To the Graduate Council:

I am submitting herewith a dissertation written by Stuart Lansing Watson, Jr., entitled "Photochemically Induced Polymerization and Modification of Polymers." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

James F. Kinstle

James F. Kinstle, Major Professor

We have read this dissertation
and recommend its acceptance:

Richard Payne

J. E. Sprinkle

Clifford Woods, III

Accepted for the Council:

Vice Chancellor
Graduate Studies and Research

PHOTOCHEMICALLY INDUCED POLYMERIZATION AND MODIFICATION OF POLYMERS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Stuart Lansing Watson, Jr.

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This thesis is dedicated to my wife, Ann, whose assistance, patience, understanding, and love made this work possible.

ABSTRACT

The interaction of triplet benzophenone and amines containing alkyl groups was investigated with respect to formation of free radicals capable of initiating polymerization. The three different types of systems investigated included homogeneous solution polymerization, homogeneous solution graft polymerization, and heterogeneous graft polymerization onto an insoluble substrate.

Combinations of benzophenone and triethylamine or N,N-diethylaniline in benzene were subjected to ultraviolet irradiation and were found to efficiently initiate polymerization of methyl methacrylate and 2-ethylhexyl methacrylate. Triplet benzophenone abstracted hydrogen from the carbon atom alpha to the nitrogen atom of the amine to form a semibenzpinacol radical and an amine-derived radical. The semibenzpinacol radical did not initiate polymerization of 2-ethylhexyl methacrylate at room temperature, and the amine-derived radical initiated polymerization of methyl methacrylate and 2-ethylhexyl methacrylate. Triethylamine was found to be significantly more effective than N,N-diethylaniline upon interaction with triplet benzophenone for initiation of free radical polymerization.

Ultraviolet irradiation of poly(styrene-co-N,N-diethylaminostyrene) with benzophenone and 2-ethylhexyl methacrylate in benzene yielded primarily grafted terpolymer. Ultraviolet irradiation of poly(styrene-co-vinylbenzophenone) with N,N-diethylaniline and 2-ethylhexyl

methacrylate in benzene yielded primarily homopolymer poly(2-ethylhexyl methacrylate).

High density polyethylene was photochlorinated and then reacted with diethylamine in toluene to incorporate amino groups. The modified polyethylene was suspended in a solution of benzophenone and methyl methacrylate or 2-ethylhexyl methacrylate in benzene. Upon ultraviolet irradiation, benzophenone abstracted hydrogen from the modified polyethylene and formed reactive free radicals which initiated graft polymerization.

To investigate pathways for efficient formation of carbon-nitrogen bonds in polyethylene, a study of the photochemical reactions of nitrosyl chloride, nitrogen dioxide, and nitric oxide with polyethylene was accomplished. Upon ultraviolet irradiation of nitrosyl chloride with low molecular weight hydrocarbons, the oxime is formed. However, upon ultraviolet irradiation of nitrosyl chloride with high density polyethylene, the only functionalities found were the gem-chloronitroso group, the nitrate, and the chlorinated methylene group. Ultraviolet irradiation of nitrogen dioxide with high density polyethylene incorporated nitro groups into the polymer, and ultraviolet irradiation of nitric oxide with high density polyethylene produced the nitro and nitrate groups.

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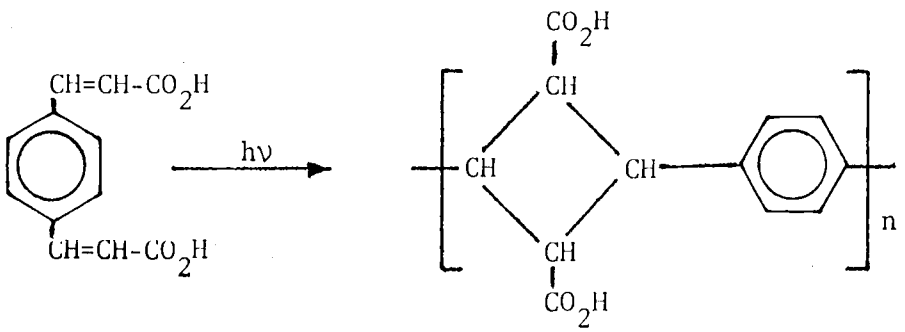
CHAPTER I

GENERAL INTRODUCTION

Photochemical processes have long been important in polymer chemistry. Originally, polymer chemists sought additives to stabilize polymers against degradation induced by ultraviolet radiation. Today, photochemical processes are becoming significant in industry[1] because of their inherently low energy requirements, the selective activation and specific reactivity of electronically excited molecules, and the exact control of the reaction allowed by instantaneously starting and stopping irradiation. These photochemical processes can be used to synthesize polymers, to beneficially modify existing polymers, and to degrade polymers for both economic and ecological considerations. This study is concerned with the first two of these groups.

Polymers can be synthesized photochemically by both step growth and chain growth mechanisms. The step growth mechanism requires that a photochemical reaction occur as each linkage is formed. An example of a photochemical step growth polymerization[2] is given in Equation 1.

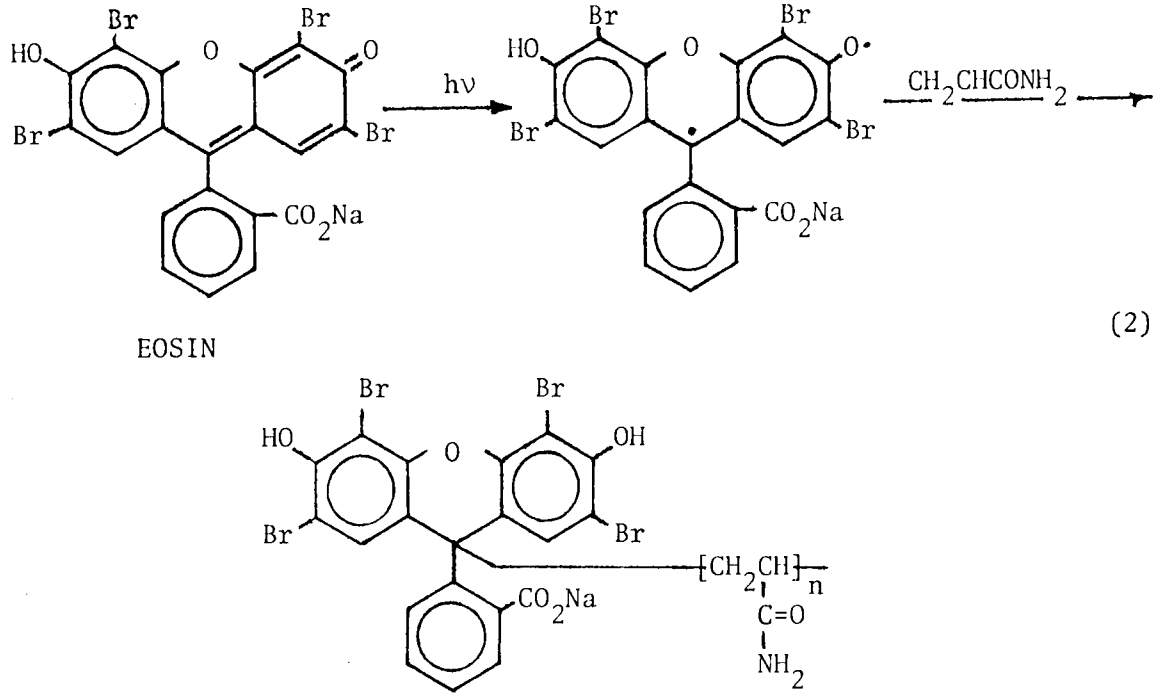


(1)

In the chain growth mechanism, the photochemical reaction yields a reactive species, usually a free radical, which initiates polymerization of the monomer.

Initiation of chain growth polymerization by photochemical processes has been the subject of intense research.[3-9] Tazuke[6] and Hutchison and Ledwith[9] have listed six mechanisms by which a species in an electronically excited state (I^*) can initiate free radical polymerization. These mechanisms are direct additions of I^* to the monomer to produce a diradical, energy transfer from I^* to the monomer to produce a reactive excited state monomer molecule, homolytic fragmentation of I^*, hydrogen abstraction by I^*, electron transfer between I^* and another molecule to produce two free radicals, and fragmentation of I^* when I represents a ground state charge transfer complex.

Smets, DeWinter, and Delzenne[10] provided an example of direct addition of I^* to the monomer molecule to produce a diradical by demonstrating that acrylamide can be polymerized by irradiation with eosin to yield polyacrylamide chains which contain eosin as shown in Equation 2.



(2)

Support for the addition mechanism included formation of 100% grafted polyacrylamide when polyvinylamine containing pendant eosin units was irradiated in the presence of acrylamide. Initiation by energy transfer has been illustrated by the photochemically induced polymerization of methyl methacrylate by uranyl ions.[11] The proposed mechanism for the reaction is given in Equations 3 through 5 where R• represents a free radical.

$$ {}^{1}UO_2^{2+} \xrightarrow{h\nu} {}^{3}UO_2^{2+} \xrightarrow{CH_2C(CH_3)CO_2CH_3} {}^{1}UO_2^{2+} + {}^{3}CH_2C(CH_3)CO_2CH_3 \qquad (3) $$

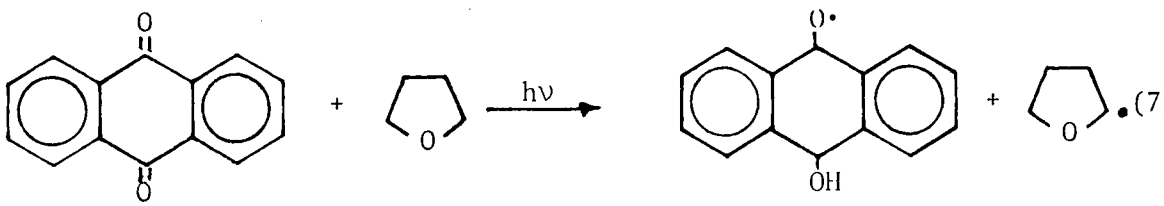
$$ {}^{3}CH_2C(CH_3)CO_2CH_3 + CH_2C(CH_3)CO_2CH_3 \longrightarrow 2\ R\cdot \qquad (4) $$

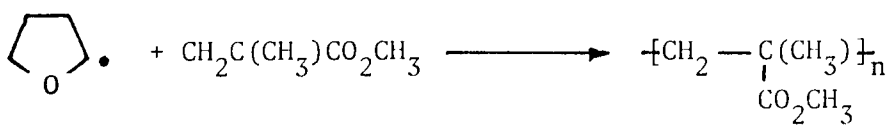
$$R\cdot + CH_2C(CH_3)CO_2CH_3 \longrightarrow \text{-}[CH_2-C(CH_3)(CO_2CH_3)]_n\text{-} \quad (5)$$

Benzoin and benzoin alkyl ethers are widely used as photoinitiators, and they are known to form free radicals by homolytic fragmentation.[12] The products of the fragmentation are given in Equation 6, where ϕ represents a phenyl group and R represents hydrogen or an alkyl group.

$$\phi\text{-}C(=O)\text{-}CH(OR)\text{-}\phi \xrightarrow{h\nu} \phi\text{-}C(=O)\cdot + \cdot CH(OR)\text{-}\phi \quad (6)$$

The recent study by Ledwith and coworkers[13] on photoinitiation of polymerization by anthraquinone demonstrated that the initiation process was hydrogen abstraction from the tetrahydrofuran solvent. Equations 7 and 8 give the proposed pathway.

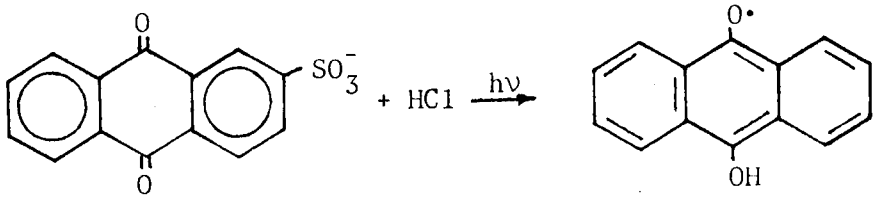




(8)

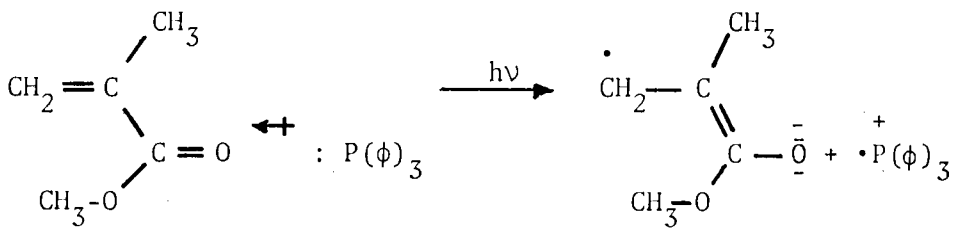
An example of the electron transfer mechanism is the initiation of polymerization using sodium anthraquinone-2-sulfonate in the presence of chloride ions.[14] The excited state anthraquinone sulfonate interacts with

a chloride ion via electron transfer to produce a chlorine atom, and this chlorine atom initiates the polymerization reaction. The proposed mechanism is outlined in Equation 9.



(9)

Many examples of free radical polymerization photoinitiated by irradiation of charge transfer complexes are known,[6] and the study by Mao and Eldred[15] is a classic case. Triphenylphosphine forms a ground state charge transfer complex with methyl methacrylate. Irradiation of this complex yields free radicals which initiate polymerization. The suggested mechanism for this process is shown in Equation 10.

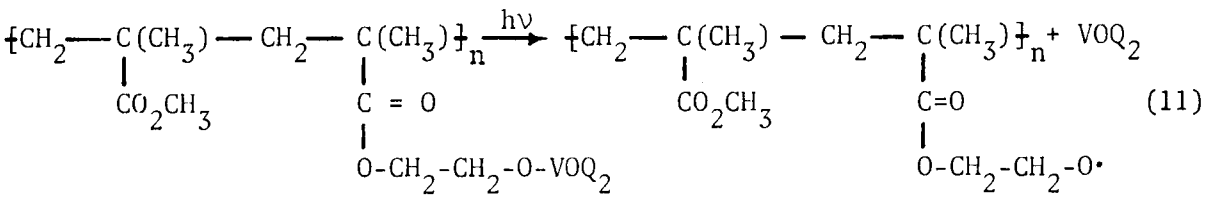


(10)

In addition to being used to initiate free radical polymerization, photochemical reactions can also be used to modify previously formed polymers.[16-18] This area may be classified into seven subdivisions including photografting, photocrosslinking, photochemical addition to polymers, photochemical isomerization, photoinduced rearrangements,

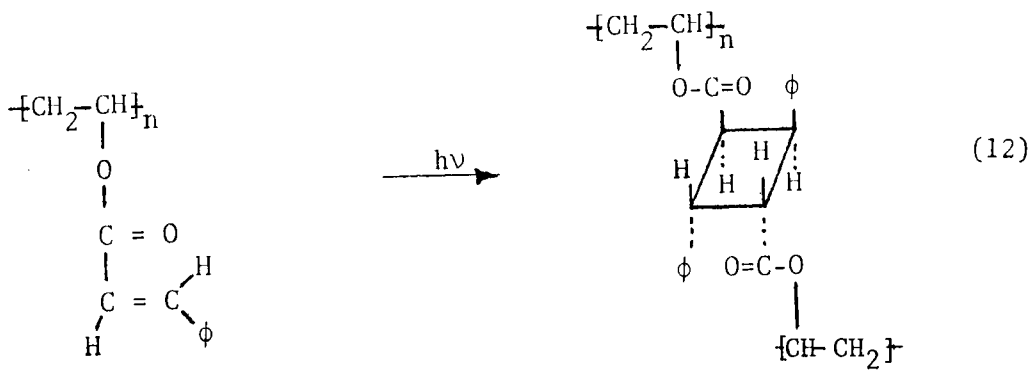
photochemical dissociation reactions, and photochemical substitution reactions.

Aliwi and Bamford[19] recently demonstrated that efficient grafting of methyl methacrylate could be accomplished photochemically using polymer substrates containing vanadium chelates. The mechanism of the grafting initiation is given in Equation 11 where Q represents the 8-quinolyloxo ligand.



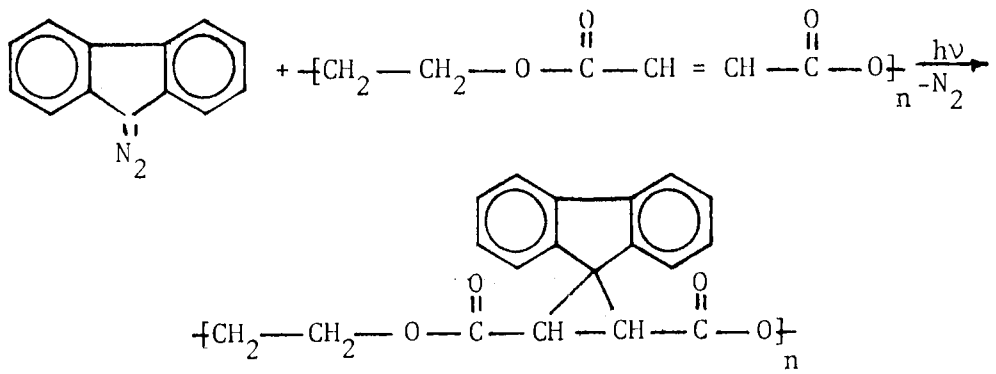
(11)

The photocyclodimerization of polyvinylcinnamate has been extensively studied.[17] The major product of the reaction is an α-truxillic type cyclobutane ring which results in a crosslink if the cinnamate groups are pendant from two different polymer chains. Equation 12 gives the structure of the uncrosslinked and crosslinked polymers.



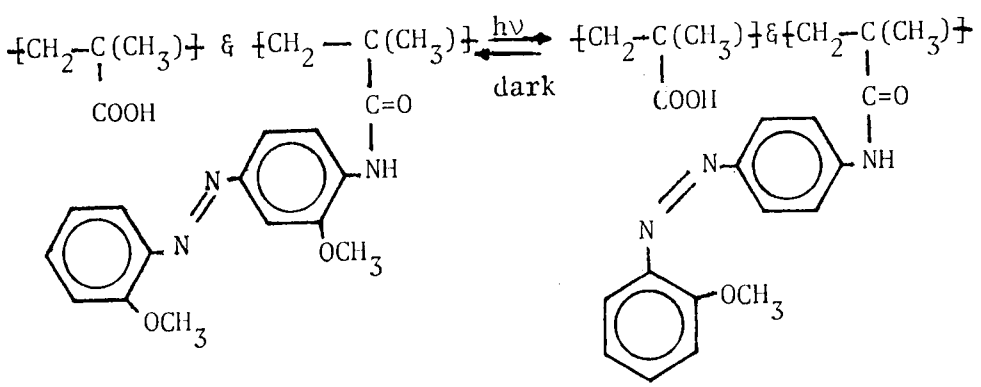
(12)

A photochemical addition to a polymer has been described by Schulz.[17] Diazofluorenone was photolyzed to yield a carbene in the presence of an unsaturated polyester. The carbene added to the double bond in the polyester to form a spirocyclopropane group are shown in Equation 13.



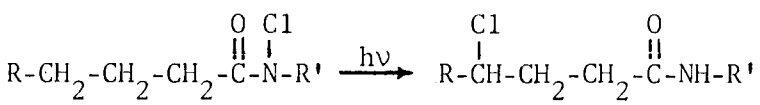
(13)

Photochemical isomerization was demonstrated by Lovrien and Waddington[20] who studied the cis-trans isomerization process in azo dyes bound to poly(acrylic acid). They synthesized a copolymer of methacrylic acid and a methacrylate containing an trans azo dye and observed a photochemical isomerization to the cis isomer upon irradiation as shown in Equation 14.



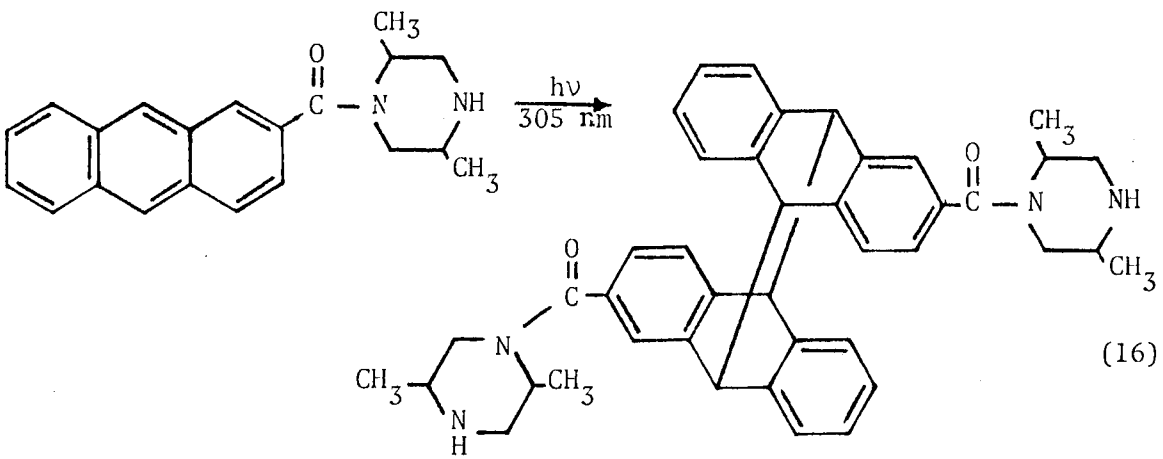
(14)

Schulz[17] has provided a unique example of a photochemically induced rearrangement of a polymer. N-Chloronylon 66 was dissolved in hexafluoroisopropanol and irradiated. The chlorine on the nitrogen was replaced by hydrogen, but the amount of chlorine in the sample remained constant. Therefore, in analogy to the results of model compounds, it was proposed that a rearrangement as given in Equation 15 had occurred.



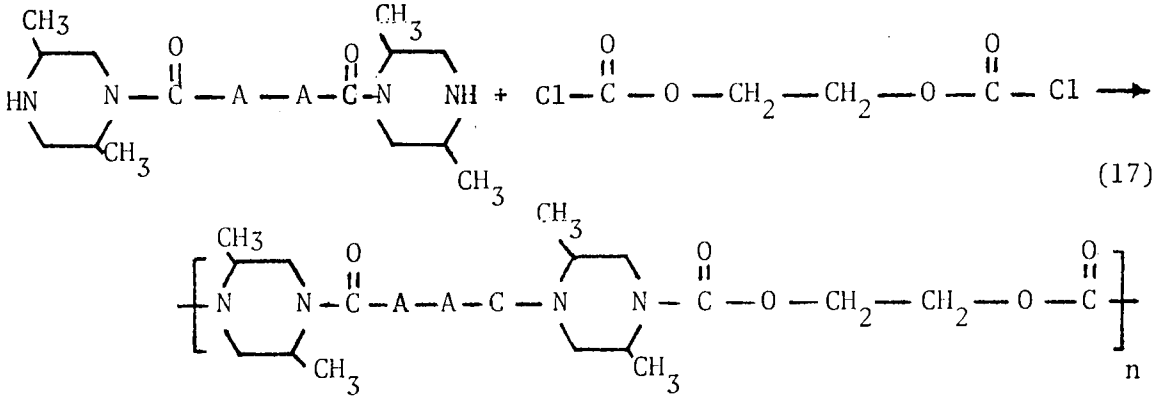
(15)

Smets[18] demonstrated a photodissociation reaction based on the photochemistry of anthracene, which forms a thermally stable dimer upon irradiation at 305 nm. Upon irradiation at 360 nm the dimer reverts back to the anthracene monomer. Equation 16 shows the dimerization of 2-(2',5'-dimethylpiperazine carboxyl)anthracene.



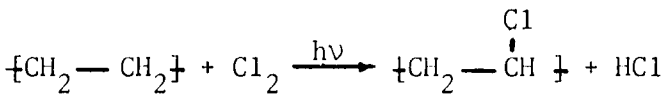
(16)

The dimer was polymerized to a polyurethane by reaction with ethyleneglycolbischloroformate as shown in Equation 17 where anthracene is abbreviated as A. Upon irradiation at 360 nm the anthracene dimer



(17)

reverted back to the monomers breaking the polymer chain. The final type of photomodification of polymers consists of photochemical substitution reactions. The most common example of this reaction is the photochlorination of polyethylene[21] given in Equation 18.



(18)

This document will relate a series of studies on photochemically induced formation and modification of polymers. First, the photochemical initiation of polymerization of methyl methacrylate and 2-ethylhexyl methacrylate using the interaction of amines and excited state benzophenone will be studied. Next, this initiation reaction will be utilized to induce selective grafting of 2-ethylhexyl methacrylate onto polystyrene in homogeneous solution. Third, this same photochemical

interaction of amines and excited state ketones will be used to form grafts of poly(methyl methacrylate) and poly(2-ethylhexyl methacrylate) onto an insoluble polymer substrate, high density polyethylene. The fourth section will relate studies on the photochemical substitution reactions of a series of nitrogen oxides upon photochemical interaction with polyethylene.

The monomers employed in this study were methyl methacrylate and 2-ethylhexyl methacrylate. Methyl methacrylate polymerizes by free radical processes to yield a primarily atactic material which is amorphous and has a glass transition temperature of about 105°C.[22] 2-Ethylhexyl methacrylate also polymerizes by free radical processes to yield a polymer with a glass transition temperature of about -10°C.[22]

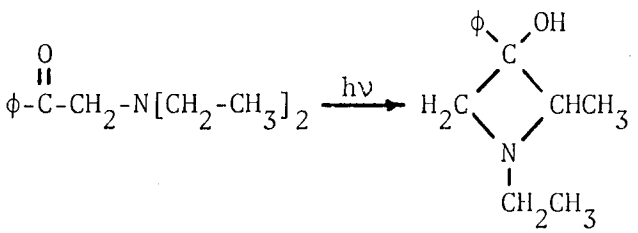
The polymer substrates used were polystyrene and polyethylene. The polystyrene was low molecular weight, atactic polymer with a glass transition temperature of about 100°C.[22] The polyethylene employed was highly crystalline, high density polyethylene in the form of a film, and it had a crystalline melting point of about 130°C.

CHAPTER II

PHOTOCHEMICALLY INDUCED POLYMERIZATION OF METHYL METHACRYLATE AND 2-ETHYLHEXYL METHACRYLATE

A. Introduction and Background

In 1966 Clasen and Searles[23] reported a unique, photochemical synthesis of 1-ethyl-3-phenylazetidin-3-ol by ultraviolet irradiation of N,N-diethylphenacylamine, as given in Equation 19. This apparent



(19)

hydrogen abstraction by the excited state ketone from the carbon atom alpha to the nitrogen atom of the amine to yield a diradial intermediate sparked intense research efforts in both academic and industrial laboratories. While the academic effort has been oriented toward a determination of the scope and mechanism of the reaction,[24] industrial research has concentrated on the use of the reaction to photochemically induce free radical polymerization.[25-33]

This chapter relates a study on the free radical polymerization of methyl methacrylate (MMA) and 2-ethylhexyl methacrylate (2EHMA) initiated by the photochemical interaction of benzophenone (BP) and amines. Reaction mixtures containing ketone, amine, monomer, and solvent are very

complex (a qualitative representation of one such system is given in Figure 1), and many different reactions are possible upon ultraviolet irradiation. Some of these reactions may be important in initiation of free radical polymerization and must be considered.

The oxygen atom of the carbonyl group of ketones has two electrons in each of two nonbonding orbitals.[9] Upon absorption of radiant energy, approximately 350 nm wavelength for BP,[35] an $n \rightarrow \pi^*$ absorption results, in which one of the electrons in one of the nonbonding orbitals is promoted to a π antibonding orbital. This absorption process is "forbidden" because of the poor spatial overlap between the n and π orbital systems, causing the weak absorbance observed. Analogous to the $n \rightarrow \pi^*$ absorption, fluorescence is also "forbidden." The initially formed excited state is usually a singlet, but in BP the lowest energy triplet lies slightly lower in energy than the first excited singlet,[37] allowing rapid, quantitative intersystem crossing to the triplet.[38] Conversion of triplet BP to the ground state by phosphorescence is also "forbidden," allowing a relatively long lifetime of 6×10^{-3} sec for triplet BP in rigid solvents at low temperature.[39]

The formation of triplet BP removes electron density from the oxygen atom, and experimental results[40] indicate that a substantial portion of the unpaired spin density of the electron promoted to the π system resides on the phenyl groups. The unpaired electron remaining in the n orbital is probably localized on the oxygen atom of the carbonyl. The resulting electron deficient oxygen atom reacts chemically in a manner similar to an alkoxy radical.[41]

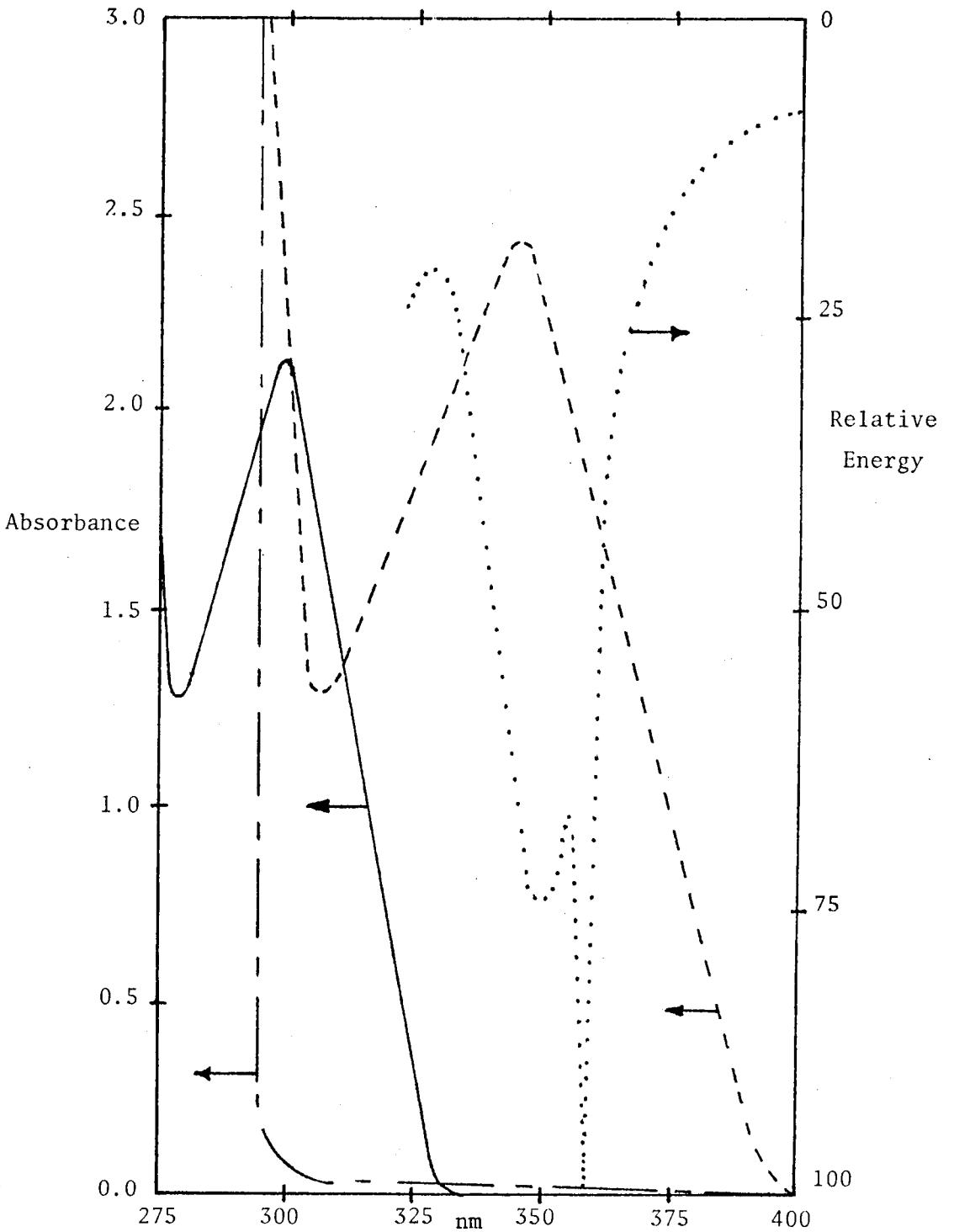
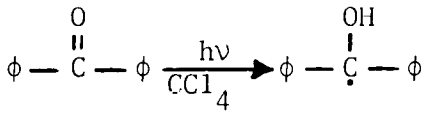


Figure 1. Qualitative representation of absorbance of reactants and emission of lamps in a polymerization system.

Methyl methacrylate (4.00 M, ——— – ———), N,N-diethylaniline[34] (0.001 M,——), benzophenone[35] (0.02 M, – – – –), lamp emission[36] (.....).

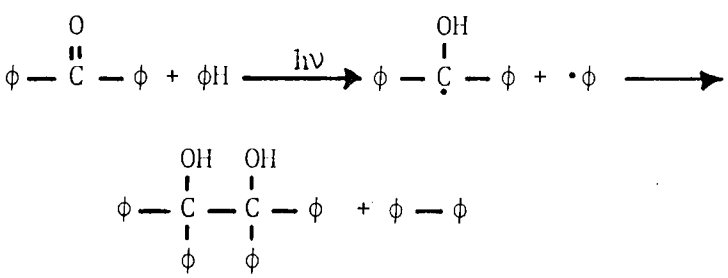
A well known reaction of alkoxy radicals is hydrogen abstraction, and this reaction is observed with triplet BP. Schuster and Weil[42] irradiated BP in carbon tetrachloride solution and identified the semibenzpinocol radical (BPH) given in Equation 20. Since the abstracted



(20)

hydrogen could not originate from the solvent, it was concluded that triplet BP must abstract hydrogen from ground state BP. An ESR study of irradiation of BP in hexadeuteriobenzene also showed the presence of BPH,[43] containing hydrogen, confirming the ability of BP to abstract hydrogen from ground state BP. The two free radicals formed by this hydrogen abstraction reaction are BPH and a very reactive phenyl-type radical. The phenyl-type radical is capable of initiating free radical polymerization.[44]

In addition to abstracting hydrogen from ground state BP, triplet BP can also abstract hydrogen from the solvent. Irradiation of BP in benzene gives BPH and phenyl radicals by way of hydrogen abstraction to ultimately yield benzpinacol and biphenyl[45,46] as seen in Equation 21. Benzene



(21)

interacts with triplet BP by another pathway in addition to the abstraction reaction.[47] While the lifetime of triplet BP is 6×10^{-3} sec in rigid solvents at low temperature, the lifetime in benzene solution at room temperature is only 1×10^{-5} sec.[39] Schuster and coworkers[48] suggested that the quenching of triplet BP observed was due to the reversible formation of a diradical adduct of triplet BP with benzene, given in Equation 22. They provide support for this process

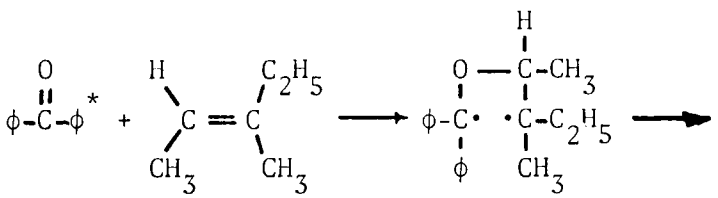


(22)

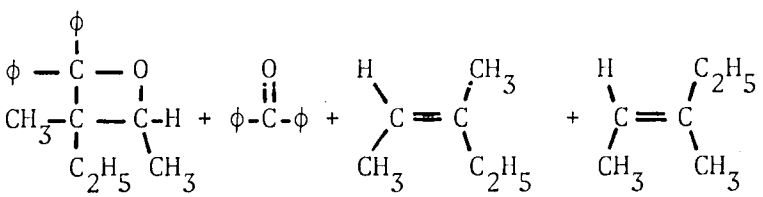
by noting a small kinetic isotope effect for the interaction of triplet BP with benzene and hexadeuteriobenzene. The reactive phenyl radical formed by hydrogen abstraction from benzene is capable of initiation,[44] while the proposed diradical adduct may also be capable of initiation of polymerization.

In addition to abstraction from ground state BP and benzene solvent, triplet BP should also abstract hydrogen from the monomer present in the reaction mixture.[49] MMA and 2EHMA contain abstractable hydrogens. Abstraction from the methyl group of the methacrylate portion of either monomer would yield a stabilized allylic radical. Additionally, abstraction could occur from the carbon atom alpha to the ester oxygen atom in both monomers. Abstraction reactions from 2EHMA are also possible from the long ester chain, which contains a methine and several methylene carbons. Free radicals formed from the monomers by such abstraction reactions may also initiate polymerization.

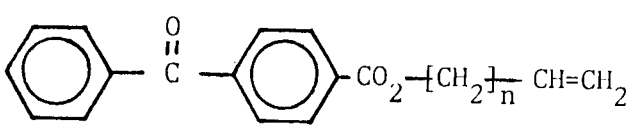
Yang, Cohen, and Shani[50] demonstrated that triplet BP reacts with olefins to form oxetanes as well as isomerizing the olefins. Direct energy transfer from triplet BP to the olefin was eliminated as a possible pathway for the isomerization since the triplet level of the olefin should be substantially higher than the triplet level of BP. They suggested the reversible formation of the diradical intermediate shown in Equation 23.



(23)



Winnick and Hsiao[51] provided support for this occurrence with their study of the phosphorescence lifetimes of a series of ω-alkenyl esters of 4-benzophenone carboxylic acid (I).



I

When the length of the ester chain was sufficient to allow intramolecular contact between the carbonyl and the olefin, the phosphorescence lifetime was significantly reduced. Turro[52] and Hammond[53] have provided different

interpretation. They suggested that the triplet carbonyl forms an exciplex with the π system of the olefin. This exciplex can decay to ground state reactants, or it can proceed to the diradical intermediate for oxetane formation or olefin isomerization. Kuhlmann and Schnabel[54] recently investigated the possibility of this type of interaction of triplet BP with MMA and discovered an efficient reaction. Interaction of 2EHMA with triplet BP should be very similar to the observed reaction of MMA with triplet BP. If the diradical intermediate is formed between the methacrylate monomer and triplet BP, it should be capable of efficient initiation of free radical polymerization.

The primary reaction of interest in a photochemically induced free radical polymerization reaction mixture containing ketone, amine, monomer, and solvent is the interaction of the triplet ketone and the amine. This interaction is very complex and several pathways have been suggested for the reaction. Roth and Lamola[55] devised a generalized scheme for the different pathways, and it is given in a modified form in Figure 2. The scheme depicts three different initial reactions for the triplet ketone with the amine. First, electron transfer from the amine to the ketone can occur resulting in the formation of radical ions. The radical ions formed can subsequently undergo proton transfer to yield neutral radicals. Second, the triplet ketone can directly abstract hydrogen from the carbon atom alpha to the nitrogen of the amine to form neutral free radicals. Third, an exciplex can be formed between the triplet ketone and the amine. The exciplex may yield either radical ions or neutral free radicals. Some or all of these reactions may be reversible.

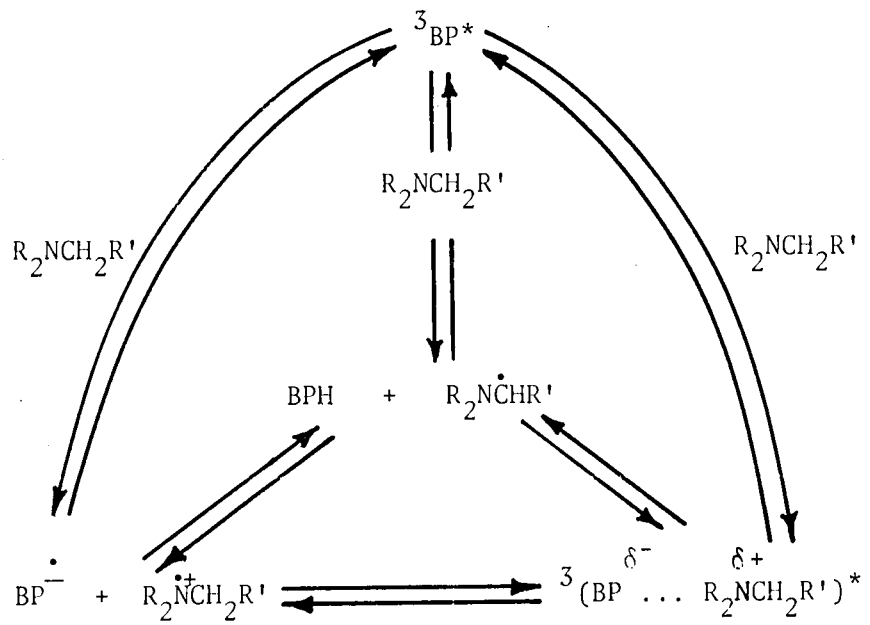
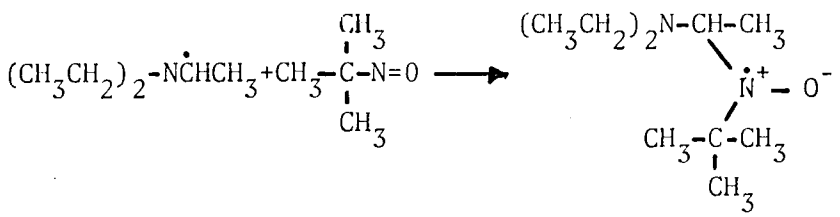


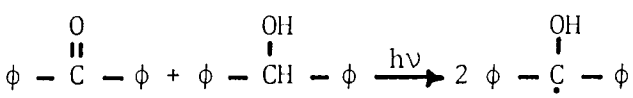
Figure 2. Possible interaction pathways for triplet benzophenone with amines.

The presence of neutral free radicals in the reaction of triplet BP and amines has been well established. Leaver and Ramsey[56] irradiated BP in 1-aminobutane, 2-aminopropane, triethylamine (TEA), and tributylamine and trapped the resulting radicals with 2-methyl-2-nitrosopropane. In each case the radical observed originated from hydrogen abstraction from the carbon atom alpha to the nitrogen. Equation 24 gives the reaction observed for TEA. The BPH adduct with 2-methyl-2-nitrosopropane was not



(24)

observed in any system studied, but in each case the adduct of a hydrogen atom with 2-methyl-2-nitrosopropane was obtained. It appeared that BPH transferred a hydrogen atom. This supposition was tested by irradiation of BP with benzhydrol as shown in Equation 25.

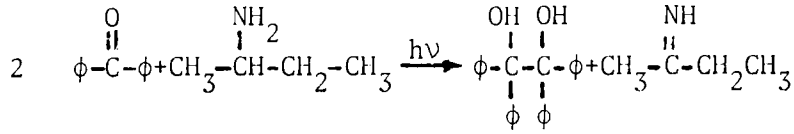


(25)

This reaction is known to yield BPH,[57] but in this system Leaver and Ramsey[56] were again only able to identify the hydrogen atom adduct. BPH has been observed in ESR experiments. Davidson and coworkers[58] irradiated BP and N,N-dimethylaniline and analyzed the ESR spectrum of the formed BPH. From these data the conclusion may be drawn that triplet BP interacts with

amines containing alkyl groups to form BPH and a carbon-centered radical alpha to nitrogen in the amine.

During the reaction of triplet BP with amines, there is significant evidence that triplet BP does not directly abstract hydrogen.[59] BP is photoreduced by 2-butylamine as shown in Equation 26. However, the rate



(26)

of photoreduction is an order of magnitude less than the rate of interaction of triplet BP with 2-butylamine. Additionally, the quantum yield for photoreduction of BP by 2-butylamine is only about 1.1, considerably less than the theoretical maximum of 2.0. This reduction in quantum yield could be caused by light-absorbing transients, but these species were not observed in this system. It could also be caused by disproportionation of the formed free radicals back to reactants or by disproportionation of two amine free radicals. Both of these processes were ruled out by photoreduction of BP by optically active 2-butylamine. The recovered amine exhibited an optical rotation identical to the original amine, indicating no racemization. Finally, photoreduction of BP with cyclohexylamine and cyclohexylamine-1-d yielded a kinetic isotope effect of about 1.6. This value is significantly less than the value of about 2.7 obtained in deuteration experiments on the photoreduction of benzhydrol,[60] in which the initial attack of triplet BP is at the carbon-hydrogen bond alpha to the hydroxyl.[59] In view of these facts, a mechanism other than direct hydrogen abstraction must be occurring.

Evidence for electron transfer from the amine to the triplet carbonyl is plentiful. Davidson and coworkers[61] flash photolyzed tri-4-tolylamine with BP in acetonitrile and identified the BP radical anion and the amine radical cation in the spectrum of the resulting solution. Later, Arimitsu and Masuhara performed a laser photolysis study on solutions of BP and N,N-diethylaniline (DEA).[62] In acetonitrile solution they also found the BP radical anion and the DEA radical cation. In a chemically induced dynamic nuclear polarization investigation, Roth and Manion[63] found that N,N-diethyl-4-toluidine reversibly transferred an electron to the excited state ketone.

The occurrence of neutral free radicals and radical ions upon interaction of triplet ketones with amines neither proves nor precludes the existence of an exciplex, formation of which may precede or compete with the formation of neutral free radicals or radical ions. The exciplex has been observed. Arimitsu and Tsubomura[64] discovered emission from a complex of BP and N,N-dimethylaniline at 77°K after irradiation. The emission was broad and had a maximum at about 475 nm. They also observed emission from BP complexes with DEA and N-methyldiphenylamine. The emission maxima shifted to longer wavelength with decreasing ionization potential of the amine and with an increase in the dielectric constant of the solvent. These results indicate that the complexes have charge transfer character. In addition to formation by irradiation of ground state reactants, the exciplex can also be formed by reaction of radical ions. Park and Bard[65] reacted BP radical anion with tri-4-tolylamine radical cation in acetonitrile and observed emission with a maximum at

581 nm. They attributed this emission to a charge transfer complex between the ketone and the amine. Formation of an exciplex by reaction of neutral free radicals is not likely, particularly in view of the lack of any disproportionation to starting materials when BP was photoreduced by optically active 2-butylamine,[59] as previously discussed.

Thus far it has been shown that neutral free radicals, radical ions, and exciplexes can be formed upon irradiation of BP and amines. Upon formation of neutral free radicals, some process is occurring, in addition to photoreduction, to cause quenching of triplet BP. The formation of radical ions is reversible, and during the recombination of radical ions the exciplex is formed. The exciplex can also be observed upon irradiation of the ketone with amines. It would be pleasing to unify the entire system by ascribing the initial interaction of the triplet ketone and the amine to an exciplex which can decay to ground state reactants resulting in quenching, which can form neutral free radicals, or which can form radical ions which reversibly form the exciplex and decay to ground state reactants. Conclusive proof of this unified process has not yet been found, but indirect evidence indicates that this pathway is occurring. Yip and coworkers[66] measured the rate of quenching of acetone phosphorescence with a series of amines in several solvents of widely different dielectric constant. Within experimental error, the rate constant for quenching of the acetone triplet remained the same for solvents of dielectric constant from 1.89 to 80 for a given amine. However, the authors provided calculations that indicated that formation of radical ions is feasible only in solvents of very high dielectric

constant. Additionally, the logarithm of the rate constants for quenching correlated linearly with the ionization potential of the amines. This led to the conclusion that a charge transfer complex was reversibly formed as the mechanism of quenching. The charge transfer complex will proceed to formation of radical ions only in solvents of high dielectric constant. Arimitsu and coworkers[67] tested this hypothesis in a significant study on the photoreduction of triplet BP by amines. Upon reaction of triplet BP with DEA in benzene, formation of BPH and not the BP radical anion was observed. However, in acetonitrile triplet BP was converted to only the BP radical anion. In solvents of intermediate polarity, a mixture of BPH and BP radical anion was observed. Calculations were accomplished to determine the free energy of the radical ions in solution. In benzene solvent the radical ions were of higher energy than triplet BP, thus their formation should be difficult. In acetonitrile, the energy level of the radical ions was below that of triplet BP, congruent with the observation of their formation. With TEA, however, triplet BP was converted to BPH over the entire spectrum of solvent dielectric constant employed. Calculations indicated that formation of radical ions in the BP-TEA system should not be highly favored even in acetonitrile, as was observed. In view of the information discussed, the evidence points to the initial formation of an exciplex between triplet BP and the amine. This exciplex will yield radical ions or neutral free radicals depending on the solvent employed and the nature of the amine used.

The amines utilized in this study are TEA and N,N-diethylaniline (DEA), and benzene is the only solvent employed. Based on the preceding

discussion, interaction of TEA or DEA with triplet BP in benzene should lead to formation of neutral free radicals and not radical ions. However, addition of MMA or 2EHMA to the benzene solution should raise the dielectric constant of the medium. This should not affect the formation of neutral free radicals with TEA, but it will probably result in the formation of some radical ions as well as neutral free radicals in the DEA system.

If radical ions are formed in the BP-DEA system, the possibility of ionic polymerization exists because the BP radical anion is known to initiate polymerization of MMA.[56] To test this supposition, BP has been irradiated with triphenylamine and methyl acrylate in a polar solvent.[29] In this system only radical ions can be formed since there are no carbon-hydrogen bonds alpha to the nitrogen atom of the amine. Polymerization of the methyl acrylate monomer did not occur. Therefore, the expected formation of radical ions in the BP-DEA system should by analogy not lead to ionic polymerization of similar vinylic monomers.

The relative effect of the various reactions of triplet BP with ground state BP, benzene solvent, monomer, and amine with respect to initiation of free radical polymerization is of interest. Pseudo first order rate constants for these interactions have been calculated using literature values, and the results are given in Table I. The value of the rate constant for DEA is not known, and the value for N,N-dimethylaniline is used as a model. The rate constants for each reaction are the rate constants for initial interaction of triplet BP with the particular species. This initial interaction is usually considered to be exciplex

TABLE I

PSEUDO FIRST ORDER RATE CONSTANTS FOR
THE REACTIONS OF TRIPLET
BENZOPHENONE

Reactant	[Reactant], M	$k, M^{-1}\ sec^{-1}$	$k[Reactant], sec^{-1}$	Reference
TEA	0.02	2.3×10^9	4.6×10^7	69
DEA[a]	0.02	2.7×10^9	5.4×10^7	69
MMA	1.00	6.9×10^7	6.9×10^7	54
BENZENE	10.00	1.0×10^4	1.0×10^5	45
BP	0.02	3.3×10^5	6.6×10^3	42

a. The rate constant for DEA is not available. The value given is for N,N-dimethylaniline.

formation. Compared with the calculated values for interaction with amine or monomer, reaction of triplet BP with ground state BP or benzene solvent is negligible. Interaction of triplet BP with monomer can be competitive with the interaction of triplet BP with amine. However, the fraction of the interactions in each case that result in free radicals capable of initiating polymerization is not known and must be determined by experiment, as discussed in the following results and discussion section.

In addition to interaction of triplet BP with the various species present in the reaction mixture, other photochemical pathways are possible. The amine DEA has an $n \rightarrow \pi^*$ transition at 303 nm.[34] While this absorption is considerably removed from the emission of the lamps employed in this study, which emit primarily at 366 nm,[36] some absorption may occur. However, direct energy transfer from the excited state DEA to the monomer, either MMA or 2EHMA, should not occur because the triplet energy of DEA is considerably lower than the expected value for the triplet energy of methacrylate monomers.[70-72] MMA[73] and 2EHMA also have an $n \rightarrow \pi^*$ transition similar to that discussed for BP, but the absorption is at shorter wavelength than the absorption in BP. Little interaction would be expected with the emission of the lamps used. However, in concentrated monomer solutions such as those employed in polymerization reactions, some excitation of this transition in the methacrylate monomers might occur. The excited state monomer would then undergo reactions similar to those observed with triplet BP, particularly the interaction with amines. This interaction has been observed upon irradiation of MMA with tertiary amines containing carbon-hydrogen bonds alpha to the nitrogen atom.[74] It was found

that the amines increased the rate of free radical polymerization, and abstraction of hydrogen from the carbon atom alpha to nitrogen in the amine was suggested as the principal mechanism of free radical production.

The neutral free radicals formed by the reaction of triplet BP and TEA or DEA have been shown to be BPH and the amine-derived radical. The amine-derived radical should be very reactive and the lack of observation of it in early ESR experiments[58] attests to its reactivity. BPH is a persistent radical,[75] and its unpaired spin density can be delocalized over both phenyl groups. Additionally, BPH is sterically hindered from coupling easily with another free radical or adding to a double bond. Therefore, it would be expected that the amine-derived radical should efficiently initiate polymerization, but it is doubtful that BPH would be capable of initiation.

Braun and Becker[76-77] studied initiation of free radical polymerization by BPH and concluded that it is not capable of initiation at room temperature, although they did find evidence for initiation at 60°C. Hutchison, Lambert, and Ledwith[78] also investigated the fate of BPH in the polymerization of MMA. They found that BPH was only a terminating species at 30°C, but that at 70°C some initiation occurred.

Most of the information available on the use of triplet ketones and amines to initiate polymerization is contained in the patent literature and deals with irradiation of very complex mixtures.[25-28,31] Two reports have appeared in which basic studies were performed on the use of triplet BP and amines to initiate polymerization. McGinniss[33] described work in which a series of alkyl amines were irradiated with BP to polymerize MMA,

but few experimental details were discussed. The major contribution was by Sandner, Osborn, and Trecker[29] who used the interaction of triplet BP and TEA to initiate the polymerization of methyl acrylate. The initial part of their work was concerned with a comparison of reactions in which methyl acrylate was irradiated with BP only, BP and TEA, or TEA only and significant polymerization was achieved only when both BP and TEA were present. However, these workers used the monomer without removing the inhibitor, and proved only that the interaction of BP and TEA was sufficient to surpass the induction period caused by the inhibitor. Additionally, neither sample size nor percent conversion was reported for these reactions, causing analysis of the data to be difficult. Much of the remainder of the report by Sandner, Osborn, and Trecker discusses the results on the amount and quantum yield of BP photoreduction upon irradiation with various hydrogen donors. However, the authors make no mention of the possibility of light absorbing transients which are often observed upon irradiation of BP with hydrogen donors.[53,79] These light absorbing transients also absorb in the $n \rightarrow \pi^*$ region of BP, sometimes causing an increase in absorption with irradiation. These transients can remain long after irradiation has ceased. The loss of BP in the work of Sandner, Osborn and Trecker was measured by the use of ultraviolet spectrophotometry in the $n \rightarrow \pi^*$ region of BP, and several of the values exceed 100% of original after irradiation. This indicates that light absorbing transients were present and casts doubt on the accuracy of the data.

In the following section a series of several sets of reactions will be described on the use of triplet BP and TEA or DEA to initiate free radical polymerization of MMA and 2EHMA. While the photochemically induced polymerization of MMA using BP and TEA has previously been reported, the use of DEA and the polymerization of 2EHMA using these systems has not. Additionally, the complex components of the reaction mixtures will be systematically varied using purified reactants to determine the effects of the various species on the polymerization system.

B. Results and Discussion

Preliminary experiments on the polymerization of 2EHMA and MMA indicated that the rate of polymerization of 2EHMA was greater than the rate of polymerization for MMA. Values of the rate constants for polymerization of MMA are available, but the values for 2EHMA have not yet been determined. Therefore, an initial attempt was made to estimate the rate of polymerization of 2EHMA as compared to MMA. Equation 27 gives the general rate expression for free radical polymerization of vinyl monomers.[80] R_p is the rate of polymerization; k_p and k_t are the rate

$$R_p = k_p \left(0.5\, R_i\, k_t^{-1}\right)^{0.5} [M] \qquad (27)$$

constants for propagation and termination. R_i is the rate of initiation, and M represents the monomer. Rearrangement of Equation 27 yields Equation 28 in which the rate constants unique for a particular monomer are separated.

$$R_p = (k_p k_t^{-0.5})\ (0.5\ R_i)^{0.5}\ [M] \qquad (28)$$

Use of the same initiator, initiator concentration, and monomer concentration should allow the estimation of relative rates of polymerization from known values of k_p and k_t as shown in Equation 29.

$$\frac{R_{p_1}}{R_{p_2}} = \frac{(k_{p_1} k_{t_1}^{-0.5})\ (0.5\ R_i)^{0.5}\ [M_1]}{(k_{p_2} k_{t_2}^{-0.5})\ (0.5\ R_i)^{0.5}\ [M_2]} = \frac{k_{p_1} k_{t_1}^{-0.5}}{k_{p_2} k_{t_2}^{-0.5}} \qquad (29)$$

Using this approach with known values for k_p and k_t,[81] Table II was constructed yielding relative rates of polymerization for a series of methacrylate esters with MMA arbitrarily set to unity. The trend toward increased rates of polymerization with longer ester chain length is very pronounced. From these data the rate of polymerization of 2EHMA is expected to be at least two to three times that of MMA if other variables are maintained constant.

This estimation was tested by thermally polymerizing 2EHMA and MMA using 2,2'-azobis-(2-methylpropionitrile)(AIBN) as the initiator to yield poly(2-ethylhexyl methacrylate)(P2EHMA) and poly(methyl methacrylate) (PMMA), assuming that the efficiency of initiation by AIBN-derived radicals is the same for both monomers. The results are given in Tables III - VI. MMA is known to polymerize thermally at a low rate, and this was found when MMA was maintained at 50°C in the absence of AIBN, as given in Table III. The results for the AIBN initiated reactions of MMA are detailed in Table IV. No pure thermal initiation of polymerization

TABLE II

RELATIVE RATES OF POLYMERIZATION FOR METHYACRYLATE ESTERS

Ester	k_p[a], $\underline{M}^{-1}sec^{-1}$	k_t[a], $\underline{M}^{-1}sec^{-1}$	Temperature °C	$k_p k_t^{-0.5}$, $\underline{M}^{-0.5}sec^{-0.5}$	Relative R_p
Methyl	143	12.2×10^6	30	4.09×10^{-2}	1.00
Ethyl	126	7.35×10^6	30	4.65×10^{-2}	1.14
Propyl	467	45.1×10^6	30	6.95×10^{-2}	1.70
Butyl	369	10.2×10^6	30	1.16×10^{-1}	2.84

a. Values taken from reference 81.

TABLE III

THERMAL POLYMERIZATION OF METHYL METHACRYLATE AT 50°C IN BENZENE

Reaction	[MMA],M	Volume,ml	Time,hr	PMMA Formed	
				g	%
III A	4.00	25	0.0	0.00	0.0
III B	4.00	25	1.0	0.04	0.4
III C	4.00	25	2.0	0.07	0.7
III D	4.00	25	3.0	0.08	0.8
III E	4.00	25	4.0	0.10	1.0

TABLE IV

THERMAL POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY 2,2'-AZOBIS-(2-METHYLPROPIONITRILE) AT 50°C IN BENZENE

Reaction	[MMA],M	[AIBN],M	Volume,ml	Time,hr	PMMA Formed	
					g	%
IV A	4.00	2.44×10^{-3}	25	0.0	0.00	0.0
IV B	4.00	2.44×10^{-3}	25	1.0	0.27	2.7
IV C	4.00	2.44×10^{-3}	25	2.0	0.57	5.7
IV D	4.00	2.44×10^{-3}	25	3.0	0.85	8.5
IV E	4.00	2.44×10^{-3}	25	4.0	1.09	10.9

TABLE V

THERMAL POLYMERIZATION OF 2-ETHYLHEXYL METHACRYLATE AT 50°C IN BENZENE

Reaction	[2EHMA],M	Volume, ml	Time,hr	P2EHMA Formed	
				g	%
V A	0.50	25	0.0	0.00	0.0
V B	0.50	25	1.0	0.00	0.0
V C	0.50	25	2.0	0.00	0.0
V D	0.50	25	3.0	0.00	0.0
V E	0.50	25	4.0	0.00	0.0

TABLE VI

THERMAL POLYMERIZATION OF 2-ETHYLHEXYL METHACRYLATE INITIATED BY 2,2'-AZOBIS-(2-METHYLPROPIONITRILE) AT 50°C IN BENZENE

Reaction	[2EHMA],M	[AIBN],M	Volume,ml	Time,hr	P2EHMA Formed	
					g	%
VI A	0.50	2.44×10^{-3}	25	0.0	0.00	0.0
VI B	0.50	2.44×10^{-3}	25	1.0	0.18	7.3
VI C	0.50	2.44×10^{-3}	25	2.0	0.31	12.5
VI D	0.50	2.44×10^{-3}	25	3.0	0.47	19.0
VI E	0.50	2.44×10^{-3}	25	4.0	0.60	24.2

of 2EHMA was observed in the absence of AIBN as given in Table V, and the results for the AIBN initiated polymerizations of 2EHMA are presented in Table VI. The data for the AIBN initiated polymerizations of both MMA and 2EHMA are plotted in Figure 3 with the values for MMA corrected for pure thermal initiation by subtracting the amount of PMMA formed in the absence of AIBN. The straight lines were drawn based on the results of a linear regression analysis of the data. The value of the slope for 2EHMA is 6.01% hr^{-1}, and the value of the slope for MMA is 2.52% hr^{-1}. The ratio of the slopes is 2.38, indicating that 2EHMA polymerizes at about two to three times the rate for MMA, in strong agreement with the previous estimation.

In the AIBN initiated polymerization reactions just described and in the photochemically induced polymerization reactions to be discussed later, the monomer concentrations for MMA (4.00 M) and 2EHMA (0.50 M) differ greatly. Polymer formation was determined gravimetrically, and the ratio of mass (1.98:1.00) and ratio of polymerizability (2.38:1.00) for 2EHMA to MMA require the large difference in monomer concentration for ease and accuracy in weighing the product. This difference in concentration will not affect the comparibility of the data since polymer formation is always presented as percent conversion.

North and Reed[82] have studied free radical polymerization of a series of alkyl methacrylates and also observed the increase in the rate of polymerization as the ester group size increases. Their analysis indicated that the phenomenon occurred in the termination reaction, and they divided the termination process into three separate areas. The first

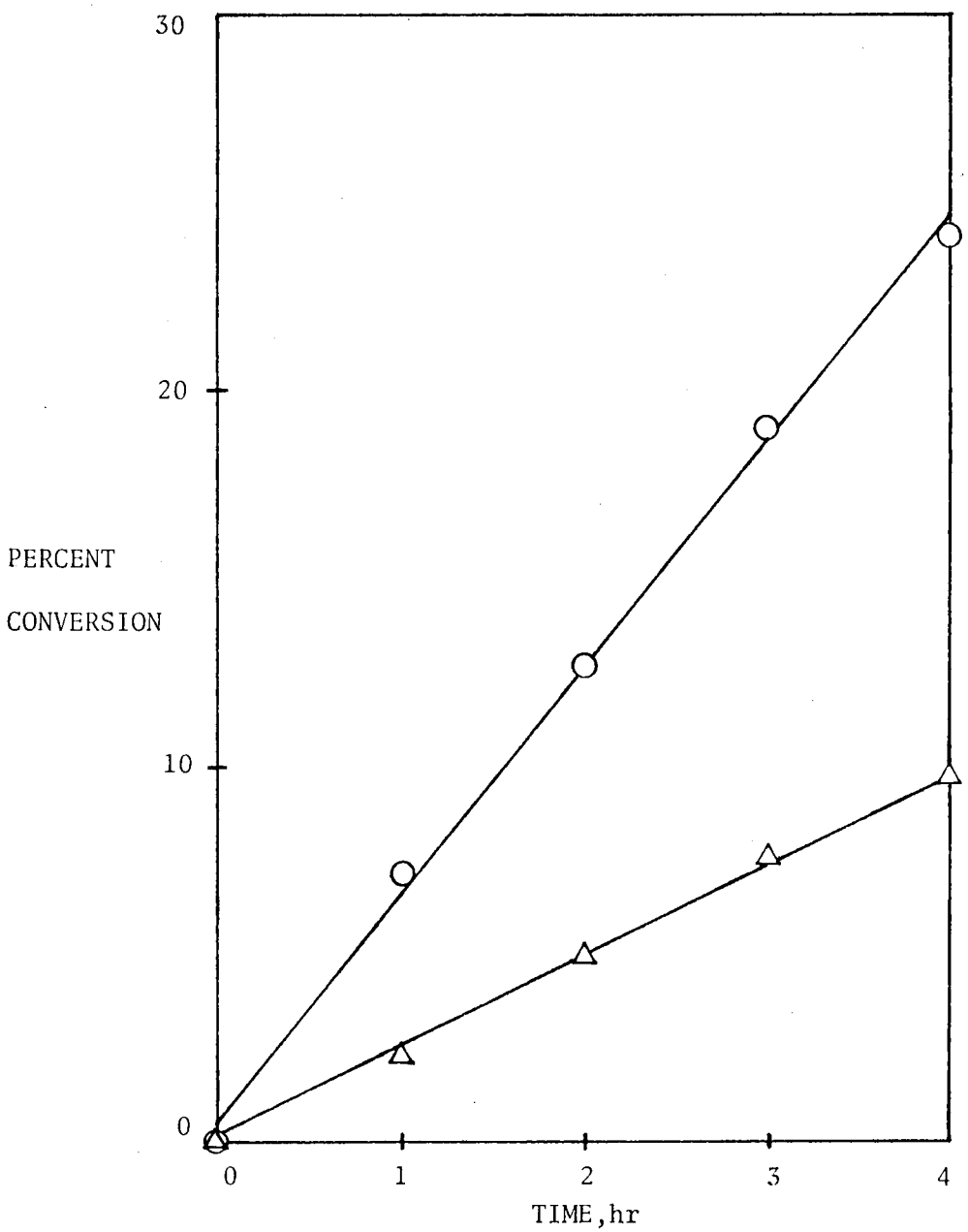


Figure 3. Thermal 2,2'-azobis-(2-methylpropionitrile) initiated polymerization of 2-ethylhexyl methacrylate and methyl methacrylate at 50°C

Circles: 2-ethylhexyl methacrylate, triangles: methyl methacrylate.

area is translational diffusion of the centers of gravity of the two macroradicals to a proximity where the two radicals are able to come into contact. The second area is segmental diffusion or rearrangement to allow reaction to occur between the two radicals. The third area is the actual reaction, either combination or disproportionation. North and Reed concluded that segmental diffusion controlled the rate of termination. The present results which show that 2EHMA polymerizes at a greater rate than MMA are reasonable in the context of the analysis by North and Reed. Segmental diffusion should proceed more easily in MMA than in 2EHMA, yielding increased rates of termination in MMA as compared to 2EHMA. This increased rate or rate constant for termination gives a decreased rate of polymerization for MMA due to the inverse relationship between the rate of polymerization and the rate constant for termination, as previously seen in Equation 27 (p 29).

The photochemically induced polymerizations to be discussed in this section were accomplished in sets of five reactions, and each set of reactions is presented in a separate table. Each particular set was accomplished with simultaneous irradiation of each reaction vessel in the photoreactor to allow equal irradiation for each vessel. This procedure allows direct comparisons between the reactions in a particular table. Comparisons of data between different tables contain the inherent possibility of a slight change in light intensity between reactions. However, the reactions were quite reproducible indicating that the light source was very stable.

Table VII contains the results of irradiation of MMA alone and with various combinations of BP and TEA. Reaction VIIA demonstrates that no polymerization is observed in the absence of irradiation, even if both BP and TEA are present. Polymerization of MMA does occur in benzene upon irradiation even in the absence of BP and TEA, as seen in Reaction VIIB. The observed polymerization of MMA in the absence of both BP and TEA is a photochemical and not a thermal effect. Although MMA is known to polymerize at a low rate thermally, extended dark reactions at room temperature, to be discussed later, and the control, Reaction VIIA, demonstrate that the small amount of polymerization observed is due to irradiation and not due to the rise in temperature in the photoreactor (22°C - 32°C) observed during irradiation. Additionally, a small amount of thermal initiation of polymerization of MMA was observed at 50°C during the AIBN initiated polymerization reactions, but no thermal initiation of polymerization of 2EHMA was observed, as previously discussed. However, during irradiation of 2EHMA alone in benzene, to be more fully discussed later, a small amount of polymerization was observed, providing further confirmation that the polymerization observed in Reaction VIIB is photochemical in origin. The initiation of polymerization could be caused by impurities in the monomer or the solvent, but this is not likely due to the purification procedure employed. The probable pathway is slight absorption of the radiation by MMA to yield an excited state species which is similar in reactivity to triplet BP. The excited state MMA could then abstract hydrogen creating reactive free radicals which could initiate polymerization.

TABLE VII

METHYL METHACRYLATE, BENZOPHENONE, AND TRIETHYLAMINE COMBINATIONS IN BENZENE SUBJECTED TO ULTRAVIOLET IRRADIATION

Reaction	[MMA],M	[BP],M	[TEA],M	Volume,ml	Irradiation Time, min	PMMA Formed	
						g	%
VII A	4.00	0.02	0.02	25	0	0.00	0.0
VII B	4.00	0.00	0.00	25	180	0.55	5.5
VII C	4.00	0.02	0.00	25	180	0.55	5.5
VII D	4.00	0.00	0.02	25	180	0.81	8.1
VII E	4.00	0.02	0.02	25	180	2.29	22.9

Another possible reaction of the excited state molecule is alpha bond cleavage, given in Equation 30. This reaction would lead to very

$$CH_2{=}C(CH_3)CO_2CH_3^{*} \longrightarrow CH_2{=}\dot{C}{-}CH_3 + {\cdot}\dot{C}(=O){-}O{-}CH_3 \longrightarrow CO_2 + \dot{C}H_3 \qquad (30)$$

reactive methyl and vinylic radicals. This type of reaction, with the subsequent formation of carbon dioxide, has been observed often in esters, but usually with irradiation by higher energy light.[83] Support for a reaction of this type can be seen by comparing Reactions VIIB and VIIC. Addition of BP to MMA has little effect on the amount of polymerization observed. This result indicates that initiation by hydrogen abstraction from monomer or solvent, either by triplet BP or excited state monomer, does not lead to appreciable initiation of polymerization.

Addition of TEA to MMA yields a slight increase in polymerization (compare Reactions VIIB and D). The increase is small but reproducible, and appears in each set of reactions to be discussed. The cause for the observed increase is probably due to abstraction of hydrogen from the carbon atom alpha to nitrogen in the amine by the excited state monomer. This effect has been observed by other workers,[74] as previously discussed in Section A of this chapter.

Comparison of Reactions VIIIB and C allows a conclusion to be drawn on the interaction of triplet BP and MMA which has been investigated by Kuhlmann and Schnabel.[54] Despite the occurrence of efficient interaction

between triplet BP and MMA, few, if any, of these interactions lead to free radical initiating species. Thus, the interaction between triplet BP and MMA which was observed by Kuhlmann and Schnabel must lead primarily to quenching of triplet BP.

Inspection of Reaction VIIE indicates the dramatic increase in polymerization observed when both BP and TEA are present in the irradiated reaction mixture. This increase is most likely due to efficient formation of a free radical initiating species upon interaction of triplet BP and TEA. As previously discussed in Section A of this chapter, this interaction leads to net hydrogen abstraction from the alpha carbon atom in the amine.[24] This amine-derived radical probably is the initiating species, while the concurrently formed BPH is not capable of initiating polymerization of MMA near room temperature.[78]

Table VIII presents the results of irradiation of various combinations of MMA with BP and DEA. The control, Reaction VIIIA, again demonstrates that no polymerization is observed in the absence of irradiation. As previously observed, a small amount of MMA polymerizes upon irradiation, even in the absence of both BP and DEA, as shown in Reaction VIIIB. Addition of BP to the reaction mixture in Reaction VIIIC shows little effect on the amount of PMMA formed. A small increase in the percent conversion is noted in Reaction VIIID, presumably due to hydrogen abstraction from the amine. Reaction VIIIE gives the results for the reaction in which both BP and DEA are present with the monomer, and a significant increase in PMMA formation is noted. However, a comparison of Reaction VIIIE using DEA and Reaction VIIE using TEA indicates that DEA

TABLE VIII

METHYL METHACRYLATE, BENZOPHENONE, AND N,N-DIETHYLANILINE COMBINATIONS IN BENZENE SUBJECTED TO ULTRAVIOLET IRRADIATION

Reaction	[MMA],M	[BP],M	[DEA],M	Volume,ml	Irradiation Time, min	PMMA Formed	
						g	%
VIII A	4.00	0.02	0.02	25	0	0.00	0.0
VIII B	4.00	0.00	0.00	25	180	0.40	4.0
VIII C	4.00	0.02	0.00	25	180	0.53	5.3
VIII D	4.00	0.00	0.02	25	180	0.72	7.2
VIII E	4.00	0.02	0.02	25	180	1.25	12.5

is much less effective than TEA with respect to initiation of polymerization of MMA.

To preclude the possibility that the observed differences in the ability of TEA and DEA to initiate polymerization of MMA were due to a variation in light intensity, a set of reactions were accomplished in which combinations of BP and TEA or DEA with MMA were irradiated simultaneously. The results are given in Table IX. The amounts of polymerization noted are very similar to the amounts previously observed, and TEA is significantly more effective in initiating polymerization than DEA. The rate constants for interaction of triplet BP with TEA or DEA were previously given in Table I (p 25), and the value for TEA (2.3×10^9 $\underline{M}^{-1}$ sec^{-1}) is less than the estimated value for DEA (2.7×10^9 $\underline{M}^{-1}$ sec^{-1}). Therefore, the decrease in ability to initiate must occur after the initial formation of the exciplex and is probably due to the quenching of triplet BP by rapid reversible formation of radical ions. Other factors may also be affecting the relative ability of the amines to initiate polymerization. When the amine-derived radical is formed from DEA, it may be more sterically hindered with respect to attacking the monomer than the TEA-derived radical because of the bulky phenyl group. Additionally, the DEA-derived radical may be stabilized by the presence of the phenyl group. Interaction of the carbon-centered radical through the nitrogen atom could allow the unpaired spin density to be delocalized into the phenyl group.

Extended dark reactions of MMA with BP and TEA or DEA were accomplished to investigate the possibility of thermal polymerization of

TABLE IX

RELATIVE EFFECTIVENESS OF TRIETHYLAMINE AND N,N-DIETHYLANILINE FOR POLYMERIZATION OF METHYL METHACRYLATE IN BENZENE

Reaction	[MMA],M	[BP],M	Amine	[Amine],M	Volume,ml	Irradiation Time, min	PMMA Formed	
							g	%
IX A	4.00	0.02	--	0.00	25	0	0.00	0.0
IX B	4.00	0.02	DEA	0.02	25	180	1.22	12.2
IX C	4.00	0.02	DEA	0.02	25	180	1.30	13.0
IX D	4.00	0.02	TEA	0.02	25	180	2.19	21.9
IX E	4.00	0.02	TEA	0.02	25	180	2.06	20.6

MMA at room temperature. The results are given in Table X, and the lack of PMMA formation substantiates the previous statement that the polymer formation observed in Reaction VIIB of Table VII (p 40) must be due to irradiation.

The same sets of reactions were repeated using 2EHMA as the monomer, and the results are similar to those observed with MMA. Table XI gives the results for irradiation of 2EHMA with combinations of BP and TEA. A small amount of polymerization is noted with 2EHMA alone in Reaction XIB, and a moderate increase can be seen in Reaction XIC when BP is added to the monomer. This increase could be due to abstraction of hydrogen from the long ester chain in 2EHMA to yield a reactive carbon-centered radical. Additionally, an increase is noted in Reaction XID when TEA is irradiated with the monomer. This increase was previously observed in the MMA reactions and is presumably due to hydrogen abstraction from the amine by the excited state monomer. The expected significant increase in polymerization of 2EHMA is seen in Reaction XIE, in which both TEA and BP are present with the monomer.

Irradiation of 2EHMA with combinations of BP and DEA were also accomplished, and the results are detailed in Table XII. Small amounts of polymerization are observed when the monomer is irradiated alone or with BP or DEA. The greatest amount of polymerization is noted in Reaction XIIE when both BP and DEA are present, but the amount is significantly less than that observed with TEA.

Similar to the reactions with MMA, combinations of BP and TEA or BP and DEA were irradiated simultaneously with 2EHMA to determine if the

TABLE X

DARK REACTIONS OF METHYL METHACRYLATE IN BENZENE

Reaction	[MMA],M	[BP],M	Amine	[Amine],M	Volume,ml	Time,hr	PMMA Formed	
							g	%
X A	4.00	0.00	--	0.00	25	360	0.00	0.0
X B	4.00	0.02	DEA	0.02	25	360	0.00	0.0
X C	4.00	0.00	--	0.00	25	360	0.00	0.0
X D	4.00	0.02	TEA	0.02	25	360	0.00	0.0

TABLE XI

2-ETHYLHEXYL METHACRYLATE, BENZOPHENONE, AND TRIETHYLAMINE COMBINATIONS IN BENZENE SUBJECTED TO ULTRAVIOLET IRRADIATION

Reaction	[2EHMA],M	[BP],M	[TEA],M	Volume,ml	Irradiation Time, min	P2EHMA Formed	
						g	%
XI A	0.50	0.02	0.02	25	0	0.00	0.0
XI B	0.50	0.00	0.00	25	120	0.13	5.2
XI C	0.50	0.02	0.00	25	120	0.21	8.5
XI D	0.50	0.00	0.02	25	120	0.22	8.9
XI E	0.50	0.02	0.02	25	120	0.67	26.9

TABLE XII

2-ETHYLHEXYL METHACRYLATE, BENZOPHENONE, AND N,N-DIETHYLANILINE COMBINATIONS IN BENZENE SUBJECTED TO ULTRAVIOLET IRRADIATION

Reaction	[2EHMA],M	[BP],M	[DEA],M	Volume,ml	Irradiation Time, min	P2EHMA Formed	
						g	%
XII A	0.50	0.02	0.02	25	0	0.00	0.0
XII B	0.50	0.00	0.00	25	120	0.12	4.7
XII C	0.50	0.02	0.00	25	120	0.23	9.2
XII D	0.50	0.00	0.02	25	120	0.28	11.4
XII E	0.50	0.02	0.02	25	120	0.37	14.9

differences observed between TEA and DEA in Tables XI and XII were due to variations in light intensity, and the results are presented in Table XIII. As expected from the MMA results, TEA consistently yields a greater amount of polymer formation.

In analogy to the dark reactions accomplished for MMA, extended dark reactions were investigated in 2EHMA with combinations of BP and TEA or DEA. The results are presented in Table XIV, and the lack of polymerization noted indicates that BP and DEA or TEA do not initiate polymerization of 2EHMA without ultraviolet irradiation.

The work of Braun and Becker[76,77] and the work of Hutchison, Lambert, and Ledwith[78] demonstrated that BPH does not initiate polymerization of MMA at or near room temperature. Similarly, BPH should not initiate polymerization of 2EHMA, but this has not yet been proven. Irradiation of BP with benzhydrol (BOH) will yield BPH[57] as previously given in Equation 25 (p 19), and this reaction was employed to determine if BPH is capable of initiating polymerization of 2EHMA. The results are detailed in Table XV where a comparison of Reactions XVC and XVB and E shows that BPH is not an initiating species. Additionally, comparison of Reactions XVD and E indicates that the presence of BOH in the BP and TEA reaction mixture decreases polymer formation. This result indicates that BPH is a terminating species only during polymerization of 2EHMA at or near room temperature.

In summary, the results in this chapter allow several conclusions to be drawn. Both MMA and 2EHMA polymerize upon irradiation in benzene. The amount of polymerization is slightly increased upon addition of

TABLE XIII

RELATIVE EFFECTIVENESS OF TRIETHYLAMINE AND N,N-DIETHYLANILINE FOR POLYMERIZATION OF 2-ETHYLHEXYL METHACRYLATE IN BENZENE

Reaction	[2EHMA],M	[BP],M	Amine	[Amine],M	Volume,ml	Irradiation Time, min	P2EHMA Formed	
							g	%
XIII A	0.50	0.02	--	0.00	25	0	0.00	0.0
XIII B	0.50	0.02	DEA	0.02	25	120	0.42	16.9
XIII C	0.50	0.02	DEA	0.02	25	120	0.41	16.5
XIII D	0.50	0.02	TEA	0.02	25	120	0.71	28.2
XIII E	0.50	0.02	TEA	0.02	25	120	0.74	29.8

TABLE XIV

DARK REACTIONS OF 2-ETHYLHEXYL METHACRYLATE IN BENZENE

Reaction	[2EHMA],M	[BP]	Amine	[Amine],M	Volume,ml	Time,hr	P2EHMA Formed	
							g	%
XIV A	0.50	0.00	--	0.00	25	360	0.00	0.0
XIV B	0.50	0.02	DEA	0.02	25	360	0.00	0.0
XIV C	0.50	0.00	--	0.00	25	360	0.00	0.0
XIV D	0.50	0.02	TEA	0.02	25	360	0.00	0.0

TABLE XV

EFFECT OF BENZHYDROL ON PHOTOINDUCED POLYMERIZATION OF 2-ETHYLHEXYL METHACRYLATE IN BENZENE

Reaction	[2EHMA],M	[BP],M	[TEA],M	[BOH],M	Volume,ml	Irradiation Time, min	P2EHMA Formed	
							g	%
XV A	0.50	0.02	0.00	0.02	25	0	0.00	0.0
XV B	0.50	0.02	0.00	0.00	25	120	0.12	4.8
XV C	0.50	0.02	0.00	0.02	25	120	0.07	2.8
XV D	0.50	0.02	0.02	0.02	25	120	0.56	22.6
XV E	0.50	0.02	0.02	0.00	25	120	0.69	27.8

either TEA or DEA, but it is affected little by the addition of BP. Addition of both BP and TEA or DEA to the monomer dramatically enhances the amount of polymerization that occurs upon irradiation. This enhancement is probably due to efficient interaction of triplet BP and the amine to form BPH and the amine-derived radical. BPH does not initiate polymerization of MMA or 2EHMA near room temperature, and TEA is significantly more effective in initiating polymerization than DEA upon interaction with triplet BP.

CHAPTER III

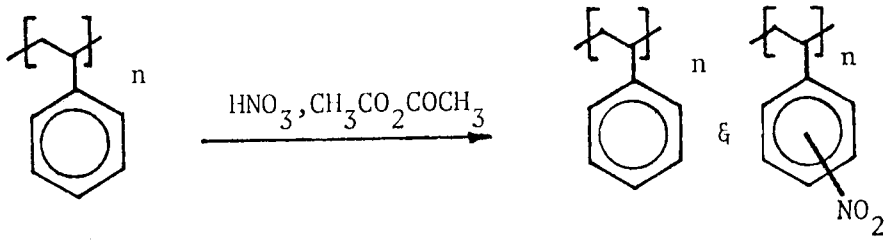
PHOTOCHEMICALLY INDUCED HOMOGENEOUS GRAFT POLYMERIZATION OF 2-ETHYLHEXYL METHACRYLATE ONTO MODIFIED POLYSTYRENE

A. Introduction and Background

In the previous chapter the polymerization of methyl methacrylate (MMA) and 2-ethylhexyl methacrylate (2EHMA) by the photochemical interaction of triplet benzophenone (BP) and triethylamine or N,N-diethylaniline (DEA) was investigated. The interaction of triplet BP and the amine leads to the formation of a semibenzpinacol radical (BPH) and a carbon-centered amine-derived radical by hydrogen abstraction from the carbon atom alpha to the nitrogen atom of the amine. The amine-derived radical was proposed to be the initiating species for polymerization of both MMA and 2EHMA, while BPH functions only as a terminating species. This formation of free radicals which are dissimilar in their ability to initiate polymerization should allow the formation of polymeric substrates onto which selective graft polymerizations could be accomplished.

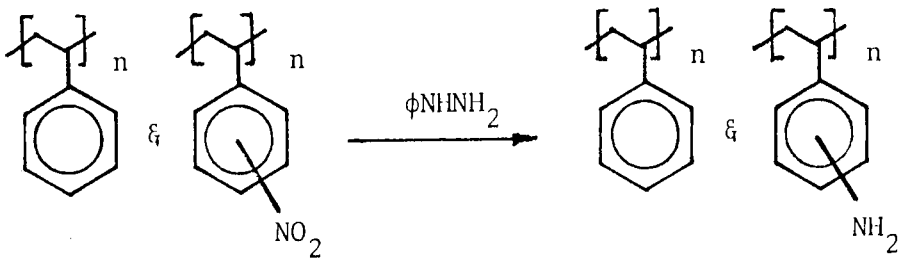
Two different photoreactive polymers have been synthesized by modifying polystyrene (PS) for studying the graft polymerization. The first photoreactive polymer contains the amine functionality and is polystyrene-co-N,N-diethylaminostyrene (PDEA). The second substrate contains the ketone functionality and is poly(styrene-co-vinylbenzophenone) (PBP).

The synthesis of PDEA is detailed in Chapter VI and will only be outlined here. Low molecular weight PS was treated with nitric acid to incorporate nitro groups[84,85] as shown in Equation 31. The PS containing



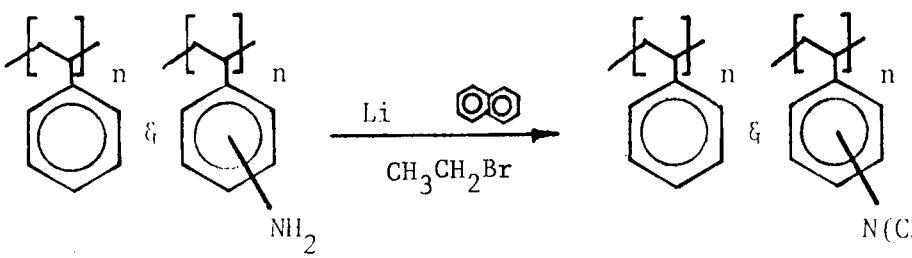
(31)

nitro groups was then treated with hot phenylhydrazine to reduce the nitro groups quantitatively to the amino[84,85] as given in Equation 32. The PS containing amino groups was then converted quantitatively to PDEA



(32)

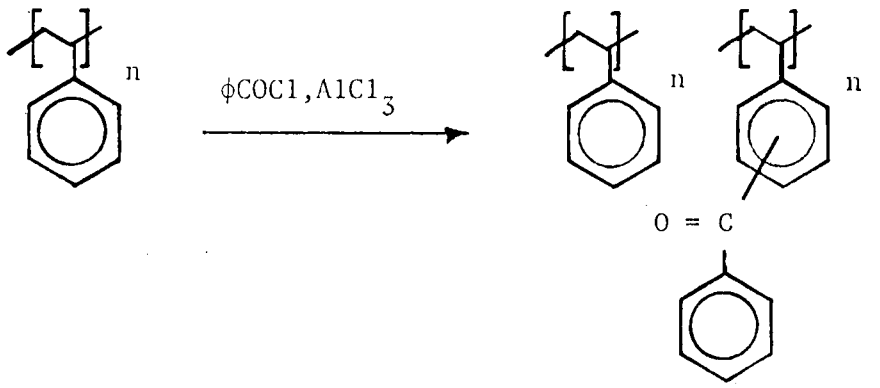
using lithium naphthalenide and ethyl bromide,[86] which is depicted in Equation 33. This is the first reported synthesis of this copolymer.



(33)

However, since the original disclosure of this synthetic pathway,[87] another method of preparing PDEA has appeared,[88] but the two syntheses are completely different.

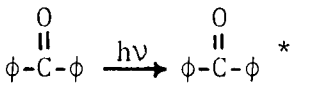
The synthesis of PBP was first reported in 1958 by Merril, Unruh, and Robertson,[89] and, later, Greber and Egle[90] improved on the original synthesis. The copolymer is made by benzoylating PS with benzoyl chloride and aluminum chloride. Equation 34 outlines the synthesis of PBP.



(34)

The photochemistry of PDEA has not previously been investigated, but David, Demarteau, and Geuskens[91] have accomplished a thorough investigation of polyvinylbenzophenone. In discussing their work, polyvinylbenzophenone will be abbreviated PVP to distinguish it from poly(styrene-co-vinylbenzophenone) (PBP) used in the present investigation. David and coworkers initially studied the ultraviolet absorption spectra of BP, PVP, and 4-propylbenzophenone. They reported that the spectrum of 4-propylbenzophenone was identical to that of BP, and the absorption spectrum of PVP which they published is identical to the absorption spectrum of BP[35] in the $n \rightarrow \pi^*$ region.

Next, David and coworkers studied the quantum yield for photoreduction of BP and 4-propylbenzophenone in 2-propanol according to Equation 35 through 38. The quantum yield for acetone formation in this system



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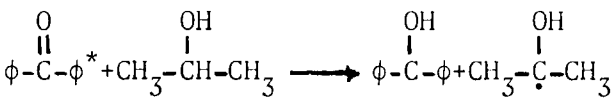

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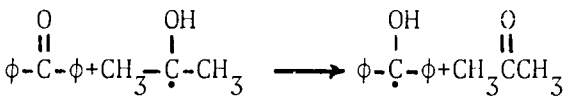
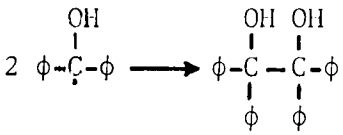


(37)



(38)

approaches unity. Specifically, they found the quantum yield for acetone formation upon irradiation of BP in 2-propanol to be 0.86 and the quantum yield for acetone formation upon irradiation of 4-propylbenzophenone in 2-propanol to be 0.82. These results indicate that the alkyl group of 4-propylbenzophenone has little effect on the photoreduction process.

A similar procedure was used to study PVP. Irradiation of 4-propylbenzophenone with 0.1 M 2-propanol in benzene solution gave a quantum yield of 0.58. However, irradiation of PVP with 0.1 M 2-propanol in benzene gave a quantum yield of 0.25, which was considerably less than the small molecule system. David, Demarteau, and Geuskens proposed that the large difference in quantum yield values was due to the reduced accessibility of the excited state carbonyl inside the macromolecular coil.

David and coworkers also irradiated PVP to determine the fate of the macromolecule. In the analysis of the reaction pathways, they considered three possible processes. The first process was hydrogen abstraction by the excited state carbonyls followed by combination of the formed semibenzpinacol-type radicals leading to cyclization which would decrease the viscosity of the sample. The second process was again hydrogen abstraction by the excited state carbonyl followed by intermolecular radical coupling which would cause gel formation. The third process was composed of reactions of the main chain leading to chain scission which would lower the viscosity of the sample.

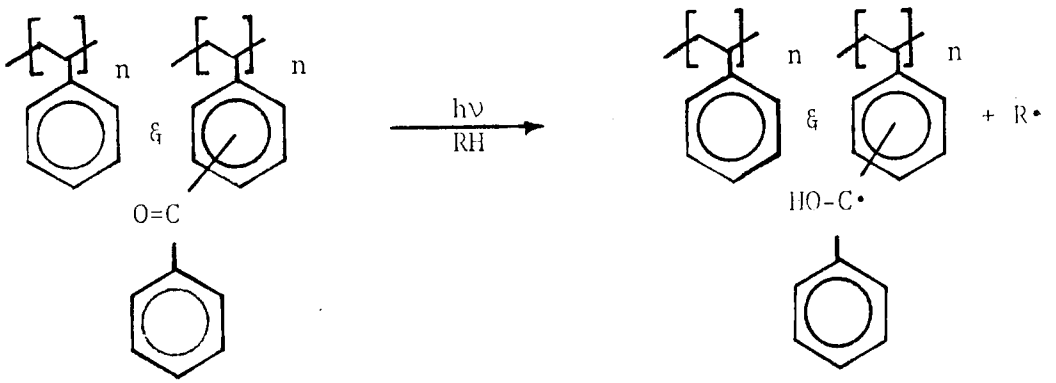
The proposed possible reactions were tested initially with dilute solutions of PVP in benzene which was 0.1 M in 2-propanol. A rapid decrease in viscosity was observed with very little gel formation. These phenomena were attributed to intramolecular cyclization of the radicals. The lack of formation of any appreciable amount of gel eliminated the possibility of extensive intermolecular radical coupling. The viscosity decrease was attributed to intramolecular cyclization and not to rupture of the main chain because of the extremely low quantum yield for propane formation (2×10^{-4}) upon irradiation of 4-propylbenzophenone.

Irradiation of PVP in concentrated solutions or in solid films always led to extensive gel formation. This effect was attributed to intermolecular coupling of radicals. Gel formation as high as 100% was obtained upon prolonged irradiation.

Several significant conclusions can be drawn from the work of David, Demarteau, and Geuskens with respect to irradiation of PBP with hydrogen donors such as DEA. First, in dilute solutions little, if any, gel formation is expected. Second, the photoreactivity of PBP will be significantly reduced from that of BP due to the presence of the macromolecule. Third, irradiation of solutions of BP and PBP containing equivalent concentrations of the carbonyl group will lead initially to equal population of the first excited singlet due to the equivalence of the ultraviolet absorption spectra for BP and PVP.

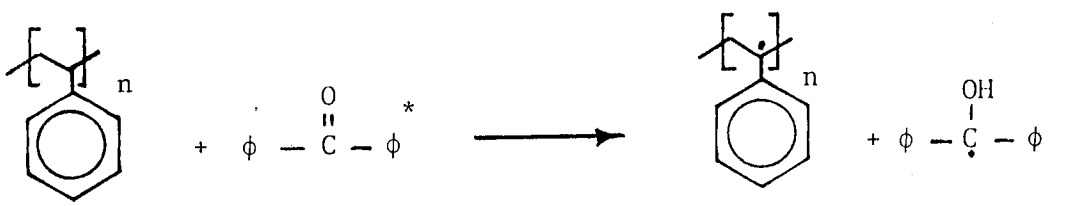
Sumitomo, Nobutoki, and Susaki[92] have studied the photochemistry of PBP and attempted to photochemically graft MMA onto PBP. These workers reported a series of eight reactions in which they used two different temperature ranges, three different concentrations of PBP, two different concentrations of MMA, two different solvents, three different concentrations of methanol as an additive, and two different irradiation times. In view of the wide number of variables employed in a limited number of reactions, analysis of their results in a consistent manner is difficult.

Basically, Sumitomo and coworkers were attempting to form a semibenzpinacol-type radical pendant to the polymer chain as described in Equation 39, where RH is a hydrogen donor. The hydrogen donors employed were MMA, benzene, methanol, and toluene. It is now known that BPH does not initiate polymerization of MMA near room temperature.[76-78] Therefore, this system is not inherently designed for efficient graft formation.



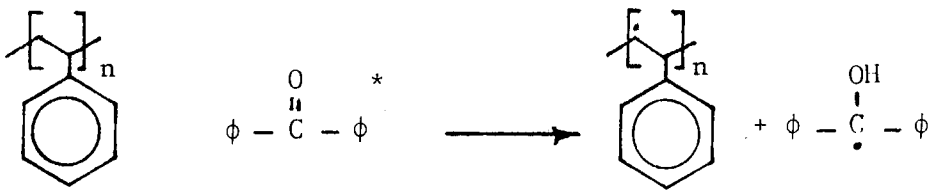
(39)

The various interactions of triplet BP with monomer, solvent, amine, and ground state BP were investigated earlier in Chapter II. It was found that the interaction of triplet BP with amine and monomer dominated the interaction of triplet BP with benzene solvent and ground state BP. Additionally, it was determined experimentally that the interaction between triplet BP and amine led to free radical initiating species much more efficiently than the interaction of triplet BP with the monomer. The reactions in this chapter have an additional complication, and that complication is the presence of a PS or modified PS main chain in the reaction mixture. The possibility exists for triplet BP to abstract hydrogen from the PS methine carbon (Equation 40) or from the PS methylene



(40)

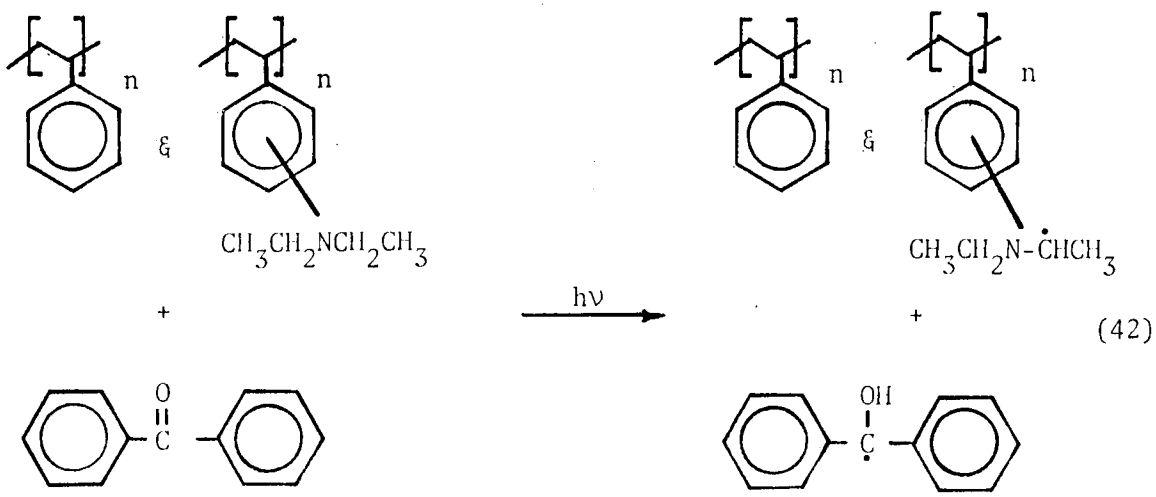
carbon (Equation 41), and these reactions must be investigated. Either of these abstraction reactions would yield a free radical on the PS chain capable of initiating graft polymerization.



(41)

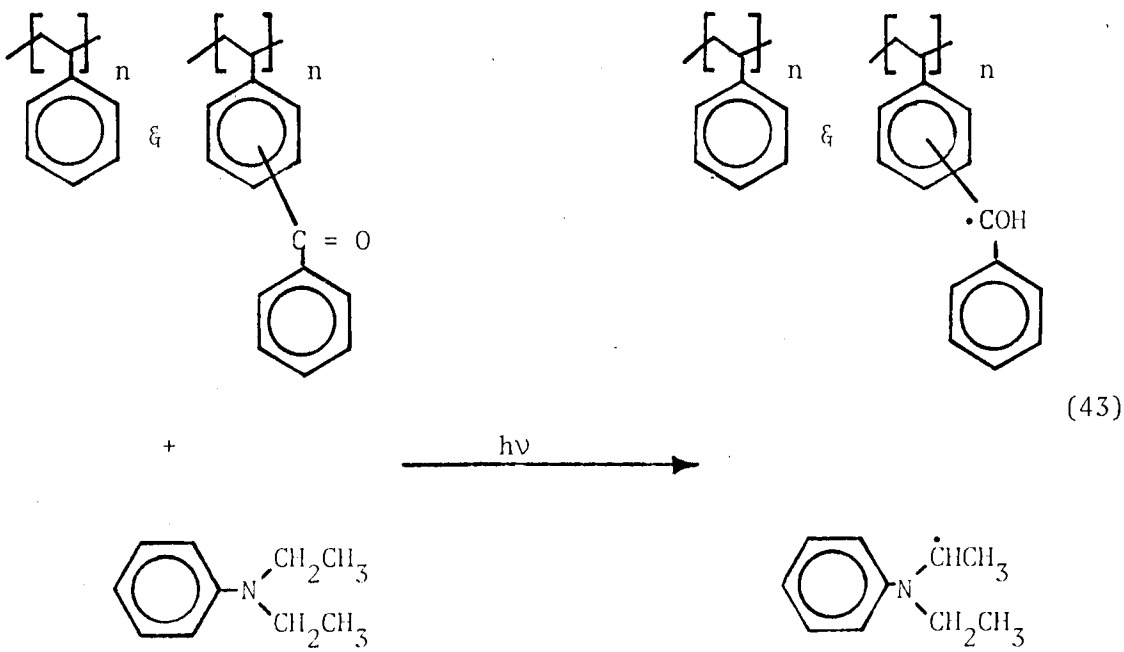
Using toluene as a model for reaction at the methine carbon (Cumene would be a better model, but the rate constant for interaction of cumene with triplet BP is not available), and a repeat unit concentration for PS of 0.1 M, the rate constant for interaction of triplet BP with toluene (8×10^6 M^{-1} sec^{-1})[93] yields a pseudo first order rate constant of 8×10^5 sec^{-1} for the interaction of triplet BP with the methine carbon of PS. Using cyclohexane as a model for the interaction of triplet BP with the methylene carbons of the PS chain, and taking one-sixth of the value of the rate constant for interaction of triplet BP with cyclohexane ($0.17 \times 3.3 \times 10^6$ M^{-1} sec^{-1})[93] to give a value for each methylene carbon, a pseudo first order rate constant of 5.6×10^4 sec^{-1} is calculated for the interaction of triplet BP with the methylene carbon of PS at a repeat unit concentration of 0.1 M. Comparison of either of these values with those given in Table I(p 25) indicates that these interactions are negligible in comparison with the interaction of triplet BP and the amine.

Before discussing the results of the various photochemically induced grafting reactions, the combinations of free radicals to be formed will be described. Irradiation of PDEA and BP is shown in Equation 42. Formation of the two radicals shown in the presence of a reactive monomer should lead primarily to graft formation because the amine-derived



(42)

radical, which is proposed to be the initiating species, is pendant from the PS chain. Irradiation of PBP and DEA is shown in Equation 43. In



(43)

this system the reactive amine-derived radical is not pendant from the PS chain, and homopolymer is expected to be formed upon formation of these two radicals in the presence of a reactive monomer. However, some

graft formation is expected because the semibenzpinacol-type radicals are not sufficiently stable to prevent coupling with growing radical chains.

B. Results and Discussion

While each of the sets of reactions previously described in Chapter II were accomplished with simultaneous irradiation of the reactants, the irradiations to be described in this section were all accomplished individually. The light source appeared to be very stable, but comparisons between reactions must be viewed with the inherent possibility of a slight variation in light intensity. This possible variation would affect the amount of polymer formation observed, but it would not be expected to affect the relative proportions of graft polymer and homopolymer.

The reactions and results are detailed in Table XVI. In each of the six reactions the initial reaction mixture was approximately 1.3% by weight in PS, PBP, or PDEA. Additionally, in each reaction in which a ketone was present, either as BP or PBP, the concentration of ketone was always 0.02 M. The concentration of the amine was always 0.02 M, either as DEA or PDEA.

Inspection of the results of Table XVI shows that significant polymerization is achieved only when both ketone and amine are present in the reaction mixture. However, the combination of BP and PDEA in Reaction XVIE yields significantly more poly(2-ethylhexyl methacrylate) (P2EHMA) than the combination of DEA and PBP in Reaction XVIC. This

TABLE XVI

POLYSTYRENE, POLYSTYRENE COPOLYMERS, 2-ETHYLHEXYL METHACRYLATE, BENZOPHENONE, AND N,N-DIETHYLANILINE COMBINATIONS IN BENZENE SUBJECTED TO ULTRAVIOLET IRRADIATION

Reaction[a]	Polymer Substrate Type	g	Additive Type	g	Vol. ml	[2EHMA] M	[Ketone] M	[Amine] M	P2EHMA Formed g	%
XVI A	PS	0.250	BP	0.091	25	0.50	0.02	0.00	0.031	1.2
XVI B	PS	0.251	DEA	0.080	25	0.50	0.00	0.02	0.040	1.6
XVI C	PBP[b]	0.252	DEA	0.080	25	0.50	0.02	0.02	0.102	4.1
XVI D	PBP[b]	0.251	NONE	0.000	25	0.50	0.02	0.00	0.019	0.8
XVI E	PDEA[c]	0.252	BP	0.091	25	0.50	0.02	0.02	0.277	11.1
XVI F	PDEA[c]	0.250	NONE	0.000	25	0.50	0.00	0.02	0.014	0.6

a. Irradiation time was 300 sec.

b. Poly(styrene-co-vinylbenzophenone) containing 31 mole % vinylbenzophenone.

c. Poly(styrene-co-N,N-diethylaminostyrene) containing 25 mole % N,N-diethylaminostyrene.

apparent decreased reactivity of PBP compared to BP could be due to steric hindrance with respect to exciplex formation between the ketone and the amine. Approach of DEA to the carbonyl of PBP may be sterically hindered by the presence of the adjacent pendant phenyl groups and by the outer phenyl group of the vinylbenzophenone repeat unit. This steric hindrance may not be as great in the PDEA system. The amine functionality is probably para to the main chain, allowing direct approach to the unshared pair of electrons on the amine by the electron deficient orbital of triplet BP.

The actual situation in question is whether graft or homopolymer P2EHMA is formed in Reactions XVIC and E. The homopolymer was extracted from the reaction mixtures, and the results are given in Table XVII. As expected the PBP substrate yields primarily homopolymer while the PDEA substrate yields primarily graft polymer.

In the PBP-DEA system the reactive radical is the small molecule species as previously shown in Equation 43 (p 63) while the semi-benzipinacol-type radical is pendant from the PS chain. Some of the growing P2EHMA chains will react with the semibenzpinacol-type radicals, and it is of interest to investigate the possible interactions. The two interactions are combination, leading to graft formation, and disproportionation, leading to homopolymer formation.

Winnik and coworkers[94] studied the photoreactions of n-alkyl esters of 4-benzophenone carboxylic acid as shown in Equation 44. They found that disproportionation of the intermediate radical back to ketone starting material occurred 5.7 times as often as cyclization. This

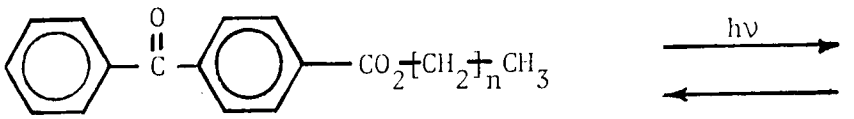
TABLE XVII

DISTRIBUTION OF POLY(2-ETHYLHEXYL METHACRYLATE) AS HOMOPOLYMER AND GRAFT TERPOLYMER

Reaction	Polymer Substrate	% P2EHMA in Homopolymer[a]	% P2EHMA in Graft Terpolymer[b]
XVII A	PBP	69	31
XVII B	PDEA	23	77

a. % P2EHMA in Homopolymer calculated by dividing the amount of homopolymer P2EHMA extracted from the reaction mixture by the total amount of P2EHMA formed and multiplying the result by 100.

b. % P2EHMA in Graft Terpolymer calculated by subtracting % P2EHMA in Homopolymer from 100.



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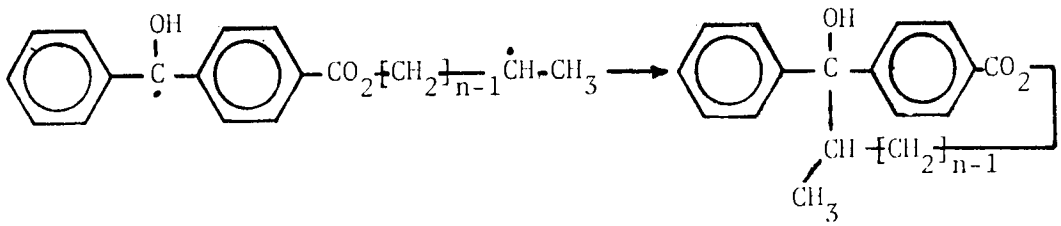


observation is similar to the results of Leaver and Ramsey,[56] previously discussed in Chapter II, that BPH will not add to 2-methyl-2-nitroso-propane, but will only transfer a hydrogen. These data are in qualitative agreement with the results in Table XVII which show that the semi-benzpinacol-type radicals which are pendant from the PBP chain predominantly disproportionate with growing P2EHMA chains instead of coupling.

In addition to reaction with the semibenzpinacol-type radicals, the growing P2EHMA chains could also undergo chain transfer. The most likely site of chain transfer in the PBP substrate would be to the tertiary benzylic carbon on the main chain. This abstraction reaction would terminate the growing homopolymer chain and initiate the growth of grafted polymer, increasing the amount of grafted P2EHMA observed.

The results for graft and homopolymer P2EHMA in the BP-PDEA system are shown in Reaction XVIIB. As described in the experimental discussion in Chapter VI, the value for grafted P2EHMA is a lower limit. This is

due to the extreme changes in solubility of the PDEA substrate upon extensive grafting by P2EHMA. For example, the terpolymer containing large amounts of grafted P2EHMA was slightly soluble in pentane, which is normally a nonsolvent for PS. However, some homopolymer is formed by chain transfer processes. The long alkyl group of the monomer 2EHMA is a likely site for chain transfer. This process would terminate the grafted chain and initiate homopolymer formation.

In summary, two significant conclusions can be drawn from the results discussed in this chapter. First, in spite of the fact that the amine and ketone photoinitiation process has been studied and used widely, this is the first direct observation that the two formed radicals differ in their ability to initiate polymerization. Second, the difference in their ability to initiate polymerization is significant and can be used to selectively and efficiently form graft polymers to suitable substrates in homogeneous solution.

CHAPTER IV

PHOTOCHEMICALLY INDUCED HETEROGENEOUS GRAFT POLYMERIZATION OF METHYL METHACRYLATE AND 2-ETHYLHEXYL METHACRYLATE ONTO MODIFIED POLYETHYLENE

A. Introduction and Background

In the previous chapter it was demonstrated that polymers containing alkyl amines could be reacted with triplet benzophenone (BP) to form reactive amine-derived radicals in homogeneous solution. These radicals initiated the graft polymerization of 2-ethylhexyl methacrylate (2EHMA) onto polystyrene very efficiently. In this chapter reactions will be described in which a similar procedure is used to graft methyl methacrylate (MMA) and 2EHMA onto high density polyethylene (HDPE) film, with the major difference being that the monomer will be grafted heterogeneously to an insoluble substrate suspended in the solution.

HDPE has a very low surface energy,[95] and inks, coatings, and adhesives demonstrate little adhesion to untreated HDPE. Because surface properties have a great deal of influence on the practical usefulness of materials, modification of the surface of HDPE has received a great deal of attention. The most successful treatments involve micropitting the surface to develop very small craters. The ink, coating, or adhesive is then applied and becomes physically adhered to the roughened surface.[96]

Grafting of various polymers to HDPE is important because of the advantageous properties available with different polymers. For example,

poly(methyl methacrylate) (PMMA) has a higher surface energy than HDPE[95] and would promote adhesive bonding. Poly(2-ethylhexyl methacrylate) (P2EHMA) has a surface energy similar to HDPE,[97] but the glass transition temperature of P2EHMA is very low[22] causing it to be a viscous liquid at room temperature, with the adhesive properties inherent with such systems.

The use of BP to photochemically induce graft polymerization has been studied by Oster and his coworkers.[98,99] They used specially prepared polyethylene (PE) into which BP has been milled. Irradiation of this system led to hydrogen abstraction from PE by triplet BP, as seen in Equation 45. The radical site created on the polymer chain was presumed

$$\text{-}[CH_2]\text{-} + \phi\text{-}\overset{\overset{O}{\|}}{C}\text{-}\phi^* \longrightarrow \text{-}[\dot{C}H]\text{-} + \phi\text{-}\overset{\overset{OH}{|}}{\dot{C}}\text{-}\phi \qquad (45)$$

to be the initiating species of free radical graft polymerization.

The system used in the present study did not have the BP incorporated into the HDPE substrate. The insoluble HDPE film employed was suspended in a solution of BP and the monomer, MMA or 2EHMA, in benzene. In view of the short lifetime of triplet BP in benzene solution,[39] it is of interest to obtain an estimation of the fraction of BP triplets in solution which will be capable of diffusing to the HDPE substrate for reaction. Assuming that the BP triplet can be approximated as a spherical particle of radius 0.4 nm, the Stokes-Einstein Equation[100] may be used to calculate its diffusion coefficient. The Stokes-Einstein Equation is given in Equation 46, where D represents the diffusion coefficient, k is Boltzmann's constant, T is the temperature, η is the viscosity of the medium, and r is the radius of the

$$D = \frac{kT}{6\pi\eta r} \tag{46}$$

spherical particle. Einstein[100] related the diffusion coefficient to the distance that the particle will travel in a particular time, and his relationship is given in Equation 47, where X represents distance

$$D = 0.5\ X^2\ \tau^{-1} \tag{47}$$

and τ is the time interval. Combination of Equations 46 and 47 yields Equation 48 in which X represents the distance the particle will diffuse in a particular direction. At a temperature of 30°C, using the lifetime

$$X = \left[\frac{\tau kT}{3\tau\eta r}\right]^{1/2} \tag{48}$$

of triplet BP to be 1×10^{-5} sec in a benzene solution[39] of viscosity 0.564 cp,[101] Equation 48 reveals that triplet BP will diffuse about 1.4×10^{-5} cm before deactivation. Comparison of the distance of diffusion with the depth of the solvent (about 1 cm) shows that only a small fraction of the BP triplets will be active in forming free radicals on the HDPE substrate capable of initiating free radical polymerization.

In view of the apparently low efficiency of this system to initiate graft polymerization, a comparison with Oster's process[98,99] is required. In the majority of the systems that were employed by Oster to photochemically induce graft polymerization, BP was blended into the PE. Upon irradiation, some of the BP triplets would abstract hydrogen to

form reactive radicals on the polymer chain. However, the efficiency of those radicals formed inside the substrate is subject to diffusion effects. First, the semibenzpinacol radical formed would not be capable of easy diffusion away from the polymer radical because of the highly viscous nature of the solid polymer. A large percentage of these radicals would disproportionate or couple resulting in no graft polymerization. Second, formation of graft polymers would be dependent on the relatively slow diffusion of the monomer into the substrate. Formation of these types of graft polymers, inside the substrate, might change the physical properties of the substrate but would probably not have a significant effect on the surface properties. The BP which was near the surface of the substrate would not be as highly affected by the radical recombination and monomer diffusion problems. However, if BP is soluble, even to a small extent, in the solution containing the monomer, the BP near the surface of the polymer substrate will tend to diffuse out into the solution.

The problems inherent in blending the BP with the PE substrate are not present in the system under present consideration. The primary site of reaction should be near the substrate surface where triplet BP abstracts hydrogen to form reactive radicals which initiate graft polymerization of the monomer. This process depletes the concentration of both monomer and BP near the substrate, and the concentration gradient thus formed will cause diffusion of more BP and monomer toward the substrate, allowing further graft polymerization to occur.

The presence of the absorbing species, BP, in the solution around the PE substrate does create a problem not found in Oster's system. That problem is an "inner-filter" effect caused by the radiation having to pass through a considerable amount of solution before reaching the reaction zone near the substrate. An estimate of the magnitude of this effect can be calculated using Equation 49,[102] where A is absorbance,

$$A = \varepsilon\, b\, C \tag{49}$$

ε is the molar absorptivity, b is the path length, and C is the molar concentration. The molar absorptivity for BP at 366 nm, the wavelength of greatest emission of energy of the lamps employed,[36] is about 55 $\underline{M}^{-1}$ cm^{-1}.[35] For a path length of 0.5 cm at a BP concentration of 0.02 $\underline{M}$. Equation 49 yields an absorbance of 0.55. This value of absorbance can be related to transmittance (T) by means of Equation 50,[102] which yields

$$A = \log T^{-1} \tag{50}$$

a transmittance of 0.28 for an absorbance of 0.55. Thus, the majority of the radiation will be absorbed by the BP in solution, but a sufficient amount should reach the region near the substrate for the photoreaction to occur.

In Chapter II it was demonstrated that both MMA and 2EHMA in benzene solution undergo a small amount of polymerization upon irradiation, and that addition of only BP does not significantly increase that amount. However, comparison of the reactive zone for graft polymer formation around the film substrate (about 3×10^{-5} cm considering both top and

bottom of the film) with the total depth of solution (about 1 cm) allows the prediction that the majority of polymer formation will not be due to graft formation, but it will occur as a result of irradiation of the solution away from the substrate. This process will then yield inherently low graft efficiency, which is defined as the amount of graft polymer formed, divided by the total amount of graft and homopolymer formed. Additionally, the low efficiency of polymer formation in solutions containing only BP, monomer, and benzene allows the added prediction that the percent conversion of monomer to polymer per unit time will also be relatively low.

The preceding discussion indicates that the process of grafting MMA or 2EHMA to HDPE will be a very inefficient process. However, the surface of the substrate represents only a minute portion of the bulk of the material. The HDPE film used in the present study was about 0.038 mm in thickness. If the surface is considered to be the outer 20 Å of both the top and bottom of the film,[103] it constitutes only about 1×10^{-2}% of the total thickness. If the density of the surface region is the same as the density of the bulk of the film, the weight of the surface is also only about 1×10^{-2}% of the total weight of the film. Therefore, an increase in film weight of only 1% due to polymer grafted to the surface of the film could cause dramatic changes in the surface properties.

As previously stated, the HDPE will be modified by incorporation of alkyl amine groups to enhance hydrogen abstraction from the polymer substrate by triplet BP. The route taken to incorporate the amine functionality included photochlorination of the substrate followed by

reaction with the amine. The mechanism of photochlorination of PE is well known[104] and is given in Equations 51 through 54. At low degree of

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\cdot \tag{51}$$

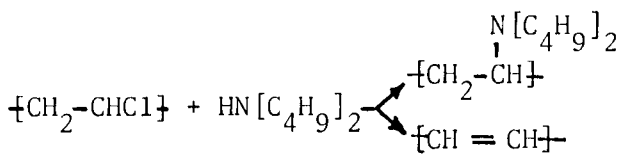
$$Cl\cdot + \text{-}CH_2\text{-} \longrightarrow \text{-}\dot{C}H\text{-} + HCl \tag{52}$$

$$\text{-}\dot{C}H\text{-} + Cl_2 \longrightarrow \text{-}CHCl\text{-} + Cl\cdot \tag{53}$$

$$\text{-}\dot{C}H\text{-} + Cl\cdot \longrightarrow \text{-}CHCl\text{-} \tag{54}$$

chlorination the monochlorinated methylene unit is formed,[21,105] but at a high degree of chlorination (about 20% by weight) the gem-dichlorinated units begin to occur.

Adylov, Ilina, Krentsel, and Shishkina[106] have studied the reaction of several amines with chlorinated high density polyethylene (CLPE). The amines they studied included aniline, dibutylamine, and ammonia, and their CLPE contained between 1.29% and 60.86% chlorine. (It must be noted that the abstract[106] of this paper is incorrect in that it reports N,N-dibutylaniline instead of dibutylamine and 6.86% instead of 60.86% chlorine.) It was found that dehydrochlorination occurred in addition to amination, as shown in Equation 55. Also, these workers found that the percentage of dehydrochlorination increased as the chlorine percent in the substrate increased.



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The procedure employed for formation of the CLPE used in the present study is detailed in Chapter VI and basically consists of irradiation of HDPE mounted in the center of a cell containing gaseous chlorine. The CLPE thus formed was reacted with diethylamine to form the diethylaminated polyethylene (NEPE) substrate.

After formation of NEPE, the surface of the substrate will probably contain amine groups, unsaturated ethylenic units, and methylene groups. Previously in Chapter III it was found that interaction of triplet BP with alkyl amines predominated over the interaction of triplet BP with methylene units. Additionally, in Chapter II it was found that the interaction of triplet BP with olefins was efficient, but that it results primarily in quenching of triplet BP. Therefore, it is expected that interaction of triplet BP with NEPE will result primarily in formation of amine-derived radicals by hydrogen abstraction from the carbon atom alpha to the nitrogen atom of the amine. However, the concentration of amine groups is low, and some hydrogen abstraction from the methylene units will probably occur.

B. Results and Discussion

The photoreactions described in this section were accomplished in groups of three. Each group of three received equal amounts of

irradiation while being rotated in the photoreactor. This procedure allows direct comparison between reactions within a particular group, but comparisons between reactions in different groups must be viewed with the inherent possibility of a slight change in light intensity.

When preparing the polymeric substrates for the photoinitiated grafting reactions, difficulties were encountered in attaining samples of identical size and weight; this will cause some variance in the total percent conversion of monomer to polymer and in the observed graft efficiency. Therefore, the most valid comparison between reactions is a comparison of the percent by weight of P2EHMA or PMMA in the grafted film.

The results for grafting 2EHMA to HDPE, CLPE, and NEPE are given in Table XVIII. As expected, the percent conversion of 2EHMA to P2EHMA and the percent graft efficiency are low. However, comparison of the percent by weight of P2EHMA in the grafted film demonstrates the effectiveness of the addition of amine groups to the polymer substrate. The presence of some grafted P2EHMA with the HDPE and CLPE indicates that some hydrogen abstraction by triplet BP from the methylene carbons is occurring.

To optimize the conditions for incorporation of the maximum amount of grafted P2EHMA, the effects of percent chlorine and the temperature of the reaction of diethylamine with CLPE were studied. The results are given in Table XIX, in which each vertical column represents a set of three photoinitiated grafting reactions. Inspection of the first two columns indicates that the grafting of 2EHMA maximizes at an N,N-diethylamination temperature of 50°C, while the last column indicates a

TABLE XVIII

PHOTOINITIATED GRAFTING OF 2-ETHYLHEXYL METHACRYLATE TO HIGH DENSITY POLYETHYLENE

Polymer Substrate[a]	Original Substrate g	Grafted Substrate g	P2EHMA g	Percent Conversion	P2EHMA Grafted g	Percent Graft Efficiency	Percent P2EHMA[d]
HDPE	0.0664	0.0688	0.0724	2.92	0.0024	3.31	3.49
CLPE[b]	0.0659	0.0690	0.0641	2.58	0.0031	4.48	4.49
NEPE[c]	0.0635	0.0714	0.0779	3.14	0.0079	10.14	11.06

a. Substrate irradiated for 30 min in a benzene solution which was 0.02 M in BP and 1.0 M in 2EHMA.

b. 3.47 % Cl by weight.

c. NEPE formed by reacting CLPE with 0.88 M diethylamine in toluene for 12 hr at 50°C.

d. Percent P2EHMA = $\frac{\text{grafted substrate - original substrate}}{\text{grafted substrate}} \times 100\%$

TABLE XIX

EFFECT OF PERCENT CHLORINE AND N,N-DIETHYLAMINATION TEMPERATURE ON THE PHOTOINITIATED GRAFTING OF 2-ETHYLHEXYL METHACRYLATE TO HIGH DENSITY POLYETHYLENE

Percent Chlorine[a]	Reaction Temperature[b] °C	Percent P2EHMA[c,d]	Percent Chlorine[a]	Reaction Temperature[b] °C	Percent P2EHMA[c,d]	Percent Chlorine[a]	Reaction Temperature[b] °C	Percent P2EHMA[c,d]
1.99	20	5.43	3.45	20	5.85	4.91	20	6.28
1.99	50	6.51	3.45	50	8.53	4.91	50	4.94
1.99	80	4.21	3.45	80	5.73	4.91	80	3.45

a. Percent Chlorine = Chlorine percent by weight of CLPE before reaction with diethylamine.

b. Temperature of reaction of a 0.88 M diethylamine in toluene with CLPE for 25 hr.

c. Percent P2EHMA = $\frac{\text{grafted substrate - original substrate}}{\text{grafted substrate}} \times 100\%$

d. Substrate irradiated for 30 min in a benzene solution which was 0.02 M in BP and 0.5 M in 2EHMA.

continual decrease as the temperature is raised. These results are indicative of at least three competing influences for the formation of the amine functionality and the occurrence of the dehydrochlorination reaction. First, the CLPE substrate is insoluble in the toluene solvent at all three temperatures employed. However, some solvent swelling of the substrate may occur, and this process will increase as the temperature is raised, allowing more reaction of the amine. Second, Adylov[106] found that the relative proportion of dehydrochlorination increased as the percent chlorine increased, and this effect is probably beginning to appear at the highest percent chlorine substrate. Third, the activation parameters for the two competing processes favor an increase in dehydrochlorination over amination as the temperature is increased.[107]

The effect of the time of the reaction of diethylamine with CLPE was also investigated, and the results are presented in Table XX. The data indicate that the greatest incorporation of grafted P2EHMA is obtained at an amine reaction time of 12 hr. This effect is unusual and may be due to increased dehydrochlorination at long reaction times, resulting in less hydrogen abstraction from methylene units. Some of the chlorinated methylene units may be sterically constrained from undergoing amine substitution, but they may eventually undergo dehydrochlorination.

The same series of reactions were accomplished using MMA instead of 2EHMA, and the results are presented in Tables XXI through XXIII. The data are not as definitive as those for 2EHMA, but the same trends are present. The decreased effectiveness for MMA as compared to 2EHMA is

TABLE XX

EFFECT OF TIME OF REACTION OF DIETHYLAMINE WITH CHLORINATED POLYETHYLENE ON THE PHOTOINITIATED GRAFTING OF 2-ETHYLHEXYL METHACRYLATE TO HIGH DENSITY POLYETHYLENE

Reaction Time[a] hr	Original Substrate g	Grafted Substrate g	P2EHMA g	Percent Conversion	P2EHMA Grafted g	Percent Graft Efficiency	Percent P2EHMA[b,c]
6	0.0796	0.0857	0.1491	6.01	0.0061	4.09	7.12
12	0.0724	0.0793	0.1770	7.14	0.0069	3.90	8.67
24	0.0782	0.0834	0.1698	6.85	0.0052	3.06	6.23

a. Time of reaction of 0.88 M diethylamine in toluene with CLPE (3.50% chlorine by weight) at 50°C.

b. Percent PMMA = $\frac{\text{grafted substrate - original substrate}}{\text{grafted substrate}} \times 100\%$

c. Substrate irradiated for 30 min in a benzene solution which was 0.02 M in BP and 0.5 M in 2EHMA.

TABLE XXI

PHOTOINITIATED GRAFTING OF METHYL METHACRYLATE
TO HIGH DENSITY POLYETHYLENE

Polymer Substrate[a]	Original Substrate g	Grafted Substrate g	PMMA g	Percent Conversion	PMMA Grafted g	Percent Graft Efficiency	Percent PMMA[d]
HDPE	0.0718	0.0744	0.0829	3.32	0.0026	3.14	3.49
CLPE[b]	0.0640	0.0661	0.0550	2.20	0.0021	3.82	3.18
NEPE[c]	0.0621	0.0649	0.0544	2.18	0.0028	5.15	4.31

a. Substrate irradiated for 30 min in a benzene solution which was 0.02 M in BP and 1.0 M in MMA.

b. 3.47 % Cl by weight.

c. NEPE formed by reacting CLPE with 0.88 M diethylamine in toluene for 12 hr at 50°C.

d. Percent PMMA = $\frac{\text{grafted substrate - original substrate}}{\text{grafted substrate}} \times 100\%$

TABLE XXII

EFFECT OF PERCENT CHLORINE AND N,N-DIETHYLAMINATION TEMPERATURE ON THE PHOTOINITIATED GRAFTING OF METHYL METHACRYLATE TO HIGH DENSITY POLYETHYLENE

Percent Chlorine[a]	Reaction Temperature[b] °C	Percent PMMA[c,d]	Percent Chlorine[a]	Reaction Temperature[b] °C	Percent PMMA[c,d]	Percent Chlorine[a]	Reaction Temperature[b] °C	Percent PMMA[c,d]
1.40	20	2.87	2.96	20	3.19	4.12	20	3.15
1.40	50	4.06	2.96	50	3.18	4.12	50	2.55
140	80	3.36	2.96	80	2.26	4.12	80	2.59

a. Percent Chlorine = chlorine percent by weight of CLPE before reaction with diethylamine.

b. Temperature of reaction of 0.88 M diethylamine in toluene with CLPE for 25 hr.

c. Percent PMMA = $\frac{\text{grafted substrate - original substrate}}{\text{grafted substrate}} \times 100\%$

d. Substrate irradiated for 30 min in a benzene solution which was 0.02 M in BP and 1.0 M in MMA.

TABLE XXIII

EFFECT OF TIME OF REACTION OF DIETHYLAMINE WITH CHLORINATED POLYETHYLENE ON THE PHOTOINITIATED GRAFTING OF METHYL METHACRYLATE TO HIGH DENSITY POLYETHYLENE

Reaction Time[a] hr	Original Substrate g	Grafted Substrate g	PMMA g	Percent Conversion	PMMA Grafted g	Percent Graft Efficiency	Percent PMMA[b,c]
6	0.0711	0.0728	0.0467	1.87	0.0017	3.64	2.34
12	0.0681	0.0707	0.0594	2.38	0.0027	4.55	3.82
24	0.0657	0.0681	0.0414	1.66	0.0024	5.80	3.52

a. Time of reaction of 0.88 M diethylamine in toluene with CLPE (3.13% chlorine by weight) at 50°C.

b. Percent PMMA = $\frac{\text{grafted substrate - original substrate}}{\text{grafted substrate}} \times 100\%$

c. Substrate irradiated for 30 min in a benzene solution which was 0.02 M in BP and 1.0 M in MMA.

probably due to the previously observed higher rate of free radical polymerization for 2EHMA and because the mass of a 2EHMA unit is almost twice that of MMA. The results in Table XXI demonstrate the increased effectiveness of NEPE over HDPE and CLPE with respect to weight percent grafting of MMA. The effect of percent chlorine and the temperature and time of the N,N-diethylamination reaction are given in Tables XXII and XXIII, and the trends observed are similar to the 2EHMA results.

In summary, analysis of the ultraviolet radiation induced grafting of reactive monomers to insoluble substrates indicates that placement of the photoinitiating system near the surface of the substrate should be superior to placement inside the substrate. Similar to the results of Oster and coworkers, irradiation of BP was found to lead to hydrogen abstraction from the PE substrate leading to initiation of graft polymerization. However, it has been demonstrated that incorporation of alkyl amine groups on the substrate will enhance the formation of free radicals capable of initiating graft polymerization.

CHAPTER V

PHOTOCHEMICAL INTERACTION OF NITROGEN OXIDES AND NITROSYL CHLORIDE WITH POLYETHYLENE

A. Introduction and Background

In the previous chapter it was shown that alkyl amines incorporated onto high density polyethylene (HDPE) could be reacted with triplet benzophenone to form radicals on the HDPE which were capable of initiating graft polymerization. The efficiency of grafting could be increased by a greater concentration of alkyl amine groups on the substrate. With the objective of finding a pathway of efficient formation of carbon-nitrogen bonds on HDPE, a study of the photochemical interactions of nitrosyl chloride (NOCl) with HDPE was undertaken.

In 1919 Lynn[108] placed NOCl in heptane and found that the reddish-brown solution turned blue upon exposure to sunlight, and he eventually isolated various heptanones from the reaction mixture. Lynn repeated the experiment in 1922[109] and proposed that the blue color was due to an intermediate nitroso compound. He suggested that the nitroso compound rearranged to the oxime which was eventually hydrolyzed to the ketone, primarily 4-heptanone. Lynn's pathway for the process is shown in Equations 56 through 58. Interest in Lynn's discovery remained fairly

$$CH_3\text{-}(CH_2)_4\text{-}CH_3 + ClNO \xrightarrow{h\nu} C_3H_7 - \underset{\displaystyle NO}{\underset{|}{CH}} - C_3H_7 \qquad (56)$$

$$C_3H_7-\overset{NO}{\overset{|}{C}}H-C_3H_7 \longrightarrow C_3H_7-\overset{NOH}{\overset{\|}{C}}-C_3H_7 \quad (57)$$

$$C_3H_7-\overset{NOH}{\overset{\|}{C}}-C_3H_7 + H_2O \xrightarrow{H^+} C_3H_7-\overset{O}{\overset{\|}{C}}-C_3H_7 \quad (58)$$

dormant until the early 1950's when Eugen Müller[110] initiated a series of investigations on photooximation of hydrocarbons.

The initial reaction upon irradiation of NOCl with light of wavelength shorter than 500 nm is cleavage of the nitrogen-chlorine bond[111] as shown in Equation 59. The chlorine radical abstracts hydrogen from

$$ClNO \xrightarrow{h\nu} Cl\cdot + NO \quad (59)$$

the alkane to form hydrogen chloride (HCl) as seen in Equation 60, where

$$Cl\cdot + R\text{-}CH_2\text{-}R' \longrightarrow R\text{-}\dot{C}H\text{-}R' + HCl \quad (60)$$

R and R' represent alkyl groups. The nitric oxide (NO) formed upon photolysis of NOCl then couples with the alkyl radical as shown in Equation 61. The formed nitroso compound then rearranges to the oxime.

$$R\text{-}\dot{C}H\text{-}R' + NO \longrightarrow R\text{-}\overset{NO}{\overset{|}{C}}H\text{-}R' \quad (61)$$

Müller developed this reaction until he was able to photochemically synthesize cyclohexanone oxime from cyclohexane in very high yield with few complicating side reactions.

Cyclohexanone oxime is important industrially because it can be converted by way of the Beckmann rearrangement[112] to ε-caprolactam, the monomer from which poly(ε-caprolactam) (Nylon 6) is prepared.[111] A plant is in operation in Japan which utilizes the nitrosyl chloride route to ε-caprolactam,[1] and this reaction has been deemed the first synthetic photochemical reaction of industrial importance.[111]

While the present work was in progress two reports appeared describing the photochemical reaction of NOCl with HDPE. Pozzi, Silvers, Giuffrè, and Cernia[113] attempted to use the reaction to form oximes on the polymer, and they treated the reaction product with a mixture of hydrochloric acid, ethanol, and water to hydrolyze the expected oxime to the carbonyl. These workers were attempting to synthesize a photodegradable polymer which would decompose in sunlight. They gave no experimental details proving that the oxime or the carbonyl was actually formed, but the modified HDPE did undergo degradation upon exposure to sunlight.

Degtyareva, Kochan, Luk'yanchuk, and Shrubovich[114] soon followed with a more complete investigation on the photochemical interaction of NOCl and HDPE. These workers used infrared (IR) spectrophotometry to identify the products of the reaction. They reported the presence of the oxime, the gem-chloronitroso group, and chlorinated hydrocarbon. These products are detailed in Equation 62. The presence of the oxime

$$\text{-}[CH_2]_n\text{-} + ClNO \xrightarrow{h\nu} \text{-}\overset{NOH}{\overset{\|}{C}}\text{-} + \text{-}\overset{NO}{\overset{|}{C}}Cl\text{-} + \text{-}\overset{Cl}{\overset{|}{C}}H\text{-} \qquad (62)$$

was expected based on the results of the reaction with low molecular weight hydrocarbons. The presence of the gem-chloronitroso group was not unexpected, because it is the product of the reaction of NOCl with an oxime,[115,116] as seen in Equation 63. Additionally, precedence for the

$$\text{-C(=NOH)-} + \text{ClNO} \longrightarrow \text{-C(NO)Cl-} \qquad (63)$$

chlorinated methylene group can be found in the early work of Müller[110] who isolated trace amounts of chlorinated hydrocarbons during photochemical reactions of NOCl with low molecular weight hydrocarbons.

These data provide support for the supposition that NOCl could be used to form carbon-nitrogen bonds on HDPE. Lithium aluminum hydride can be used to reduce the gem-chloronitroso to the oxime[117] and to convert the chlorinated methylene to the hydrocarbon,[118] which would yield clean formation of the oxime.

B. Results and Discussion

Photolysis of NOCl with HDPE caused the colorless polymer to turn blue, indicative of nitroso compounds which absorb in the 630-790 nm region of the visible spectrum.[119] Significant changes were observed in the IR spectrum of the polymer, as additional absorptions appeared at 1629, 1581, 1275, 863, 668, and 612 cm^{-1} while weak absorptions at 1640 and 910 cm^{-1} disappeared. The absence of any change in absorption in the O - H stretch region, approximately 3500 cm^{-1}, was noteworthy because the oxime should have a strong absorption in this region.[120] Additionally,

the carbon-nitrogen double bond of alkyl ketoximes[121] should absorb in the range of 1652-1682 cm^{-1}, but no absorption was present in this region of the IR spectrum. These results indicate that the oxime is not formed and dictate a detailed investigation of the products of the reaction observed in the IR spectrum.

Delineation of the disappearance of absorption at 1640 and 910 cm^{-1} is straightforward. These absorptions are due to residual unsaturation in the HDPE,[96] and their disappearance is due to addition of NOCl to the double bond[122] as given in Equation 64.

$$\text{-CH=CH-} + \text{ClNO} \longrightarrow \text{-CHCl-}\underset{\displaystyle \text{NO}}{\underset{|}{\text{CH}}}\text{-} \qquad (64)$$

Several studies have been accomplished on the IR spectra of gem-chloronitroso compounds, and the absorptions of the N = O stretch are listed in Table XXIV. The strong correlation between the new absorption at 1581 cm^{-1} and the values for the gem-chloronitroso compounds suggest assignment of the 1581 cm^{-1} absorption to the gem-chloronitroso group, which probably originates from reaction of NOCl with the oxime, as described in Equation 63 (p 90).

Further reactions confirm this assignment. Nitroso compounds are easily oxidized,[119] and gem-chloronitrosoalkanes are oxidized by air to gem-chloronitroalkanes.[126] Exposure of the blue HDPE photoproduct to air resulted in disappearance of both the blue color, characteristic of nitroso groups, and the absorption at 1581 cm^{-1}. Concurrently, a new absorption appeared at 1561 cm^{-1}, which should be due to the asymmetric

TABLE XXIV

NITROGEN-OXYGEN STRETCH ABSORPTIONS IN THE INFRARED SPECTRA OF GEM-CHLORINITROSOALKANES

Compound	Absorption(cm^{-1})	Reference
2-Chloro-2-nitrosopropane	1570-1587	123
	1587	124
2-Chloro-2-nitrosobutane	1568-1585	123
3-Chloro-3-nitrosopentane	1572-1586	123
2-Chloro-2-nitroso-3,3-dimethylbutane	1570-1584	123
1-Chloro-1-nitrosocyclohexane	1564-1577	123
	1572	124
	1577	125
1-Chloro-1-nitrosocyclopentane	1568-1578	123

stretch of the gem-chloronitro group. Brown[127] has studied the IR spectrum of 2-chloro-2-nitropropane and assigned the absorption at 1565 cm^{-1} to the asymmetric stretch and the absorption at 1342 cm^{-1} to the symmetric stretch of the nitro group. The correlation between the 1561 cm^{-1} absorption in the oxidized HDPE photoproduct and Brown's assignment provides evidence for assignment of the 1561 cm^{-1} absorption as the gem-chloronitro functionality. The symmetric stretch of the gem-chloronitro group should occur at about 1342 cm^{-1}, in analogy to Brown's results, but delineation of an absorption in this region assignable to the nitro group was not possible because of the presence of the methylene deformation of HDPE.[96]

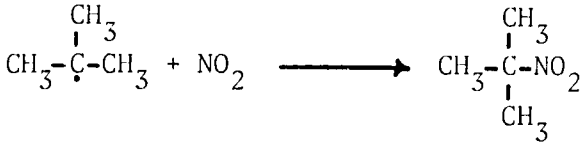
To provide further support for the assignment of the absorption at 1561 cm^{-1} to the gem-chloronitro group, one can look at the nitro groups incorporated into HDPE upon irradiation with nitrogen dioxide (NO_2). Jellinek and coworkers[128] irradiated NO_2 with low density PE and reported incorporation of nitro groups in the polymer, but the IR spectral data reported was not sufficiently precise for use in this study. Blacet, Hall, and Leighton[129] studied the photolysis of NO_2 with 2-methylpropane and determined the mechanism of the reaction upon irradiation at 313 nm to be as described in Equations 65 through 68. NO_2 absorbs over a wide

$$NO_2 \xrightarrow{h\nu} NO + O \tag{65}$$

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_3 + O \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\bullet}{C}}}-CH_3 + \dot{O}H \tag{66}$$



(67)



(68)

range of the visible and ultraviolet region,[130] and Gaedtke and Troe[131] demonstrated that irradiation of NO_2 at wavelengths shorter than 400 nm results in photolysis of NO_2 to yield NO and an oxygen atom, as found by Blacet, Hall, and Leighton[129] at 313 nm. Therefore, the mechanism of the reaction of NO_2 with HDPE upon irradiation at 366 nm as accomplished in this study, should be similar to that given in Equations 65 through 68. The IR spectrum of the photoproduct of the photolysis of NO_2 with HDPE exhibited a new absorption at 1567 cm^{-1}, which is assigned to the asymmetric stretch of a nitroalkane, in analogy to the results of Blacet, Hall, and Leighton.[129] The symmetric stretch of the nitro group is again not observable due to the methylene deformation of HDPE.[96] The correlation between the value of 1567 cm^{-1} for the asymmetric stretch of the alkyl nitro group provides further support for the assignment of the 1561 cm^{-1} absorption to the asymmetric stretch of the gem-chloronitro group, which further supports the assignment of the original 1581 cm^{-1} absorption to the gem-chloronitroso functionality.

The absorptions which appear at 668 and 612 cm^{-1} upon irradiation of NOCl with HDPE fall in the carbon-chlorine stretch region. Lüttke[124] studied the IR spectra of 2-chloropropane and 2-chloro-2-nitrosopropane,

and he assigned the absorption at 612 cm^{-1} in 2-chloropropane and the absorption at 674 cm^{-1} in 2-chloro-2-nitrosopropane to the carbon-chlorine stretch. In view of Lüttke's results, the absorption at 668 cm^{-1} may be assigned to the carbon-chlorine stretch of the gem-chloronitroso group, and the absorption at 612 cm^{-1} may be assigned to the carbon-chlorine stretch of the chlorinated hydrocarbon. However, the situation is not this simple.

HDPE was irradiated with chlorine, and the IR spectrum of the photoproduct polymer also showed new absorptions at 668 cm^{-1} and 612 cm^{-1}. Quenum, Berticat, and Vallet[105] have reported an extensive study of the IR spectra of PE chlorinated to various extents. They assigned a band between 610 and 615 cm^{-1} to the carbon-chlorine stretching mode of ⟨CHCl⟩ units in a poly(vinyl chloride) syndiotactic sequence. Additionally, they assigned a band at 660 cm^{-1} to ⟨CHCl⟩ units surrounded by PE sequences. These results allow the assignment of the absorptions at 668 and 612 cm^{-1} to various stretching modes of carbon-chlorine bonds, but specific assignment of the carbon-chlorine stretch in the gem-chloronitroso group is not possible.

The remaining unassigned changes in the IR spectrum of HDPE after irradiation with NOCl are the new absorptions which appear at 1629, 1275, and 863 cm^{-1}. These absorptions are characteristic of an alkyl nitrate, and Carrington[132] has reported an extensive study on the IR spectra of organic nitrates. He assigned the region of 1626-1639 cm^{-1} to the asymmetric stretch of the nitrate, and by analogy the 1629 cm^{-1} absorption is similarly assigned. Additionally, he assigned the 1272-1282 cm^{-1}

region to the symmetric stretch of the nitrate, and, therefore, the 1275 cm^{-1} absorption is also assigned to this mode. Finally, Carrington assigned the O - NO_2 stretch to the 855-870 cm^{-1} region, and this correlates strongly with the observed value of 863 cm^{-1} in the photoproduct HDPE spectrum. The presence of significant concentrations of the nitrate group was not expected, but further evidence for its presence will be given later.

Table XXV presents a summary of the IR assignments made for the photoreaction of NOCl with HDPE accomplished in this study, and Table XXVI gives the assignments made by Degtyareva, Kachan, Luk'yanchuk, and Shrubovich.[114] There are significant differences between the assignments.

In Table XXVI it may be noted that Degtyareva and coworkers assigned absorptions at 1560 cm^{-1} and 1720 cm^{-1} to the N = O stretch of the gem-chloronitroso group. While two absorptions for the N = O stretch have been previously observed,[124] the splitting was attributed to rotational isomerization and was not nearly as great as that proposed by Degtyareva. Additionally, both values are outside the range for the N = O stretch for gem-chloronitroso compounds previously detailed in Table XXIV (p 92). Earlier the value of 1561 cm^{-1} was assigned to the asymmetric stretch of the gem-chloronitro group, and it is probable that the absorption at 1560 cm^{-1} reported by Degtyareva and coworkers is due to this functionality, formed by oxidation of the nitroso before the IR spectrum was accomplished. Also seen in Table XXVI is the assignment by Degtyareva of the absorption at 1630 cm^{-1} to the C = N stretch of the oxime. This value is outside the range of 1652-1682 cm^{-1} given by

TABLE XXV

INFRARED SPECTRAL ASSIGNMENTS OF THE PRODUCTS OF THE PHOTOREACTION OF NITROSYL CHLORIDE WITH HIGH DENSITY POLYETHYLENE

Absorption (cm^{-1})	Assignment
1581	N = O stretch of $-\overset{\overset{\displaystyle NO}{\vert}}{C}Cl-$
668,612	C - Cl stretch of $-\overset{\overset{\displaystyle Cl}{\vert}}{C}H-$ and/or $-\overset{\overset{\displaystyle NO}{\vert}}{C}Cl-$
1629	Asymmetric stretch of $-NO_2$ in $-\overset{\overset{\displaystyle O-NO_2}{\vert}}{C}H-$
1275	Symmetric stretch of $-NO_2$ in $-\overset{\overset{\displaystyle O-NO_2}{\vert}}{C}H-$
863	O - NO_2 Stretch of $-\overset{\overset{\displaystyle O-NO_2}{\vert}}{C}H-$

TABLE XXVI

INFRARED SPECTRAL ASSIGNMENTS PROPOSED BY DEGTYAREVA, KACHAN, LUK'YANCHUK, AND SHRUBOVICH

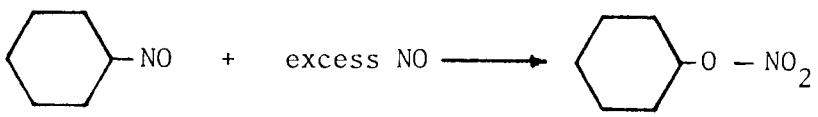
Absorption (cm^{-1})	Assignment[114]
1560	N = O stretch of $-[\overset{\overset{\displaystyle NO}{\vert}}{C}Cl]-$
1720	N = O stretch of $-[\overset{\overset{\displaystyle NO}{\vert}}{C}Cl]-$
1630	C = N stretch of $-[\overset{\overset{\displaystyle NOH}{\Vert}}{C}]-$
3620	O - H stretch of $-[\overset{\overset{\displaystyle NOH}{\Vert}}{C}]-$

Fabian, Legrand, and Poirier[121] for alkyl ketoximes, and the absorption at 1630 cm^{-1} is probably due to the asymmetric stretch of an alkyl nitrate, which has been assigned the value of 1629 cm^{-1} in the present study.

To determine the origin of the absorptions at 1720 and 3620 cm^{-1} reported by Degtyareva, NOCl was photolyzed again with HDPE, except that the NOCl was not rigorously dried. Identical results to those previously reported were obtained with the exception of an additional absorption at 1718 cm^{-1}. This absorption is assigned to the often studied carbon-oxygen stretch of a carbonyl.[133] The origin of the carbonyl is probably due to hydrolysis of the transient oxime, previously described in Equation 58 (p 88), before the oxime reacts with NOCl to form the gem-chloronitroso group, as previously shown in Equation 63 (p 90). This result suggests that the absorption at 1720 cm^{-1} reported by Degtyareva and coworkers, which they assigned to the gem-chloronitroso group, is actually due to the carbonyl, and it further suggests that the absorption at 3620 cm^{-1} is due to traces of water on their HDPE photoproduct, because water has a strong absorption in the 3600 cm^{-1} region.[134]

In summary of the discussion presented thus far, data have been presented indicating that the products of the photoreaction of NOCl with HDPE are the alkyl nitrate, the gem-chloronitroso group, and the chlorinated methylene functionality. Some oxime is formed, but it is converted to the gem-chloronitroso by reaction with NOCl, or it is converted to the carbonyl by hydrolysis by traces of water. If the analysis and discussion presented are accepted, the conclusion must be reached that the IR assignments in the work of Degtyareva, Kachan, Luk'yanchuk, and Shrubovich are incorrect.

The evidence for the unexpected alkyl nitrate presented to this point has only been a strong correlation of IR absorptions, and the presence of the nitrate warrants further investigation. The occurrence of an alkyl nitrate in the photochemical reaction of NOCl with hydrocarbons is not completely without precedence because Müller reported that a trace of this produce was present in his early work.[110] A clue to the origin of the nitrate may be found in the work of Donaruma and Carmody,[135] who reacted nitrosocyclohexane with NO and obtained cyclohexylnitrate as the major product, as shown in Equation 69.



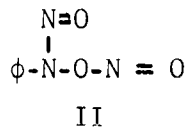
(69)

Referring back to Equations 59 and 61 (p 88), it is observed that NO is formed upon photolysis of NOCl and that the nitroso is an intermediate in the formation of the oxime. Thus the two reactive species employed by Donaruma and Carmody for formation of the nitrate are present in the reaction mixture of NOCl with HDPE.

In 1897 Bamberger[136] reacted NO with nitrosobenzene and isolated benzene diazonium nitrate as seen in Equation 70. In 1918[137] he repeated

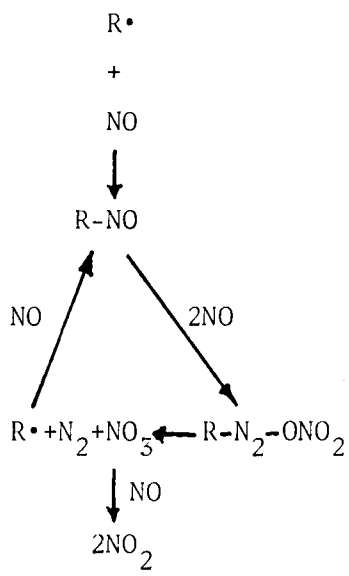
$$\phi - NO + 2NO \longrightarrow \phi - N = N - ONO_2 \qquad (70)$$

the experiment and postulated the formation of a nitritonitrosoamine intermediate (II) which rearranged to the diazonium nitrate. Little work was done on extending Bamberger's results to alkyl systems until



II

Brown[138] reported in 1954 a study on the reaction of NO with alkyl free radicals. However, Brown was unable to isolate either the nitritonitrosoamine intermediate or the alkyl diazonium nitrate. He did observe what he termed a nitrosoalkane catalyzed disproportionation of NO into molecular nitrogen (N_2) and NO_2. He extended Bamberger's proposed mechanism based on the assumption that the formed alkyl diazonium nitrate decomposed spontaneously to regenerate the alkyl radical. Brown's suggested pathway is given in Equation 71. The report by Brown



(71)

led to several extensive investigations on the reaction of NO with nitrosoalkanes.[139-143] Kinetic evidence[141] indicates that the reaction is third order, first order in nitrosoalkane and second order in NO,

supporting Brown's pathway. An alkyl diazonium nitrate has never been isolated, and it has been postulated that these species are stable only when conjugated,[144] such as in Bamberger's benzene diazonium nitrate. In the gas phase, radical recombination of the alkyl radical and nitrogen trioxide (NO_3) formed by rupture of the diazonium nitrate usually does not occur,[140-142] but in solution, such as in the work of Donaruma and Carmody[135] previously shown in Equation 69 (p 100), some radical recombination does occur resulting in the formation of the nitrate.

If this process is occurring during photolysis of NOCl with HDPE to form the alkyl nitrate, N_2 should be present in the gaseous products of the reaction. A significant portion of the reaction gas mixture could not be liquified by liquid nitrogen, indicating that it was probably N_2, and mass spectrometric analysis of the gas demonstrated that it was primarily N_2.

To this point it has been tacitly assumed that the nitrate is formed from the alkyl nitroso intermediate and not from the gem-chloronitroso group, and an additional reaction was performed to demonstrate the validity of this assumption. NO in high concentration was allowed to react with the gem-chloronitroso group of the HDPE photoproduct for a significant period of time in the dark. New absorptions in the IR spectrum appeared at 1658 cm^{-1} and 824 cm^{-1}, and the absorption due to the gem-chloronitroso group at 1581 cm^{-1} decreased. The new absorption at 1658 cm^{-1} is assigned to the asymmetric stretch of the gem-chloronitrate, and the new absorption at 824 cm^{-1} is assigned to the O - NO_2 stretch of the gem-chloronitrate. The specific value of the

symmetric stretch of the gem-chloronitrate could not be determined because of the strong absorption by the alkyl nitrate.

The shift in the frequency of the asymmetric stretch from 1629 cm^{-1} for the alkyl nitrate to 1658 cm^{-1} for the gem-chloronitrate is consistent with the work of Burrell,[125] who reported the IR spectra for cyclohexyl nitrate and 1-chlorocyclohexyl nitrate. He assigned the asymmetric stretch of the nitrate group to the absorption at 1639 cm^{-1} in cyclohexyl nitrate and to the absorption at 1667 cm^{-1} in 1-chlorocyclohexyl nitrate.

The difference in reactivity of the alkyl nitroso group and the gem-chloronitroso group with respect to reaction with NO is understandable in view of the presumed mechanism. The initial interaction between NO and the nitroso functionality is probably attack by NO on the unshared pair of electrons of the nitrogen atom of the nitroso to form an initial nitrosonitroxide adduct, as shown in Equation 72. If chlorine is

$$R\text{-}N{=}O + NO \longrightarrow R\text{-}\overset{\overset{N=O}{|}}{N}\text{-}O\cdot \qquad (72)$$

substituted alpha to the nitroso group, as in the gem-chloronitroso functionality, electron density on the nitrogen atom should be decreased inductively, causing the observed lower rate of reaction with NO.

The isomerization of nitroso compounds to oximes is also very interesting. As discussed by Gowenlock and Lüttke,[119] it was assumed many years ago that primary and secondary nitroso compounds rapidly isomerize to oximes. These authors pointed out that this may be an incorrect assumption and that nitroso compounds may be stable until catalytically

isomerized. Donaruma[145] studied the isomerization of nitrosocyclohexane to cyclohexanone oxime and concluded that the nitroso compound does not isomerize to the oxime in a nonpolar solvent even at 80°C. However, isomerization did proceed in the presence of acid or base or in a polar solvent.

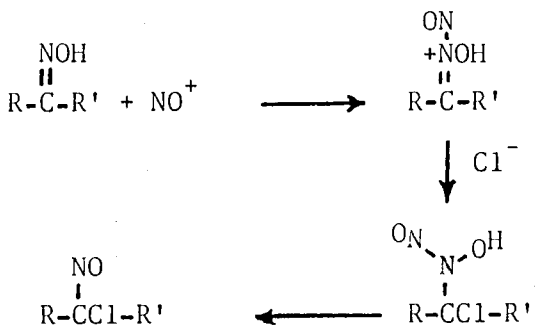
To test the effect of the medium on the products of the photoreaction of NOCl with HDPE, purified NO was irradiated for a long period of time with HDPE. The only changes observed in the IR spectrum were additional absorptions at 1629, 1567, 1275, and 863 cm^{-1}. These absorptions have been discussed previously and are assigned to nitrato and nitro alkanes. No change in the IR spectrum was observed in the oxime C = N stretch region, 1652-1682 cm^{-1}. The alkyl nitrate probably arises from the reaction of NO with the formed nitrosoalkane, and the nitro group probably arises from the formation of NO_2 by small amounts of NO_3 not undergoing cage recombination after rupture of the diazonium nitrate.

In the photoreaction of NOCl with HDPE some oxime is formed, but it is converted to the gem-chloronitroso group by reaction with NOCl. However, the absence of any oxime in the photo reaction of NO with HDPE demonstrates that HCl is required for conversion of the alkyl nitroso group to the oxime. As previously shown in Equation 60 (p 88), HCl is initially formed in the photoreaction of NOCl with HDPE.

To determine if the intermediate alkyl nitroso compound could be forced to isomerize to the oxime rather than form the nitrate, photolyses of NOCl with HDPE were accomplished with added HCl. NOCl and HCl in the mole ratios of 3:1, 1:1, ∞:0, and 1:3 were used, and in each case the ratio

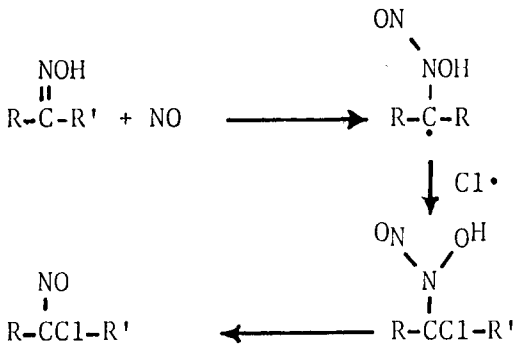
of the absorbance of the nitrate, measured at 1629 cm^{-1}, to the absorbance of the gem-chloronitroso, measured at 1581 cm^{-1}, was within 5% of 1.48. These data indicate that HCl is acting as a catalyst, and that the amount of HCl formed in the NOCl photoreaction catalyzes the formation of as much oxime as can be formed. Some process other than the HCl catalyst is the controlling process for isomerization of the nitroso, and this other process is probably the constraint of the rigid matrix of HDPE.

The last aspect of the photoreaction of NOCl with HDPE is the mechanism of the reaction of NOCl with the transient oxime to form the gem-chloronitroso group. Kissinger and Ungade[116] investigated the reaction of NOCl with a series of oximes and proposed two possible mechanisms. The first mechanism is ionic in nature and is presented in Equation 73. The second mechanism is a free radical process and is



(73)

given in Equation 74. Kissinger and Ungnade preferred the ionic mechanism because substitution of electronegative groups alpha to the oxime prevented the reaction from occurring. Whichever mechanism is operating, the N-nitrosohydroxylamine should be an intermediate. Müller and



(74)

Metzer[146] have demonstrated that N-nitrosohydroxylamines are unstable and decompose to nitroso compounds. If the stoichiometry of the reaction is correct, the formation of nitroxyl (HNO) is required. However, nitroxyl dimerizes and decomposes spontaneously to water and nitrous oxide[147-149] as shown in Equation 75. N_2O should, therefore, be present in the gaseous

$$2HNO \longrightarrow H_2O + N_2O \qquad (75)$$

products of the photoreaction of NOCl with HDPE, and a significant amount of N_2O was observed in the mass spectrum of the gaseous products.

In summary of the information presented in this chapter, it may be concluded that the photochemical reaction of NOCl with HDPE does not proceed cleanly to form the oxime as expected. IR spectral data for the assignments made are collected in Tables XXV and XXVII, and Figure 4 presents a general scheme for the reaction pathways described. It appears that Degtyareva, Kochan, Luk'yanchuk, and Shrubovich[114] incorrectly identified the products of the reaction while Pozzi, Silvers Giuffrè, and Cernia[113] assumed that a reaction which proceeds smoothly in homogeneous solution will proceed similarly in a hetereogeneous

TABLE XXVII

ADDITIONAL INFRARED SPECTRAL ASSIGNMENTS
FOR MODIFIED POLYETHYLENE

Absorption (cm^{-1})	Assignment
1718	C = O stretch of $\left\{\overset{\overset{O}{\|}}{C}\right\}$
1567	Asymmetric stretch of $-NO_2$ in $\left\{\overset{\overset{NO_2}{\|}}{CH}\right\}$
1561	Asymmetric stretch of $-NO_2$ in $\left\{\overset{\overset{NO_2}{\|}}{CCl}\right\}$
1658	Asymmetric stretch of $-NO_2$ in $\left\{\overset{\overset{ONO_2}{\|}}{CCl}\right\}$
824	O - NO_2 stretch of $\left\{\overset{\overset{ONO_2}{\|}}{CCl}\right\}$

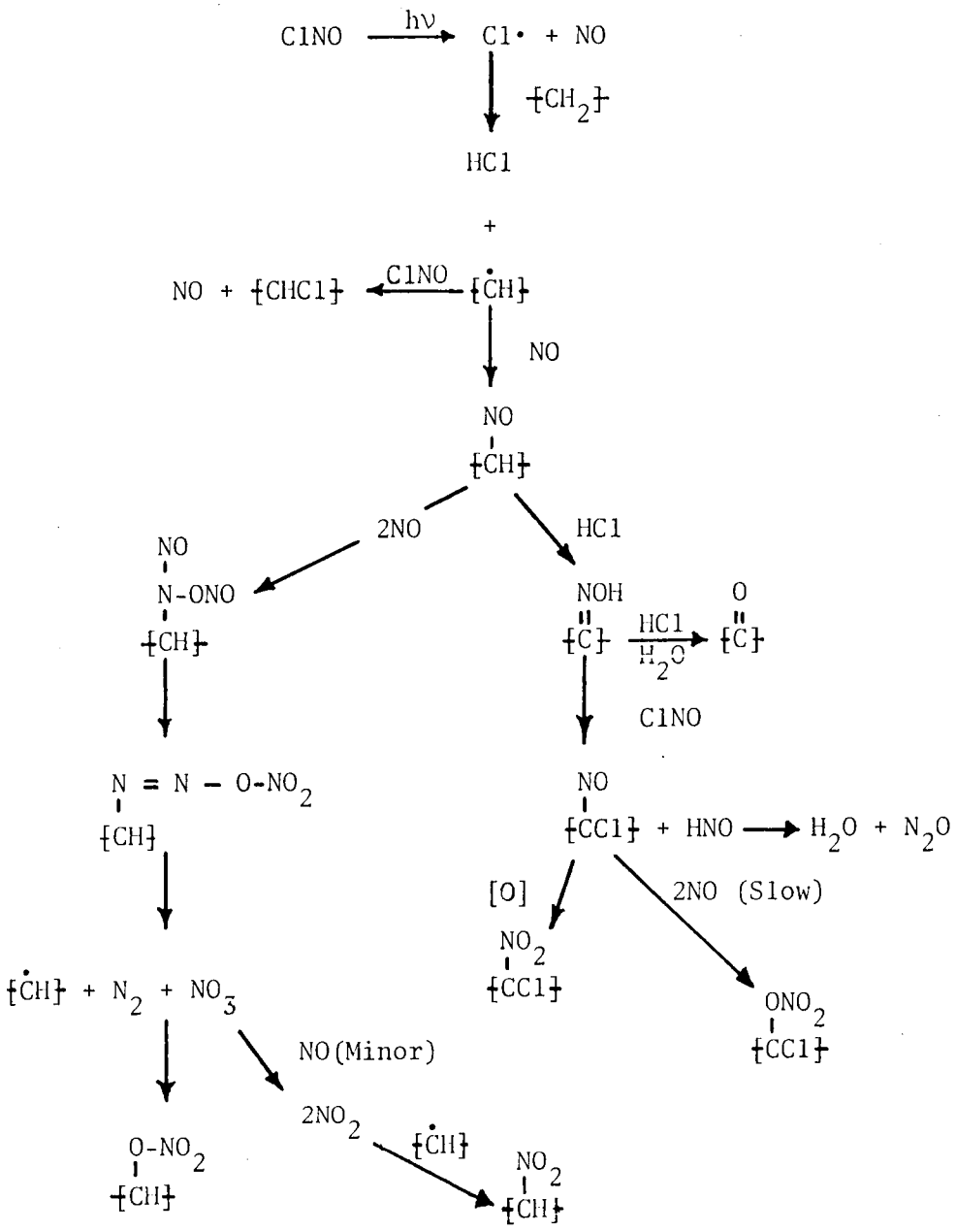


Figure 4. Pathways for the photoreaction of nitrosyl chloride with high density polyethylene.

mixture. Pozzi and coworkers probably obtained a mixture of nitrate, nitro, and nitroso functionalities, which may be a better initiator of photodegradation than the carbonyl which they sought.

HDPE is a highly crystalline material composed of linear chains,[96] and it was of interest to determine if photolysis of NOCl with low density PE, which is more amorphous than HDPE due to extensive chain branching,[96] yields the same products as observed with HDPE. The IR spectrum of the photoproduct low density PE, after photolysis with NOCl, exhibited the same absorptions as those present in the HDPE photoproduct. However, qualitative comparison of the ratio of the absorption due to nitrate compared to the absorption due to the gem-chloronitroso group indicated that a greater amount of nitrate is formed with low density PE than with HDPE. This difference is probably due to the greater number of tertiary sites in low density PE at which a formed nitroso group cannot tautomerize to the oxime and can only react with NO to yield the nitrate.

There is one large question not yet answered about the photochemical reaction of NOCl with HDPE, and that question is why the reaction proceeds so smoothly in homogeneous solution with low molecular weight hydrocarbons to yield oximes, and, yet, the oxime is not found among the products of the reaction with HDPE. In retrospect the answer is straightforward. With low molecular weight hydrocarbons, low concentrations of NOCl and high concentrations of HCl are used during photooximation reactions. The nitroso compound is formed and then rapidly isomerized to the oxime by the HCl catalyst. The HCl then forms a salt with the oxime, and the

salt precipitates from the solution, to be continuously drained from the bottom of the photoreactor.[150] The low concentration of NOCl allows isomerization of the nitroso compound before it can react with NO, and the high concentration of HCl causes the oxime salt to precipitate from solution before it can react with NOCl. In the HDPE case, some of the formed nitroso groups are constrained from isomerization to the oxime by the HDPE matrix and are susceptible to further attack by NO. If rearrangement to the oxime does occur, it cannot precipitate from the reaction and is constrained to react with NOCl.

CHAPTER VI

EXPERIMENTAL PROCEDURES

A. Materials

All materials were Reagent Grade and used as received unless otherwise specified.

Acetic anhydride: Eastman (Technical).

Acetone: Commercial Solvents (Technical).

Aluminum chloride: Baker.

Argon: Selox, passed through Drierite column.

2,2'-Azobis-(2-methylpropionitrile): Eastman, recrystallized from ethanol.

Benzene: Fisher, fractionally distilled.

Benzhydrol: Eastman, recrystallized from pentane.

Benzophenone: Eastman, recrystallized from pentane.

Benzoyl chloride: Eastman.

Bromoethane: Matheson, Coleman, and Bell, fractionally distilled.

2-Butanone: Fisher (Technical).

Carbon tetrachloride: Fisher, fractionally distilled.

Chlorine: Matheson, fractionally distilled three times and stored on phosphorous pentoxide.

Chloroform-d: Merck, Sharp, and Dohme.

Chromic chloride: Baker (Technical).

Diethylamine: Baker, fractionally distilled.

1,4-Dioxane: Fisher.

Drierite: W. A. Hammond Drierite Company.

Ethanol: Commercial solvents.

2-Ethylhexyl methacrylate: Polysciences, washed with five 100 ml portions of 0.5% sodium hydroxide in water (w/v); washed with five 100 ml portions of distilled water; dried over magnesium sulfate; fractionally distilled under reduced pressure.[151]

Hydrochloric acid, concentrated: Allied.

Hydrogen chloride: Matheson, fractionally distilled three times and stored on phosphorous pentoxide.

Lithium: A. D. Mackay, Inc.

Lithium aluminum hydride: Ventron.

Magnesium sulfate: Fisher.

Mercuric chloride: Fisher.

Methanol: Fisher.

Methyl methacrylate: Eastman, washed with five 100 ml portions of 0.5% sodium hydroxide in water (w/v); washed with five 100 ml portions of distilled water; dried over magnesium sulfate; fractionally distilled under reduced pressure.[151]

N,N-Diethylaniline: Eastman (Technical), refluxed with acetic anhydride and fractionally distilled.[152]

Naphthalene: Fisher, recrystallized from ethanol.

Nitric acid, concentrated: Mallinckrodt.

Nitric oxide: Matheson, fractionally distilled three times and stored on phosphorous pentoxide.

Nitrobenzene: Fisher, fractionally distilled.

Nitrogen: Selox, deoxygenated and dried by bubbling through two solutions of chromous ion followed by bubbling through sulfuric acid.[153]

Nitrogen dioxide: Matheson, fractionally distilled three times and stored on phosphorous pentoxide.

Nitrosyl chloride: Matheson, fractionally distilled three times and stored on phosphorous pentoxide.

Pentane: Eastman (Practical).

Phenylhydrazine: Fisher, fractionally distilled under reduced pressure.

Phosphorous pentoxide: Fisher.

Polyethylene, high density: Film of 0.038 mm thickness specially prepared by Phillips Petroleum Company from Marlex 6006 linear polyethylene (high molecular weight with a medium molecular weight distribution).[154] The density after extraction with 2-butanone was determined to be 0.955 g cm^{-3} which yielded a calculated[155,156] crystallinity of 71%.

Polyethylene, low density: Commercial film of thickness 0.032 mm.

1-Propanol: Baker.

Sodium hydroxide: Fisher.

Styrene: Aldrich, washed with five 100 cm^3 portions of 0.5% sodium hydroxide in water (w/v); washed with five 100 cm^3 portions of distilled water; dried over magnesium sulfate; fractionally distilled under reduced pressure.[151]

Sulfuric acid, concentrated: Mallinckrodt.

Tetrahydrofuran: Fisher, fractionally distilled over lithium aluminum hydride.

Tetramethylsilane: Aldrich.

Toluene: Fisher, fractionally distilled.

Triethylamine: Eastman, fractionally distilled.

Zinc: Baker.

B. Instrumentation

Ultraviolet spectra were accomplished with Carey 14 and 17 Recording Spectrophotometers (Applied Physics Corporation). Infrared spectra were accomplished with a Beckman IR5A Spectrometer and a Fourier Transform Infrared Spectrometer FTS-20 (Digilab, Inc.). Proton nuclear magnetic resonance spectra were accomplished with Varian A60, T60, and HA100 spectrometers. Mass spectra were accomplished with an Hitachi Perkin-Elmer RMU-6E Mass Spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee. All elemental analyses given are averages of at least duplicate determinations. A Wang Model 600 Advanced Programming Calculator was used to perform linear regression analyses. Density measurements were accomplished on a Density Gradient Column employing 2-propanol and water. Melting points (uncorrected) were accomplished on a Thomas Hoover Unimelt Apparatus. Surface analyses (Electron Scattering for Chemical Analysis) were accomplished on a Modified AEI ES100 spectrometer.

C. Equipment

All photochemical reactions were performed in a Rayonet Type RS Preparative Photochemical Reactor (Southern New England Ultraviolet Company) equipped with four 12.5 W RUL 3500Å lamps. The reactor had a fan incorporated in the bottom to assist cooling during irradiation. Samples were heated under vacuum with a Thelco Model 19 vacuum oven. The vacuum system used was constructed of glass and was equipped with a Welch Duo-Seal vacuum pump, a two-stage mercury diffusion pump (H. S. Martin Co.), a McLeod gauge capable of reading to 10^{-5} mm Hg (Consolidated Vacuum Corporation), a mercury manometer, a Bourdon vacuum gauge (Fisher) which was calibrated with the mercury manometer, gas storage tubes, and a gas sampling bottle for mass spectral determinations on gases. All vacuum line work was performed with illumination by a Kodak Wratten Series 1 Safelight.[157]

Three different types of vessels were used to contain the materials during irradiation. First, photolysis tubes were used for homogeneous solution samples. The photolysis tubes were constructed of Pyrex, 13 mm outer diameter (OD) and 60 cm in length. One end of the tube was sealed, and the other end was equipped with a standard taper 24/40 outer ground glass joint. The photolysis tube tops consisted of a standard taper 24/40 inner ground glass joint connected to a 4 mm oblique-bore high vacuum stopcock. Second, photolysis flasks were used for heterogeneous grafting to polyethylene film. The photolysis flasks were heavy-wall 125 ml Erlenmyer flasks (Kimax) equipped with standard taper 24/40 outer ground glass joints. The photolysis flask tops consisted of a standard

taper 24/40 inner ground glass joint connected to a 4 mm oblique-bore high vacuum stopcock. Third, photolysis cells were used for irradiation of nitrogen oxides, chlorine, and nitrosyl chloride with polyethylene. The photolysis cell was constructed of Pyrex, 43 mm OD and 31 cm in length. One end of the cell was sealed, and the other end was equipped with a standard taper 45/50 outer joint. For certain reactions a photolysis cell insert was used. It was constructed of Pyrex, 2.8 cm OD and 19 cm in length, and was sealed at both ends. Prongs were attached at both the top and bottom so that the insert would sit in the middle of the photolysis cell. The photolysis cell top consisted of a standard taper 45/50 inner joint connected to two 4 mm oblique-bore high vacuum stopcocks.

If several samples were to be irradiated simultaneously, the photolysis vessels were mounted on a round aluminum plate, 10 cm in diameter and 2 mm thick. The center of the plate was connected to a 1.2 m stainless steel tube, 7 mm OD. The tube and plate were rotated at 14 rpm in the photoreactor by Standco Stirrer (H. H. Sticht Company).

Thermal polymerizations were accomplished in polymerization tubes. The polymerization tubes were constructed of heavy wall Pyrex, 28 mm OD and 11.5 cm in length. One end of the tube was sealed, and the other end was flanged to tightly hold a septum, which was used to cap the tube. The thermal polymerizations were accomplished using a 12 l water bath equipped with a Heidolph Stirrer, Bromwell thermostat, and Cenco Heaters (Central Scientific Company) powered by a Precision Scientific Powerstat.

D. Polymerization of Methyl Methacrylate and 2-Ethylhexyl Methacrylate

1. Thermal Polymerization

The individual polymerization solutions were made by pipetting stock solutions of reactants into volumetric flasks followed by dilution to the required volume. The solutions were transferred to polymerization tubes and deoxygenated by bubbling argon through the solutions for 10 min. After deoxygenation, the tubes were immersed in the constant temperature bath for the required period of time. Upon removal from the bath, the tubes were rapidly chilled in an ice water mixture.

The method of polymer isolation depended on the monomer employed. For polymerization of methyl methacrylate, the contents of the photolysis tube were washed into 500 ml methanol with vigorous stirring. The precipitated poly(methyl methacrylate) was filtered and then dried under vacuum at room temperature for 24 hr, followed by drying under vacuum for 48 hr at approximately 50°C. For polymerization of 2-ethylhexyl methacrylate, the contents of the photolysis tube were washed into 500 ml methanol with virogous stirring. The formed poly(2-ethylhexyl methacrylate) was allowed to settle to the bottom of the beaker, and the methanol was decanted. The polymer was redissolved in benzene and transferred to a tared beaker. This solution was frozen in a dry ice and acetone bath and then placed under vacuum at room temperature for 24 hr, followed by heating to approximately 50°C for 48 hr under vacuum.

2. Photochemical Polymerization

The individual polymerization solutions were made by pipetting stock solutions of reactants into volumetric flasks followed by dilution to the required volume. The solutions were transferred to photolysis tubes and degassed with three freeze-pump-thaw cycles using a dry ice and acetone bath. The solutions were allowed to equilibrate to room temperature before irradiation. Four samples were irradiated simultaneously while revolving inside the photoreactor, and the temperature was maintained between 22°C and 32°C.

The procedures for isolating the formed polymer were the same as those previously described for thermal polymerization.

E. Photochemically Induced Homogeneous Graft Polymerization of 2-Ethylhexyl Methacrylate onto Modified Polystyrene

1. Synthesis of Polystyrene

A 0.22 g (1.3×10^{-3} mole) portion of 2,2'-azobis-(2-methylpropionitrile), 30 ml (0.26 mole) styrene, and 500 ml benzene were placed in a three-neck, round-bottom flask equipped with a condenser and nitrogen bubbler. Initially, nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen. The solution was heated to reflux for 19 hr, and the resulting solution was poured into 5 l methanol with vigorous stirring. The white solid was filtered and then dried for 14 hr at room temperature under vacuum. The dried solid was dissolved in 100 ml benzene and reprecipitated by pouring slowly into 1.5 l methanol

with vigorous stirring. The precipitated white solid was filtered and then dried for 24 hr at approximately 50°C under vacuum. The yield was 6.56 g, 24% of the theoretical yield.

2. Synthesis of Poly(styrene-co-vinylbenzophenone)

Poly(styrene-co-vinylbenzophenone) was synthesized in accordance with the procedure of Merrill, Unruh, and Robertson[89] as modified by Greber and Egle[90] using polystyrene, aluminum chloride, and benzoyl chloride in nitrobenzene. The percent benzoylation of the phenyl groups in the polystyrene substrate was determined to be 31% by ultraviolet spectrophotometry using the published spectrum of poly(vinylbenzophenone).[91]

3. Synthesis of Poly(styrene-co-N,N-diethylaminostyrene)

Poly(styrene-co-nitrostyrene) was synthesized in accordance with the procedure of Seliger using polystyrene, acetic anhydride, concentrated nitric acid, and carbon tetrachloride.[84,85] Elemental analysis indicated that 25.5% of the phenyl groups in the polystyrene substrate contained the nitro function. The elemental analysis data for 0.745 C_8H_8 and 0.255 $C_8H_7NO_2$ were as follows:

	%C	%H	%N
Calculated	83.10	6.75	3.09
Found	83.11	7.01	2.96

The poly(styrene-co-nitrostyrene) was reduced to poly(styrene-co-aminostyrene) in accordance with the procedure of Selinger[84,85] using hot phenylhydrazine. Elemental analysis data indicated quantitative

reduction of the 25.5% nitrated polystyrene. The elemental analysis data for 0.745 C_8H_8 and 0.255 $C_8H_7NO_2$ were as follows:

	%C	%H	%N
Calculated	88.99	7.71	3.31
Found	89.07	7.79	3.07

The procedure developed by Tuga, Watanabe, Fujita, and Pan[86] for alkylation of amino groups was used to alkylate the aminated polystyrene; 4.50 g (0.035 mole) naphthalene, 0.56 g (0.081 mole) lithium, and 100 ml tetrahydrofuran were placed in a 250 ml three-neck, round-bottom flask equipped with nitrogen bubbler, dropping funnel, and magnetic stirrer. The mixture was stirred for 1.5 hr, and then 1.5 g of the aminated polystyrene was added. The resulting mixture was stirred for 1.5 hr, and then a 5.25 ml (0.070 mole) portion of bromoethane was dropped into the reaction mixture over a 30 min period. The resulting mixture was stirred for an additional 1.0 hr. The solution was then poured slowly into 1.5 l methanol with vigorous stirring, and the precipitated polymer was filtered and then dried for 12 hr at room temperature under vacuum. The polymer was dissolved in 50 ml benzene, and the solution was dropped into 1.5 l methanol with vigorous stirring. The precipitate was filtered and then dried under vacuum for 24 hr at approximately 50°C. The yield was 1.65 g of light yellow powder. Elemental analysis data for 0.745 C_8H_8 and 0.255 $C_{12}H_{17}N$ were as follows:

	%C	%H	%N
Calculated	88.59	8.49	2.92
Found	88.34	8.64	2.84

The infrared spectrum of poly(styrene-co-N,N-diethylaminostyrene) showed new absorptions at 1511 and 813 cm^{-1} (disubstituted benzene ring)[158] and at 1266 cm^{-1} (tertiary aromatic amine).[158] The proton nuclear magnetic resonance spectrum in chloroform-d showed peaks at 1.0-2.4, 3.2, 6.45, and 6.95 δ units from internal tetramethylsilane standard with relative intensities of 4:1:2:2. The ultraviolet spectrum in 1,4-dioxane showed λ_{max} at 264 nm with a shoulder at 307 nm.

The analytical sample of poly(styrene-co-N,N-diethylaminostyrene) prepared as described above was used as a standard for determination of the percent diethylamination in other preparations of the polymer, using the absorption at 307 nm. The reproducibility of the synthesis was very good.

4. Irradiation Procedures

The individual polymerization solutions were made by pipetting stock solutions of reactants into volumetric flasks followed by dilution to the required volume. The solutions were then transferred to photolysis tubes and degassed with three freeze-pump-thaw cycles using a dry ice and acetone bath. The solutions were allowed to equilibrate to room temperature before irradiation.

Each sample was irradiated separately. The irradiation time was sufficiently short so that the temperature was maintained at 22 ± 1°C.

After irradiation, the contents of the photolysis tubes were washed into tared beakers. The solutions were frozen in a dry ice and acetone bath and placed under vacuum at room temperature for 24 hr to remove the

benzene solvent. The beakers were then heated to 50°C under vacuum for 48 hr to remove unreacted 2-ethylhexyl methacrylate (2EHMA). Several samples of 2EHMA were taken through this process to show that purely thermal polymerization was not occurring.

After weighing the tared beaker to determine the amount of polymerization, the product was extracted repeatedly with pentane to remove poly(2-ethylhexyl methacrylate) (P2EHMA) homopolymer and residual unreacted benzophenone or N,N-diethylaniline from the polystyrenic substrate. The pentane extract was dried and washed with methanol to separate residual unreacted benzophenone or N,N-diethylaniline from the P2EHMA homopolymer.

Further fractionation was required for the poly(styrene-co-N,N-diethylaminostyrene) (PDEA) because the PDEA containing grafted P2EHMA was slightly soluble (or at least dispersed) in pentane. Therefore, the pentane extract was dried and then extracted with 1-propanol to remove P2EHMA homopolymer. This extraction aided the separation, but it was not completely successful in separating P2EHMA homopolymer from the PDEA containing grafted P2EHMA as determined by proton nuclear magnetic resonance spectra.

Since solvent fractionation was not completely successful in resolving the amount of P2EHMA homopolymer formed in the PDEA system, a calculation was performed to determine the limit of the amount of P2EHMA homopolymer present. Integration of the proton nuclear magnetic resonance spectrum was performed on the aryl protons and the methylene protons adjacent to oxygen of the PDEA sample containing grafted P2EHMA.

From this was calculated the number of 2EHMA units per aryl unit. This same integration was performed on the homopolymer P2EHMA fraction containing a small amount of PDEA to which P2EHMA was grafted. This allowed a determination of the amount of PDEA in the homopolymer P2EHMA fraction. Knowing the number of grafted 2EHMA units per aryl unit from the first integration, the amount of PDEA containing grafted P2EHMA present in the homopolymer P2EHMA fraction was calculated and subtracted from the weight of the homopolymer P2EHMA fraction. This yielded the amount of grafted and homopolymer P2EHMA. The calculated value for the amount of homopolymer P2EHMA is a lower limit because the PDEA containing grafted 2EHMA which dissolved or dispersed in 1-propanol probably contained more 2EHMA units per aryl unit than the PDEA which was not soluble or dispersed.

F. Photochemically Induced Heterogeneous Graft Polymerization of Methyl Methacrylate and 2-Ethylhexyl Methacrylate onto Modified Polyethylene

1. Incorporation of Diethylamine Groups onto Polyethylene

A portion of high density polyethylene (HDPE) film, 4 cm wide and 20 cm in length, was placed in a continuous extractor and washed for 24 hr with 2-butanone, followed by drying for 24 hr at room temperature under vacuum. The dried film was weighed and placed in the center of a photolysis cell, which was then attached to the vacuum system and evacuated. Chlorine was admitted to the photolysis cell to a pressure of 380 mm Hg. The photolysis cell was sealed and irradiated for 5.0 hr.

The cell was then returned to the vacuum system, and the residual gases were removed. The film was then placed in the continuous extractor and washed with 2-butanone for 24 hr, after which the film was dried for 24 hr to constant weight at room temperature under vacuum. Based on the increase in weight observed, the chlorinated HDPE film contained about 3.5% chlorine. Elemental analysis data gave similar results and were as follows:

	%C	%H	%Cl
Found	82.49	13.63	4.09

A procedure similar to that of Adylov, Ilina, Krentsel, and Shishkina[106] was employed to incorporate diethylamine groups onto the chlorinated HDPE film. A 100 ml portion of toluene and 10 ml diethylamine were placed in a 250 ml three-neck, round-bottom flask equipped with a condenser, magnetic stirrer, and thermometer. The solution was heated to 50°C, and a weighed portion of the chlorinated film was added. The mixture was stirred slowly for 12 hr, after which the film was dried under vacuum at room temperature for 24 hr. Elemental analysis results on the modified HDPE film were as follows:

	%C	%H	%Cl	%N
Found	82.50	13.60	3.97	<0.01

The ESCA (Electron Scattering for Chemical Analysis) spectrum of the modified HDPE film surface indicated the concentration of nitrogen to be about one atom percent (the nitrogen atom percent in a methine unit containing an N,N-diethylamino substituent is approximately six). Several additional portions of HDPE film were chlorinated to different

percent chlorine by weight and treated with diethylamine in toluene at 20°C, 50°C, or 80°C for 6 hr, 12 hr, or 24 hr.

2. Irradiation Procedures

The individual polymerization solutions were made by pipetting stock solutions of reactants into volumetric flasks followed by dilution to the required volume. The solutions were then transferred to the photolysis flasks which contained a weighed portion of high density polyethylene (HDPE) film. The mixtures were degassed with three freeze-pump-thaw cycles using a dry ice and acetone bath. The solutions were allowed to equilibrate to room temperature before irradiation.

Three samples were irradiated simultaneously while revolving inside the photoreactor. Temperature during irradiation was held between 22°C and 32°C.

After irradiation, the contents of the photolysis flasks were washed into tared beakers. The mixtures were frozen in a dry ice and acetone bath and placed under vacuum at room temperature. The beakers containing the product were then heated to 50°C under vacuum for 48 hr. After cooling and weighing the beakers, the film was removed and extracted for 12 hr with 2-butanone in a continuous extractor. The film was then dried for 24 hr at room temperature under vacuum before weighing.

G. Photochemical Interaction of Nitrogen Oxides and Nitrosyl Chloride with Polyethylene

1. Nitrosyl Chloride Procedure

A portion of high density polyethylene (HDPE) film, 10 cm wide and 16 cm in length, was washed with 2-butanone in a continuous extractor for 24 hr, followed by drying for 24 hr at room temperature under vacuum. The film was then mounted on a photolysis cell insert with Nichrome wire and placed in a photolysis cell. The photolysis cell was attached to the vacuum system and evacuated for 24 hr at less than 10^{-5} mm Hg.

Nitrosyl chloride (380 mm Hg) or a mixture of nitrosyl chloride and hydrogen chloride (355 mm Hg/115 mm Hg, 369 mm Hg/369 mm Hg, or 132 mm Hg/358 mm Hg) was distilled into the photolysis cell, and the cell was then transported to the photoreactor in the dark. Each sample was irradiated for 3.0 hr and then returned to the vacuum system. Liquid nitrogen was used to trap the gaseous products. A portion of the gases were noncondensable, and the mass spectrum of the noncondensable gas indicated that it was primarily molecular nitrogen. The mass spectrum of the condensable gases indicated a substantial peak at mass number 44, indicative of nitrous oxide. The photolysis cell was evacuated for 24 hr at less than 10^{-5} mm Hg. The film was then removed and infrared spectra were obtained.

One product of the reaction was the gem-chloronitroso functionality, and it was subjected to additional reactions. Oxidation of the gem-chloronitroso group to the gem-chloronitro group was accomplished by

exposing the HDPE film photoproduct to air for two weeks. Reaction of the gem-chloronitroso group with nitric oxide was accomplished by distilling nitric oxide into the previously evacuated photolysis cell containing the HDPE film photoproduct to a pressure of 380 mm Hg. The nitric oxide was allowed to remain for 24 hr before removal by evacuation followed by accomplishment of the infrared spectra.

2. Nitrogen Oxides Procedures

The procedures for the nitrogen oxides were identical to those described for nitrosyl chloride except that nitrogen dioxide or nitric oxide, as required, were employed at a pressure of 380 mm Hg. Additionally, longer irradiation times were required, 14 hr for nitric oxide and 21 hr for nitrogen dioxide.

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VITA

Stuart Lansing Watson, Jr., was born in Bristol, Virginia on January 30, 1948. He attended public schools in Bristol, Tennessee, New Orleans, Louisiana, and Lincoln, Nebraska. In 1969 he graduated with a B. S. with a major in Chemistry from Carson-Newman College where he was active in the Student Government Association. In the fall of 1969, he was commissioned as an officer in the United States Air Force. From 1969 until 1973 he served on active duty as a Missile Launch Control Officer at Minot AFB, North Dakota. In the fall of 1973, he entered The University of Tennessee, where he held a teaching assistantship. In January of 1975 he was selected as a University Non-Service Fellow.

The author is a member of the American Chemical Society and Alpha Chi. He has been a joint author of several articles published in the Journal of Radiation Curing, the Journal of Medicinal Chemistry, and ACS Polymer Preprints. He has presented papers at the Southeast Regional ACS meeting in Atlanta, Georgia, and at the combined Southeast-Southwest Regional ACS meeting in Memphis, Tennessee. In May of 1970, he married Ann Moser of Jefferson City, Tennessee.