Reversible and Irreversible Light-Induced Reactions Initiated BY SPEEK/PVA Polymer Systems

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Abstract

Illumination of sulfonated poly(ether etherketone), SPEEK, and polyvinyl alcohol, PVA, in the presence of thionine (Th) results in systems exhibiting reversible redox processes. Efficient reduction of thionine took place when SPEEK/PVA/Th films were exposed to 350 nm photons. This photoreduction process involved radicals of SPEEK (sensitizer), which led to the formation of semithionine (thionine radical) as an intermediate, and finally leucothionine. Thionine was initially photoreduced (first 40 s – 50 s of illumination) via a zero-order rate law with a rate constant of $k = 1 \times 10^{-5}$ Ms^{-1}. The reaction seemed to follow dispersive kinetics after 40 s - 50 s of photolysis. Reformation of thionine was very slow and took 30-45 days for completion, but addition of distilled water (3 ml) to illuminated films accelerated the reaction which then proceeded via first-order kinetics with $k = 2.37$ s^{-1}. Unlike films, the Th photoreduction in SPEEK/PVA degassed solutions followed zero-order kinetics throughout the decay with $k = 2 \times 10^{-6}$ Ms^{-1}. In the presence of air, Th reformation-followed zero-order kinetics with a rate constant much lower than that of the reduction process ($k = 3.3 \times 10^{-8}$ Ms^{-1}). Th reduction and reoxidation were reversible in both SPEEK/PVA/Th films and solutions for more than 8 consecutive illumination cycles.

Efficient reduction of CCl_4 and $CHCl_3$ took place upon exposure to 350 nm photons that containing air saturated HCO_2H/HCO_2^- buffers and swollen SPEEK/PVA films. The highest quantum yields for the photoreduction of above halomethanes were recorded when 0.36 M formate buffers served as H atom donors at pH = 7.3 that contained swollen 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm). Both photoreductions consisted of two steps; slow initial step (induction period) followed by a linear step in which concentration of chloride ions increased rapidly compared to the initial step. Efficiency for the reduction of CCl_4 is 100 times higher

compared to the efficiency for the photoreduction of $CHCl_3$. The occurrence of post-irradiation formation of Cl^- during the reduction of CCl_4/ $CHCl_3$ in the dark confirmed that the photoreductions proceeded via a chain process.

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List of Abbreviations

BP	benzophenone
BPK	benzophenylketyl
PEEK	poly(ether ether ketone)
SPEEK	sulphonated poly(ether ether ketone)
PVA	poly(vinyl alcohol)
Th	Thionine
^{0}C	degree Celsius
EPR	electron paramagnetic resonance
ε	extinction coefficient
λ	wavelength
hr	hour
$h\nu$	photon
M	molar concentration
mM	millimolar
μM	micromolar
min	minute
nm	nano meter
OD	optical density
ϕ	quantum yield
rc	corrected rate
ri	initial rate
UV	ultraviolet
Vis	visible
E_0	energy potential
I_0	light intensity

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Chapter 1

Photo-responsive Polymers

1.1 Introduction

Polymeric and monomeric photo-responsive materials are very interesting because their properties can be reversibly altered by the presence of light.[1] Photo-responsive or light sensitive polymers have gained more interest in recent years since light is a renewable and readily available energy source. Further, light stimulation can be spatiotemporally localized and controlled.[2] Thus, polymeric systems offer a great potential to create unique systems that can be easily altered by light. The polymers may also show sharp responses to environmental changes such as physical, chemical or biochemical stimuli including pH, temperature, ultra sound, electrochemical potential, presence of enzymes, metabolites or gases and magnetic/mechanical/electric forces.[2,3] However, actuation of materials by light has gained much more attention because electromagnetic radiation is a highly efficient stimulation source.[2] Moreover, by-products are limited in most photochemical processes and many photosensitive polymers do not require additional reagents. Further, parameters such as light intensity, illumination time and wavelength are variables that can be simply altered. These variables may induce fast responses in photo-responsive systems exhibiting transformations not controlled by diffusional processes.[4] Photo-responsive polymer systems are interesting as they can result in reversible and irreversible transformations to control drug delivery, cell scaffold architectures, tissue engineering surface patterns and nano particulates. They can also be beneficial for manipulating pharmaceuticals, biological systems specifically in ophthalmology, gynecology, dermatology, holography etc., because light-responsive polymers do not require external photosensitizers, thus minimizing the potential for toxic side products.[4]

Polymers must contain chromophores, groups with pi-electrons and hetero atoms with non-bonding, valence shell electron pairs, in order to be reactive toward light.[5] Polyaniline, which has three distinct oxidation states with different colors and doping responses, is an example of a light-responsive polymer that is also synthesized by a photopolymerization method.[6] These photo-responsive polymers can experience several transformations such as ionization, isomerization, homolytic fragmentation, hydrogen abstraction, and more importantly, redox reactions. Light induced redox reactions are fairly reversible and proceed via well-known mechanisms. For these reasons they have been used extensively vastly during photoelectrochemical studies of polyimides, polyanilines, and poly(vinylcarbazols)[7]. Interestingly, irreversible photochemical reactions of such macomolecules also occur.[8] Specifically, photo-responsive polymers that generate reducing species have gained much interest in recent years as they can be applied in a variety of ways.[9-15]

1.2 Photosensitizers and Photo-initiators

Photosensitizers are molecules that absorb light and can act as donors by transferring energy to acceptor molecules or functional groups.[16] The acceptors then undergo various reactions such as polymerization, isomerization, coupling and others. Therefore, a good photosensitizer is not only a molecule that readily absorbs light, but also one that transfers energy efficiently to another molecule/group. Most common photosensitizers are aromatic compounds and some of them are capable of forming transfer complexes in the ground state even though the common phenomena is to from ‘exiplexes’ in the excited state.[16] Photo-initiators are compounds, usually organic, that absorb light and form reactive intermediates in the form of radicals, cations or anions that initiate multiple reactions. Specially, free radicals are frequently involved as key reagents in numerous redox processes. Some molecules can act as both photosensitizers and photo-initiators. Aromatic ketones such as benzophenone, is a good example for such compounds. The carbonyl orbitals not only in ketones but also in aldehydes and carboxylic acids are important in photochemistry. However, ketones and aldehydes able to absorb photons in the wavelength (λ) range between 230 – 300 nm are more photochemically reactive than carboxylic acids and their derivatives, which absorb light with 200 ≤ λ ≤ 220 nm. These absorptions of carbonyl groups correspond to an excitation of non-bonding electrons (n) on centered on the oxygen atom into an anti-bonding (π*) orbital of the carbonyl group.[16] Since n ⟶π* transitions are forbidden, such transitions are weak. The carbonyl group exhibits a polarization in the ground state, which can facilitate a nucleophilic attack by this group. The excited state is characterized by the presence of an unpaired electron, both in the π* antibonding orbital and in also in the p-type orbital of oxygen._The net result is an oxygen atom processing an unpaired electron in an 'n orbital' that is electron-deficient, whereas the carbon atom possesses excess electron density. In the triplet state, the carbonyl group is less stable because of the presence of electrons with parallel spins. Therefore, triplet carbonyl chromophores have chemical and physical characteristics close to that of a diradical and, in particular, have similarities to alkoxy radicals (RO•).[16,17] Initially, the orbital localized on the carbonyl oxygen is in the ground state. In the excited state, the π* orbital is delocalized over the

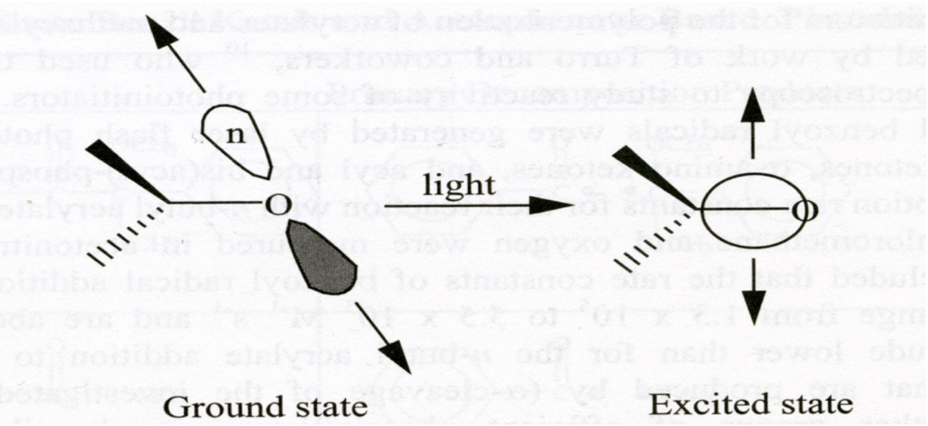

Figure 1.1: Illustration of the ketone carbonyl orbitals

entire carbonyl function, hence in an n ⟶ π* transition, the electron is further away from the oxygen and the molecule behaves like a di-radical.[16] Since they excited CO groups are similar to alkoxy radicals, they are able to yield a reducing radical via abstraction of a hydrogen atom from a donor molecule or intramolecularly from a C-H bond. For aliphatic ketones, hydrogen abstraction may occur from excited single and triplet states. In contrast, aromatic ketones abstract hydrogen solely from triplet excited states.[16] Abstraction of hydrogen is more efficient for carbonyl groups with a (n, π*) triplet state as lowest excited state. By comparison with (π, π*) triplet states as the lowest excited state, the (n, π*) triplet state is much more capable of abstracting hydrogen from donor molecules. Further the rate of hydrogen abstraction also depends on the C-H bond strength of the donor molecule. The primary products from hydrogen abstraction by carbonyl compound are an α-hydroxy, or ketal, radical ($R_2\bullet C\text{-}OH$) and the radical of the hydrogen donor molecule.[16] Photo-initiators/photosensitizers possessing carbonyl groups can either be small molecules or polymers and it was demonstrated that ketones in polymeric compounds undergo the same photoreactions as small molecules.[18]

1.3 Benzophone as a photosensitizer

Benzophenone (BP) has been studied over six decades as a model system for understanding the photochemistry and photo-physics of organic chromophores.[19] The presence of the carbonyl group which act as the chromophore, provides benzophenone to function as a highly efficient photosensitizer. Numerous photo chemical reactions initiated by this photosensitizer have been eextensively studied in the recent past.[19-24] In the presence of light, the carbonyl group of benzophenone absorbs photons of $250 \leq \lambda \leq 380$ nm and generates a singlet excited state. Then this singlet excited state undergoes an intersystem crossing transition and yield the lowest energy triplet excited state of benzophenone (T_1) which behaves as a di-radical as mentioned above. If a hydrogen atom donor is present in the system, this T_1 state of BP, easily and effectively abstracts a hydrogen atom and form α- hydroxy radical of benzophenone (benzophenyl ketyl radical, BPK). These radicals are highly reactive reducing species with a half-life of 10^{-8} s in solutions.[25,26] BPK radicals exhibit in the fluid phase a transient absorption centered at $\lambda = 545$ nm and decay via a second-order dimerization reaction with a rate constant of $k_{decay} = 1 \times 10^{9}$ $M^{-1}s^{-}1$.[27] Illustrated in Figure 1.2 is a sequence of elementary steps leading to the α-hydroxy radical of benzophenone in a solution containing 2-propanol as the H-atom donor. As shown in the second step, H-atom abstraction from 2-propanol by the triplet excited state generates two α-hydroxy radicals: one from BP and another from the alcohol. In the third step the radical from 2-propanol reduces a second BP molecule forming an additional benzophenone ketyl radical. Thus, under appropriate conditions (high concentrations of 2-propanol) two α-hydroxy radicals of BP are generate per absorbed photon.

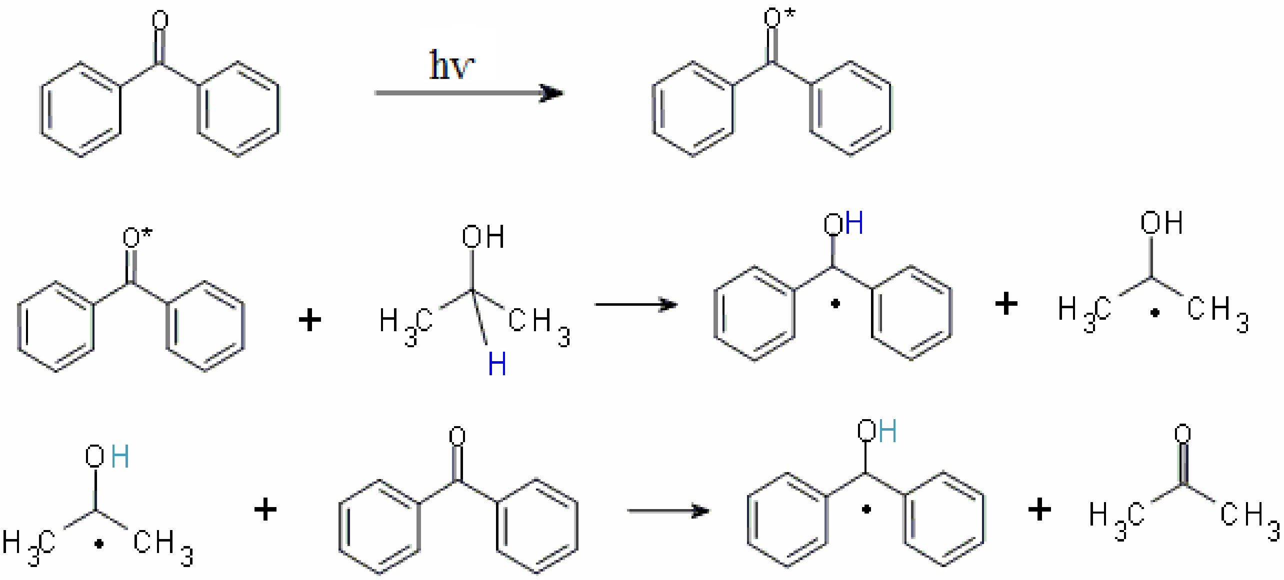

Figure 1.2: Schematic representation of the reactions leading to ketyl radicals of BP.

Aliphatic hydrocarbons with hydrogen atoms at the alpha position and also possessing electron donating heteroatoms such as O, N or S, are common H-atom donors. Hence, iso-propanol is a very good H-atom donor. The substituent groups attached to the benzophenone aromatic ring affect significantly on its reactivity. BP possessing electron donating substituents at the meta and para positions of the aromatic rings of exhibit a lower photo reactivity, while electron withdrawing substituents at these positions enhance the reactivity. The polarity of the surrounding solvent is also a factor that effects the reactivity of BP.[5]

1.4 SPEEK/PVA system

Since the combination of benzophenone and 2-propanol effectively generate α- hydroxy radicals upon illumination, our research group has designed a polymer analogue to the ketone/alcohol solution system. The purpose was to explore potential useful properties exhibited by a polymeric system that would not be possible to realize using BP/2-propanol solutions. The system that has been used by our group consists of sulphonated poly(ether etherketone), SPEEK, as the photo sensitizer and poly(vinyl alcohol), PVA, as the hydrogen atom donor.[11] Poly(ether etherketone), PEEK is a commercially available macromolecular material containing benzophenone groups which exhibits high thermal, chemical and mechanical properties. However, while polymeric alcohols dissolve in polar solvents such as water, PEEK is insoluble in most solvents at room temperature. Therefore, preparation of mixtures containing PEEK and polymeric alcohols by simple solution procedures is not possible. Adding sulphonate groups to PEEK can generate derivatives that are water-soluble, eliminating the solubility problem. Treatment of PEEK with concentrated H_2SO_4, yields SPEEK (as illustrated in figure 1.3) and the fully sulfonated SPEEK easily dissolves in water. Moreover, this addition alters the chain conformation and decreases the number of crystalline domains of the polymer, while simultaneously increasing the molecular bulkiness.[28] The degree of sulfonation affects the properties of the final product such as solubility and conductivity. PVA was chosen as the polymeric alcohol and because of the favorable physical and chemical properties of this polymer including the ability to act as hydrogen donor. The favorable properties of the polyol, including water-solubility, and low cost of production have made PVA a widely used macromolecular material. Further, PVA can be used to prepare thin, optically transparent films using solution-casting methods with chemical crosslinking.[10,11,29,30]

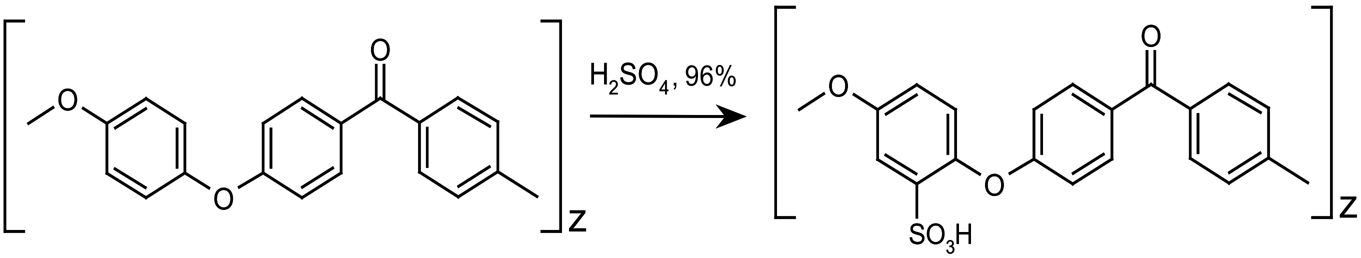

Figure 1.3: Structures of PEEK and of SPEEK generated via sulfonation.

The polymer blends were designed to be light sensitive, that is to employ photons as the energy source for the formation of reactive species. When mixtures of SPEEK and PVA are exposed to 350 nm photons or direct sunlight, the carbonyl chromophores of the benzophenone functions present in SPEEK form (n, π*) triplet states similar to those of benzophenone, followed by reaction of excited states with PVA via H atom abstraction. Accordingly, a strongly reducing α-hydroxy radical of the polyalcohol (R_2C•OH) is formed together with a radical from SPEEK (or HSPEEK•). The polyol radical can reduce another benzophenone function of a different SPEEK chain, generating a second polymeric benzophenone α-hydroxy radical.[11] This process yields two SPEEK radicals per absorbed photon. A scheme of the formation process is presented in Figure 1.4.[17] Furthermore, the sensitizing ability of SPEEK persists over long times in the presence of radical scavengers that regenerate the polyketone through the oxidation of HSPEEK•.[9]

Previous studies with the SPEEK/PVA system in both solutions and films have proven that photochemical reactions in water and in the solid state can be initiated using such polymer combination.[11-14,27] The optical spectrum of SPEEK is similar to that of benzophenone and the absorption of 350 nm photons by SPEEK (ε = 900 M^{-1} cm^{-1}) yields HSPEEK• which exhibit an absorption centered at 565 nm; (ε = 3.5 x 10^3 M^{-1} cm^{-1}), ε = extinction coefficient.[27] HSPEEK• decays in SPEEK/PVA films via second-order dimerization with k_{decay} = 4 x10^{-2} $M^{-1}s^{-1}$, whereas in air-free solutions the rate constant is 290 $M^{-1}s^{-1}$.[10] Hence the radicals have a relatively long lifetime (several minutes) in solutions free of O_2 and up to 5 h in films of SPEEK/PVA blends.[10] The polymeric HSPEEK• in PVA copolymers is easily detected optically in films illuminated under air due to the low solubility of O_2 in PVA. Under such conditions HSPEEK• reacts with O_2 according to a pseudo first-order rate law with k_{decay} = 1 x10^{-3} s^{-1}.[10] In air free solutions or in films, SPEEK• decays with a rate constant that are, at least, six orders of magnitude smaller than those of BPK radicals of benzophenone. This unusually long lifetime of the polymeric HSPEEK• enables this species to reduce various of chemicals that are not efficiently attacked by smaller

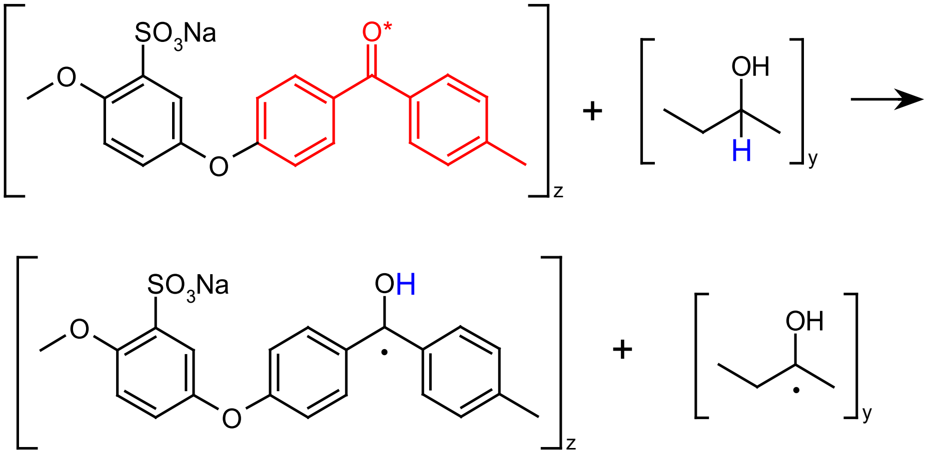

Figure 1.4: Schematic representation of the reaction leading to SPEEK and PVA radicals

radicals. Such species frequently decay via diffusion-controlled radical-radical combinations/disproportionations. Due to their fast decay, these radical are unable to attack compounds with which their reactions are slow.[10]

The unusual stability of HSPEEK• in air-free solutions, or crosslinked SPEEK/PVA blends, also enables their detection using optical and EPR methods. Moreover, the oxidation potential of HSPEEK• is 1.3 V,[27] which is similar to the value for the analog BP radical. This means that HSPEEK• is also capable of acting as a strong reducing agent. Earlier experiments have proven that SPEEK radical is able to reduce Ag^+, Au^{3+}, Cu^{2+} [27], as well as O_2 [11,12] (into H_2O_2) in both aqueous SPEEK/PVA solutions and swollen cross-linked films of the polymer. Moreover, our research group was able to reduce several organic halogenated pollutants such as CCl_4, $CHCl_3$ and $CFCl_3$ effectively by illuminating $CHCl_3$ and CCl_4 in aqueous SPEEK/ HCO_2^- solutions.[9,14,15] An important feature of this SPEEK/PVA photochemical system is that oxidation of SPEEK• regenerates the carbonyl chromophoric unit of SPEEK. This implies that overall, the only chemical change induced by the photolysis is the transformation of alcohol functional groups of PVA without altering the light sensitive SPEEK or much of the chemical and physical characteristics of the polymer mixture.

Crosslinking PVA using dialdehydes, such as glutaraldehyde has been well documented.[30-32] In the presence of a strong acid, the reaction between hydroxyl groups in PVA and aldehyde groups in glutaraldehyde yield a crosslinked structure. For our SPEEK/PVA films, glutaraldehyde was used as the crosslinking agent as it covalently links to PVA chains, immobilizing the SPEEK polymer. HCl was used as the catalyst for this reaction. SPEEK/PVA films are optically transparent, sturdy yet flexible and can be fabricated with thicknesses in the micron range, containing the polyketone as a solute and the polyol as the main component.

1.5 Halogenated Organic Pollutants

The halogenated hydrocarbons and their derivatives show low chemical reactivity as they are stable compounds. They are also non-biodegradable, hence can cause environment pollution as they have wide industrial and agricultural applications.[33] Halogenated hydrocarbons are not only valuable as industrial solvents but also used as pesticides, dyes, drugs, explosives, petrochemicals, resins, pharmaceuticals, synthetic fibers and cosmetics. Chlorinated compounds such as chloroform, carbon tetrachloride, dichloromethane and dichloroethane are the most commonly used halogenated hydrocarbons and the toxic effects of these compounds have been established in various biomedical studies.[33] Direct contact of these solvents have been reported to cause irritation, pulmonary edema, and inflammation of the respiratory tract. Moreover, higher concentration of these chlorinated hydrocarbons may cause liver injury, pathomorphological changes in liver, urological problems, carcinogenesis, neurotoxicity and adverse effects on the reproductive system.[33] There are number of ways to reduce the exposure of these chlorinated compounds such as: extraction, incineration, chemical degradation, bioremediation, super-critical water oxidation, electrochemical treatment and photochemical processes.[34] Photochemical processes are applied to treat pollutants in solutions within the concentration range of 10^{-3} M to 10^{-6} M.[35] Hence, among all these methods, photochemical techniques have been found as particular useful to degrade chlorinated compounds[36,37], specially for converting them to non-toxic compounds. Moreover, most of the conventional procedures are either slow or expensive to afford at large scale.[38-43] Futher, some of the conventional degradation processes have the drawback of converting the pollutants into even more toxic products.[40-43]

Many chlorinated aromatic compounds have been converted to less toxic compounds in recent past.[44,45] There have been reports about photochemical decomposition of CCl_4, $CHCl_3$, trichlorophenol (TCP) and pentachlorophenol (PCP) using activated H_2O_2 in the presence of UV light. Our research group has also investigated the possible degradation of CCl_4, $CHCl_3$ and Cl_3F in aqueous solutions containing SPEEK and formate buffers.[9,14,15]

1.6 SPEEK/ HCO_2^- system

Reduction of halogenated organic compounds by illuminating suspensions that contain formate (HCO_2^-) have been reported in recent past.[46,47] Oxidation of HCO_2^- generates $\bullet CO_2^-$, which is an efficient reducing radical, and can actively participate in decomposing halogenated organic compounds. The oxidation potential of $\bullet CO_2^-$ is ($E^0[\bullet CO_2^-/CO_2] = 1.8$ V), which is higher than that for the α-hydroxy radical of 2-propanol ($E^0[(CH_3)_2C\bullet OH/(CH_3)_2C{=}O, H^+]) = 1.4$ V). Thus, higher efficiencies for the reduction of halogenated compounds were anticipated if $\bullet CO_2^-$ was generated by photolysis of SPEEK. The triplet excited state of BP groups from SPEEK were expected to react with HCO_2^- via H-atom abstraction to form polymeric BPK radicals and $\bullet CO_2^-$.[9,13-15,48] The resulting $\bullet CO_2^-$ could then reduce a carbonyl group of SPEEK forming a second polyketone radical in a way analogous to the SPEEK/PVA system. In principle, $\bullet CO_2^-$ could also reduce halogenated compounds to some extent if their concentrations were high enough. However, because of the low-rate constant for the reaction between $\bullet CO_2^-$ and the halogenated methanes, the reduction of these materials was interpreted as resulting from reactions involving only HSPEEK• as the reductant.[9,13-15]

1.7 Goals and prospects of the dissertation

In this investigation we introduced some dyes in SPEEK/PVA solutions and films to study whether a reversible reduction of the coloring agents was possible. In addition, SPEEK/PVA polymer films were employed to test the possibility of eliminating halogenated organic pollutants such as CCl_4 and $CHCl_3$ from aquatic environments more efficiently than by using solutions of the polymers to photogenerate reducing radicals. Utilization of films was expected to eliminate the need of separating SPEEK and PVA from the aqueous environment after the degradation process was completed.

One of the objectives of this work was to achieve light-induced reversible systems using the photosensitive SPEEK/PVA blends in the presence of dyes. My goals were to understand the mechanism of the reduction, elucidate how the reduced dye (leuco form) was oxidized, improve the speed of the oxidation process and test other polymers that can substitute PVA as the optically transparent matrix (and also as electron donor). Further possibilities were the use of such dye-containing films for photo-imaging and photo-patterning by means of UV light. My investigations tested ways to remove photo-generated patterns using oxidation of the reduced dyes via exposure of SPEEK/PVA films to solvents (H_2O, acetonitrile, and others) containing air.

Additional photochromic properties of SPEEK-based films worth studying include their use as protective barriers in reactive clothing that chemically inactivate toxic chemicals and detoxification of contaminated water. Environmental issues caused by halogenated organic pollutants have become a global issue in recent past. Finding simple, cost-effective solution to this problem is not an easy task. Since photochemical degradation of toxic chemicals has been one of the potentially cost effective, simple and a greener approach, our investigation tested methods to reduce toxic organic halogenated compounds such as CCl_4 and $CHCl_3$ using SPEEK/PVA films in formate buffer thus establishing a new avenue for the potential remediation of halogenated organic pollutants in the environment. Our goal was to establish an efficient method and figure out the mechanism for the photo reduction of these compounds.

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Chapter 2

Light-induced reversible reactions in aqueous SPEEK/PVA solutions containing thionine

2.1 Introduction

Polymeric and monomeric photo responsive materials are very interesting because their properties can be reversibly altered by the presence of light.[1] Photo-responsive polymers have gained more interest in recent years since light stimulation can be spatiotemporally localized and controlled.[2,3,4,5] These polymeric systems offer a great potential to create unique systems that can be easily altered by light. Actuation of materials by light has gained much more attention because electromagnetic radiation is a highly efficient stimulation source.[2] Further, parameters such as light intensity, illumination time and wavelength are variables that can be simply altered. Examples of such a system are SPEEK/PVA polymer blends, which absorb light and form a reactive intermediate (SPEEK*) that is able to yield a reducing radical via abstraction of a hydrogen atom from PVA.[6] Previous studies with the SPEEK/PVA system in both solutions and films have proven that photochemical reactions in water and in the solid state can be initiated using such polymer combination.[6,7] Solution studies provide mechanistic information to understand the photochemical behavior of polymer films. In films, PVA also act as the main structural component in addition to serving as an H- atom donor. Hence, solution experiments were also performed to understand the effectiveness of PVA as a donor of H atoms.

The present investigation is centered on the photochemical properties of aqueous SPEEK/PVA solutions containing dyes in attempts to achieve a reversible reduction of the coloring agents. Thionine (Th) was anticipated to be easily transformed to the reduced form upon reacting with a SPEEK radical that forms under illumination of SPEEK/PVA polymer system. The reduced form of the dye may then experience oxidation simply by reacting with O_2. The result of such process is reforming the original form of the dye, thereby yielding a reversible photochemical system. Thiazine dyes, such as thionine and methylene blue have become important as sensitizers in photochemical, photophysical and photobiological processes.[8.9] Moreover, the electrostatic attraction between the positively charged dye and the negatively charged sulfonic groups of SPEEK may be strong enough to keep the dyes firmly bonded to the polyelectrolyte.[9] Reduction of methylene blue by the α-hydroxy radical of D-glucose (a plausible model for the SPEEK radical) occurs with a rate constant of 2.4×10^{10} M^{-1} s^{-1}.[10] Furthermore, rate constants of 3.4×10^9 M^{-1} s^{-1} and 4.4×10^9 M^{-1} s^{-1} were reported for the reduction of methylene blue by the $\bullet CH_2OH$ and $(CH_3)_2C\bullet OH$ radicals.[11] For Th, the rate of reduction of the dye by these two α-hydroxy radicals (reasonable models for HSPEEK•) were reported to be 2.6×10^9 M^{-1} s^{-1} and 4.2×10^9 M^{-1} s^{-1}, respectively.[11] Further, numerous reports are available on the reversibility of the methylene blue and thionine reduction in various systems.[12] Therefore, Th was incorporated into SPEEK/PVA polymer systems to explore the feasibility of reversible redox transformation of coloring agents.

2.2 Experimental Section

SPEEK was prepared by sulfonation of poly(ether etherketone), PEEK, supplied mainly by Solvay, with an average molar mass of $M_n = 4.0 \times 10^4$ g/mol^{-1}. Occasionally PEEK samples from Victrex, Evonik and Polyscience were also tested, ($M_n = 4.5\text{-}5.0 \times 10^4$ g/mol^{-1}); PVA ($M_n = 8.9\text{-}9.8 \times 10^4$ g/mol^{-1}) and Th were supplied by Sigma-Aldrich whereas all other chemicals were obtained from VWR. SPEEK/PVA polymer solutions were prepared according to a standard procedure,[7] which consisted of adding 0.6 mL of 10^{-4} M Th and 0.4 mL of distilled water to an optical cuvette containing 2 mL of a mixture containing 3.8×10^{-2} M SPEEK and 0.82 M PVA, resulting in a total volume of 3 mL). Necessary pH adjustments were done using 0.1 M NaOH and 0.1M HCOOH, the final acid concentration was 3.3 x 10^{-3} M. All solutions were prepared with purified water obtained from an ion-exchange resin deionizer (US filter service). The optical cuvettes were sealed with rubber septa and the solution was degassed by bubbling Ar for 15-20 min. Irradiations were carried out inside a Rayonet, RPR-100 circular illuminator that generated photons with $\lambda = 350 \pm 15$ nm by means of 16 RPR-3500A lamps. Uniform exposure of the optical cells was achieved by positioning them at the center and mid-height of the cavity inside the Rayonet, where the temperature amounted to 29 ^{0}C. The light intensity (I_0) was determined using the Amberchrome 540 actinometer.[13]

The reaction progress was monitored via recording UV-visible spectra at different illumination times on a Shimadzu UV-2450 spectrophotometer. Once the solution turned colorless after dye reduction was completed, air was introduced into the optical cell and the ensuing absorbance changes were monitored as a function of time. Finally, the same procedure of photolysis and reaction with air was repeated for 8 cycles to check the reversibility of the system. Every photochemical experiment was performed at least twice and for the desired exposure time without interruptions, followed by retrieval of samples for chemical analysis. All other measurements were conducted at room temperature (25 °C). Electron paramagnetic resonance (EPR) spectra were collected at the X-band frequency with a Bruker Biospin EMX spectrometer fitted with an ER-4119-HS perpendicular-mode cavity and a liquid nitrogen finger Dewar for low-temperature measurements. Instrument conditions were a microwave frequency of 9.386 GHz, field modulation frequency of 100 kHz, and modulation amplitude of 0.6 mT. Samples were prepared by illumination for several minutes of Ar-saturated SPEEK/PVA/Th solutions in EPR tubes.

Photolysis of the tubes occurred inside of a transparent glass Dewar either at room temperature, followed by fast freezing with liquid N_2, or with solutions frozen at 77 K.

2.3 Results and Discussion

The absorption maximum of Th detected in water at 600 nm shifts by 15 nm upon binding to SPEEK/PVA polymers. Similar behavior has been reported for highly concentrated (50 - 200 mM) solutions of deoxyadenosine monophosphate (dAMP) or deoxyguanosine monophosphate (dGMP).[14] The molar extinction coefficient (ε) of Th at 615 nm in SPEEK/PVA solutions amounted to $6.6 \times 10^{4}\ M^{-1}\ cm^{-1}$ and was obtained in the range of $2 \times 10^{-6} \leq [Th] \leq 1 \times 10^{-5}$ M where the Lambert-Beer law is obeyed.

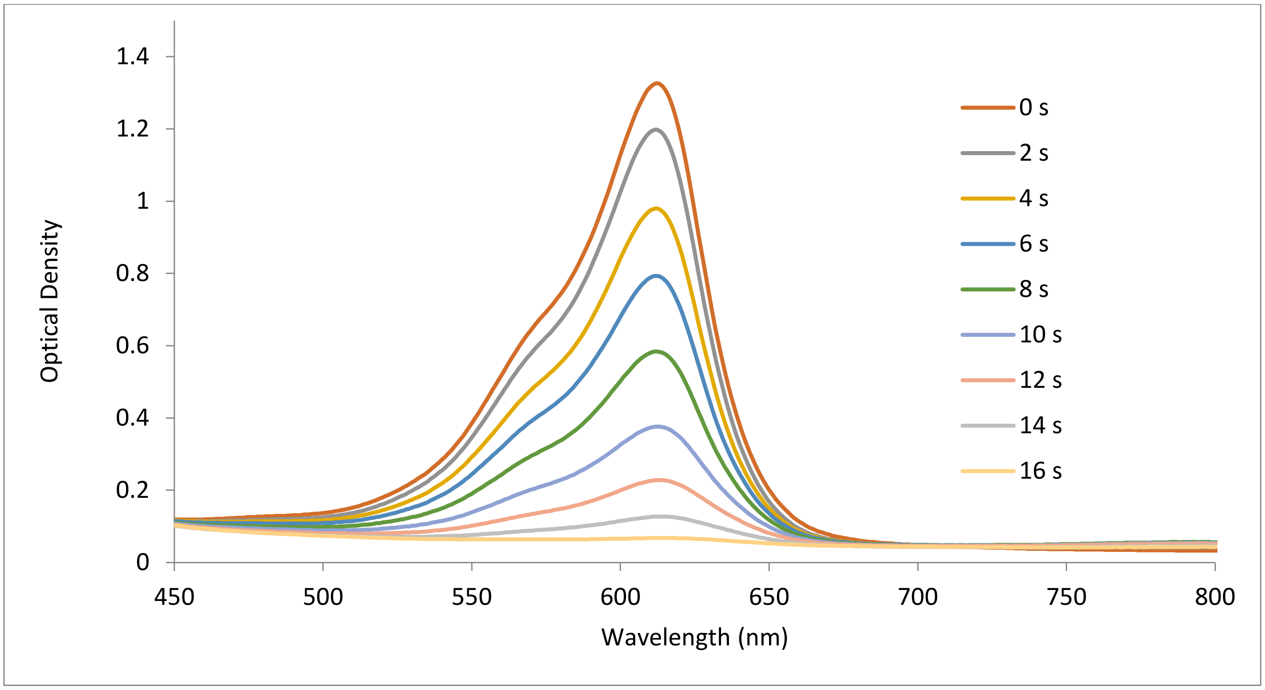

Figure 2.1: Absorption spectrum during illumination of an air-free solution with 2.0×10^{-5} M thionine, 3.8×10^{-2} M SPEEK, 0.82 M PVA, pH = 7 and $I_0 = 1.0 \times 10^{-5}$ M (hν)/s.

Despite the shift in the wavelength of maximum absorbance, (λ_{max}), the ε value compares well with the extinction coefficient determined in water, 5.6 x 10^4 M^{-1} cm^{-1}.[15] When SPEEK/PVA solutions are exposed to UV light, simultaneous formation of SPEEK and PVA radicals is anticipated.[6,7] Earlier solution work has shown that Th is reduced via a two-electron process into the leuco form, leucothionine or LTh.[16,17]

Blank experiments performed in the absence of light, SPEEK and PVA were failed to yield LTh. SPEEK/PVA solutions were then exposed to 350 nm photons for 20 mins under air as a control experiment. The photoreduction of thionine in SPEEK/PVA solutions was not detected in the presence of O_2. This was expected as the optical signal for HSPEEK• with a λ_{max} of 565 nm was not detected upon photolyzing an air saturated SPEEK/PVA solution. On the other hand, the signal was clearly visible when degassed SPEEK/PVA solutions were exposed to 350 nm photons. These findings prove that the photogenerated radicals react fast with O_2. Hence all the photoreduction experiments were carried in degassed solutions. Illustrated in Figure 2.1 is the evolution of the thionine spectrum during the photolysis of an air-free solution containing the dye and both polymers. Complete photoreduction of the dye was achieved in about (16- 18) s. The polymer radicals photogenerated in SPEEK/PVA solutions were anticipated to reduce Th to the leuco form, which explains the bleaching of the dye spectrum shown in Figure 2.1. Detection of the LTh absorptions, centered at 310 nm and 262 nm,[17] was not possible due to the strong SPEEK absorptions in that range.

Presented in Figure 2.2 is the decay of [Th] as a function of illumination time, indicating that the Th photoreduction proceeds via zero-order kinetics with a rate constant of $k = 1.37 \times 10^{-6}$ Ms^{-1}. Reduction of Th in neutral solutions is known to yield an unstable intermediate called semithionine (or thionine radical, Th•) with an optical signal centered at 770 nm ($\varepsilon = 1.72 \times 10^4$ M^{-1} cm^{-1})[18] that decays via radical-radical combination with $k = 1 \times 10^9$ M^{-1} s^{-1}.[18]

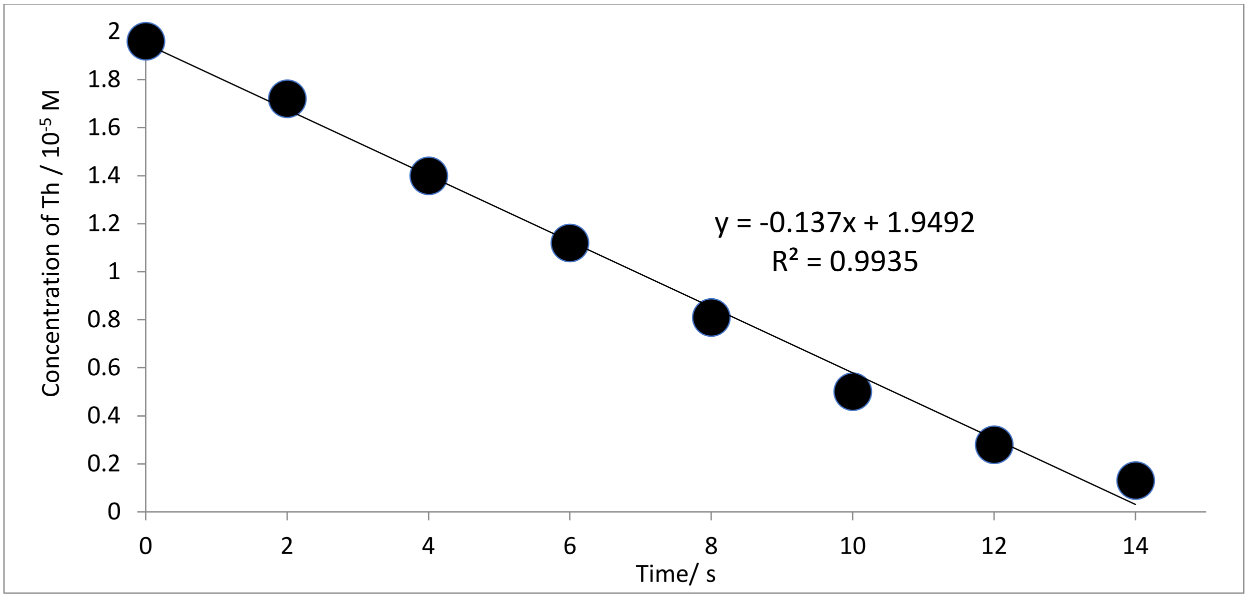

Figure 2.2: Photoreduction of 2×10^{-5} M thionine as a function of illumination time in 3.8×10^{-2} M SPEEK (Solvay) and 0.82 M PVA air free solution ($I_0 = 1.0 \times 10^{-5}$ M (hν)/s). T= 29^0 C.

However, a shift in λ_{max} of semithionine was reported when thionine was photoreduced by ferrous ions in an aqueous medium containing 60 % (W/V) poly(ethylene glycol), PEG.[19] The characteristic λ_{max} of the semithionine, which appears at around 760 nm in water, was shifted to 790 nm in the PEG solution.[19]

Similar results were obtained in Th/SPEEK/PVA solutions, where a broad and weak absorption signal with λ_{max} = 790 nm resembling the optical signal of Th•, was observed in addition to the main absorbance centered at 615 nm. This signal, shown in Figure 2.3(a), persisted for several seconds which is surprising given that such radical decays fast in water.[20] The unusual stability of the radical is probably due to strong binding of this species to SPEEK, which enables the Th radical to survive transiently, achieving a maximum [Th•] of ≈ 1 μM.

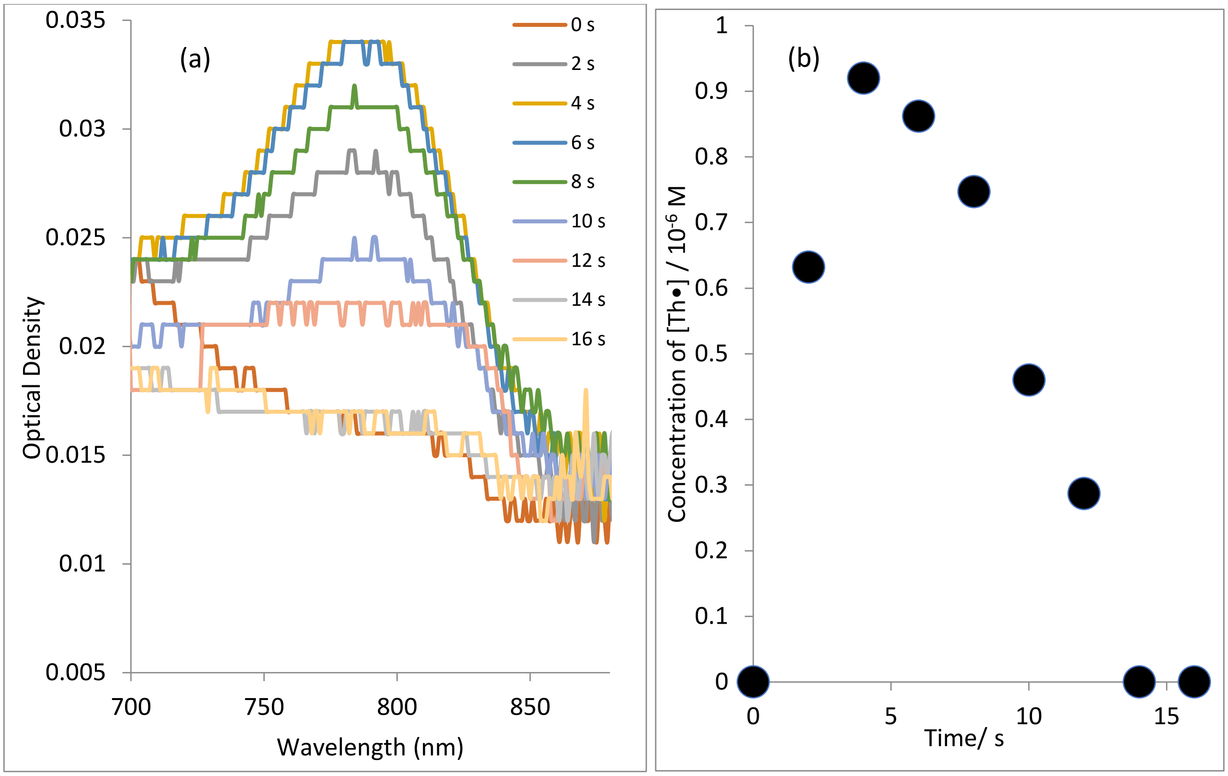

Figure 2.3: (a) Evolution of Th• spectra with time; (b) change in [semithionine] with illumination time during the photoreduction of air-free 2 x 10^{-5} M thionine in 3.8 x 10^{-2} M SPEEK (Solvay) and 0.82 M PVA at pH = 7 ($I_0 = 1.0 \times 10^{-5}$ M (hν)/s. T = 29^0 C.

The overall transformation of Th to LTh involves disproportionation of Th•. The following mechanism was proposed for the photoreduction of thionone in the SPEEK/PVA polymer system,

$$\text{SPEEK} + h\nu \longrightarrow \text{SPEEK}^* \qquad (1)$$

$$\text{SPEEK}^* + \text{PVA} \longrightarrow \text{HSPEEK}\bullet + \text{PVA}\bullet \qquad (2)$$

$$\text{PVA}\bullet + \text{SPEEK} \longrightarrow \text{HSPEEK}\bullet + \text{PVA(ox)} \qquad (3)$$

$$\text{HSPEEK}\bullet + \text{Th}^+ \longrightarrow \text{Th}\bullet + \text{H}^+ + \text{SPEEK} \qquad (4)$$

$$2\text{Th}\bullet \longrightarrow \text{LTh} + \text{Th}^+ \qquad (5)$$

In this mechanism SPEEK* represents the triplet excited state of SPEEK, HSPEEK• corresponds to the SPEEK radical after H-atom abstraction from PVA, PVA• represents the radical formed after the loss of a H-atom by the polyol, and PVA(ox) corresponds to a macromolecule in which an alcohol function was oxidized to a ketone group. Because the overall photoreaction is controlled by the initial excitation step (which occurs with an unchanging rate given the constant flux of photons entering the sample) the change in [Th] is linear with time.

In solution, formation of Th dimers and trimers are evident from shifts to shorter wavelengths in the main absorption band.[15] Spectral changes due to dimerization of Th was anticipated at high concentrations which were indeed noticed in solutions without SPEEK. Despite the high [Th] present in polymer solutions, no evidence of dimerization [no shifts in the optical signal shown in Figure 2.1] was found in the presence of SPEEK, supporting the notion that association of dye molecules was inhibited due to binding of Th to the polyelectrolyte. The fact that no Th aggregation took place in SPEEK/PVA polymer solutions can be attributed to the strong electrostatic binding of the positively charged thionine with the anionic sulfonic groups of SPEEK, which prevented interactions between dye molecules.

EPR spectroscopy was used to confirm the formation of Th radical exhibiting an absorption centered at 790 nm in Figure 2.3. Figure 2.4 a) illustrates a spectrum collected from an air-free aqueous SPEEK/PVA solution at pH = 7, without Th, that was photolyzed at 350 nm for 10 mins inside of an optically transparent glass dewar at room temperature, followed by rapid freezing with liquid N_2. A single broad and intense signal with g = 2.003 was observed at 77 K. Such a signal was previously recorded during photolysis of SPEEK/PVA solutions which is correspond to HSPEEK•.[21] All attempts to detect the PVA radical (PVA•) from the photolysis of SPEEK/ PVA blends failed in the present and past experiments.[21]

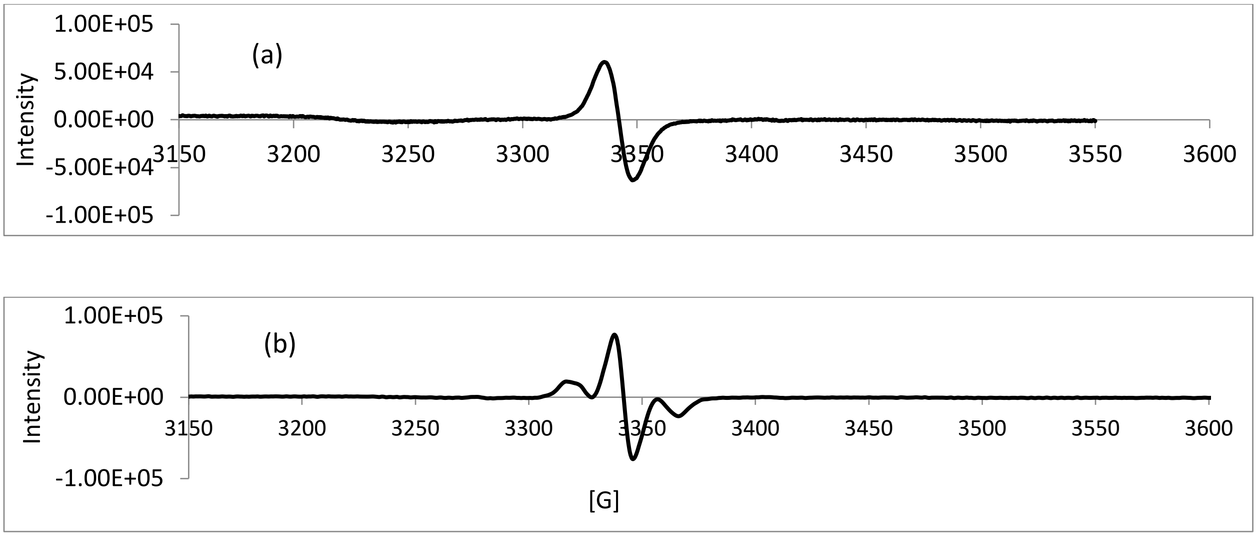

Figure 2.4: EPR spectra collected at 77 K from air-free aqueous solutions of a) SPEEK (3.8 x 10^{-2} M)/PVA (0.82 M) prepared via room temperature photolysis for 10 min followed by fast freezing under illumination with liquid N_2 b) SPEEK (3.8 x 10^{-2} M), PVA (0.82 M) and 10^{-4} M of Th prepared via room temperature photolysis for 1 min followed by fast freezing under illumination with liquid N_2 at pH = 7 with $I_0 = 1.0 \times 10^{-5}$ M (hν)/s.

Since a large amount of SPEEK was used in the experiment, such a result was not surprising as a high [SPEEK] facilitated fast scavenging of PVA• by the polyketone. Figure 2.4 b) exhibits a spectrum collected from an air-free aqueous SPEEK/PVA/Th solution at pH = 7, that was photolyzed for 5 min at room temperature, followed by rapid freezing with liquid N_2. Apart from a broad intense signal that was identified as HSPEEK•, two additional signals with g = 1.989 and g = 2.018 were observed at 77K which can attributed to signals of Th•.

Presented in Figure 2.5 is the evolution of the rate of Th photoreduction at different light intensities in solutions with pH = 7. Light intensities were changed by removing 2 bulbs at a time and were in the range of (2.0 - 12.0) x 10^{-6} M(hν)/s. The rate decreased linearly with decreasing light intensity with a gradient of 0.08 which is the average quantum yield (Φ) for the photoreduction of thionine in SPEEK/PVA polymer solutions. No significant advantage resulted when using small intensities of light. Hence, all experiments employed a high light intensity, 1 × 10^{-5} M (hv)/s, thereby avoiding a slow photoreduction of thionine.

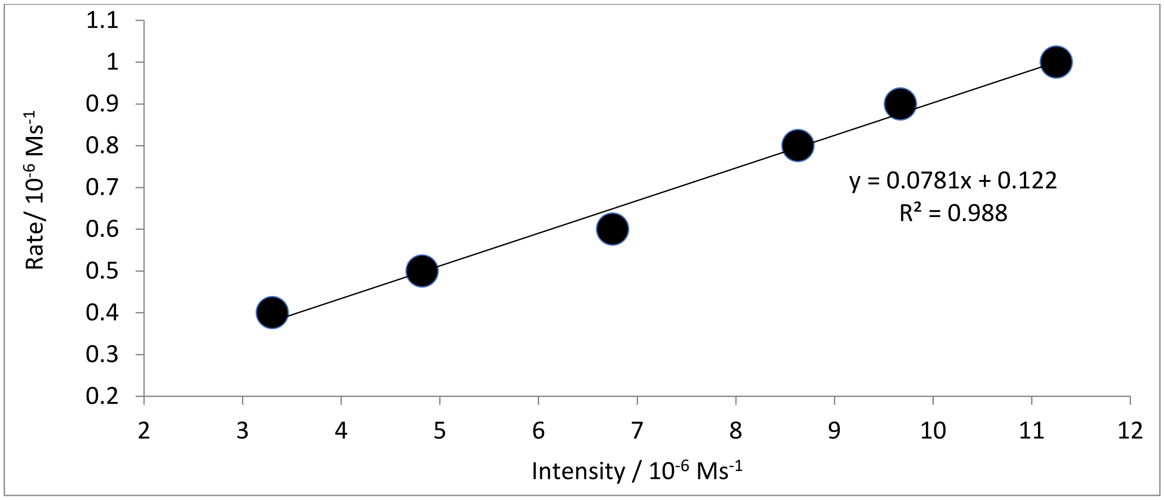

Figure 2.5: Dependence of the photoreduction rate on light intensity for degassed solutions with 3.8 x 10^{-2} M SPEEK and 0.82 M PVA at pH = 7

Displayed in Figure 2.6 is a comparison of quantum yields of thionine photoreduction as a function of pH in the range of $4 \leq pH \leq 9$; experiments in highly acidic solutions were not conducted as the quantum yields are very low at pH < 4. As the pH increases, the reaction efficiency increased smoothly from 0.03 at pH = 4.5 to 0.1 when the pH was 6.8 and remained constant thereafter. Such a behavior was expected as H_3O^+ quenches the triplet state of benzophenone via energy transfer ($k_q = 7 \times 10^8$ M^{-1} s^{-1}), thereby inhibiting radical formation.[22] An analogous quenching of the SPEEK triplet excited state by H_3O^+ was attributed to the slow photoreduction of $CHCl_3$ and CCl_4 in acidic SPEEK/HCO_2^- solutions.[23,24] The quenching effect of the hydronium ion on SPEEK* explains the low quantum yield values at low pH values and the subsequent increase in efficiency with decreasing [H_3O^+] shown in Figure 2.6. Further, HSPEEK• is a strong reducing agent in solution with an oxidation potential in the range of 1.2−1.4 V at pH = 0.[7] As is typical of α-hydroxy radicals, the potential of HSPEEK• is expected to increase in a Nernstian fashion with increasing pH. Hence the efficiency of the Th photoreduction is anticipated to increase with increasing pH. However, quenching of the SPEEK triplet excited state by hydroxide ions was

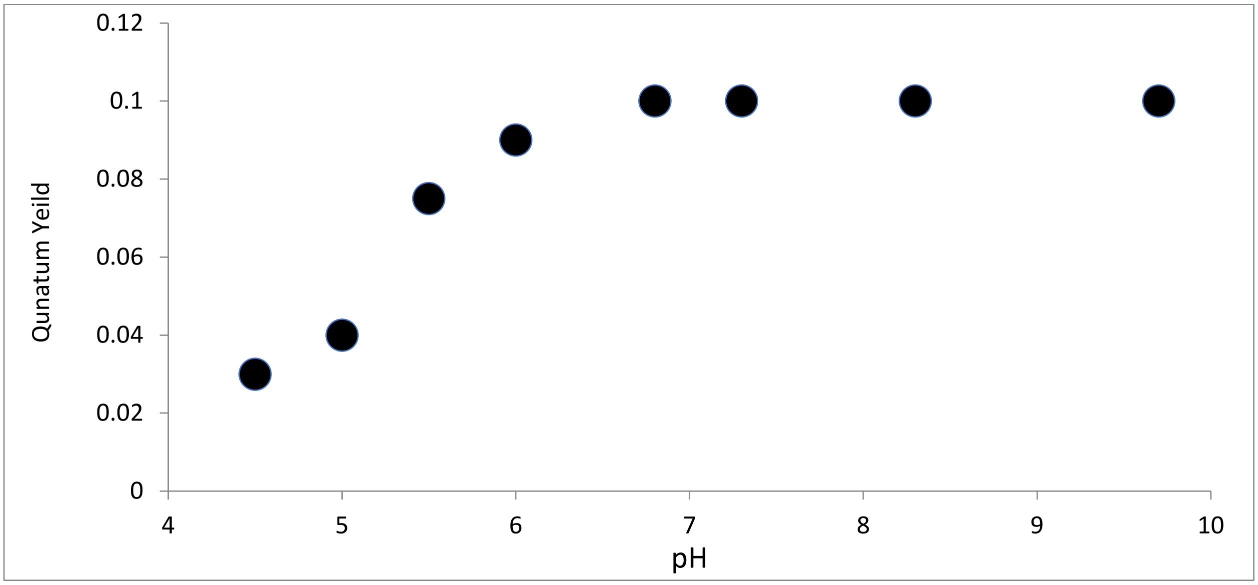

Figure 2.6: Efficiency of photoreduction of thionine as a function of pH determined via illumination of air free 3.8 x 10^{-2} M SPEEK(Solvay) and 0.82 M PVA. $I_0 = 1.0 \times 10^{-5}$ M (hν)/s. T = 29 ^{0}C.

also assumed to occur when $CHCl_3$ and CCl_4 were photoreduced in aqueous SPEEK/HCO_2^- solutions.[23,24] This assumption was based on the fact that OH- is also a quencher of the triplet excited state of benzophenone although with a lower k_q value of 5×10^6 M^{-1} s^{-1}.[25] On the other hand, the standard potential for the reduction of Th to LTh becomes increasingly negative with decreasing H_3O^+, reaching a value of about -0.2 V when pH ≈ 9.[26] The fact that a constant Φ value of 0.1 was obtained at pH ≥ 6.8 implies that the increasing reducing driving force of HSPEEK•

with augmenting basicity counteracts both the increased quenching of SPEEK* by OH^- ions and the potential of the Th/LTh couple turning more negative as $[H_3O^+]$ decreases.

The oxidation of LTh in solutions with air to reform thionine also follows zero-order kinetics with $k = 2.8 \times 10^{-8}$ Ms^{-1} (1.7×10^{-6} $Mmin^{-1}$, Figure 7). In such solutions open to air $[O_2]$ remains constant at 2.6×10^{-4} M,[20] whereas [LTh] was initially only 2×10^{-5} M. Thus, reformation of Th was expected to proceed via first-order kinetics, the observed zero-order rate law suggests that LTh was generated within SPEEK aggregates previously proposed to exist in aqueous solutions.[20]

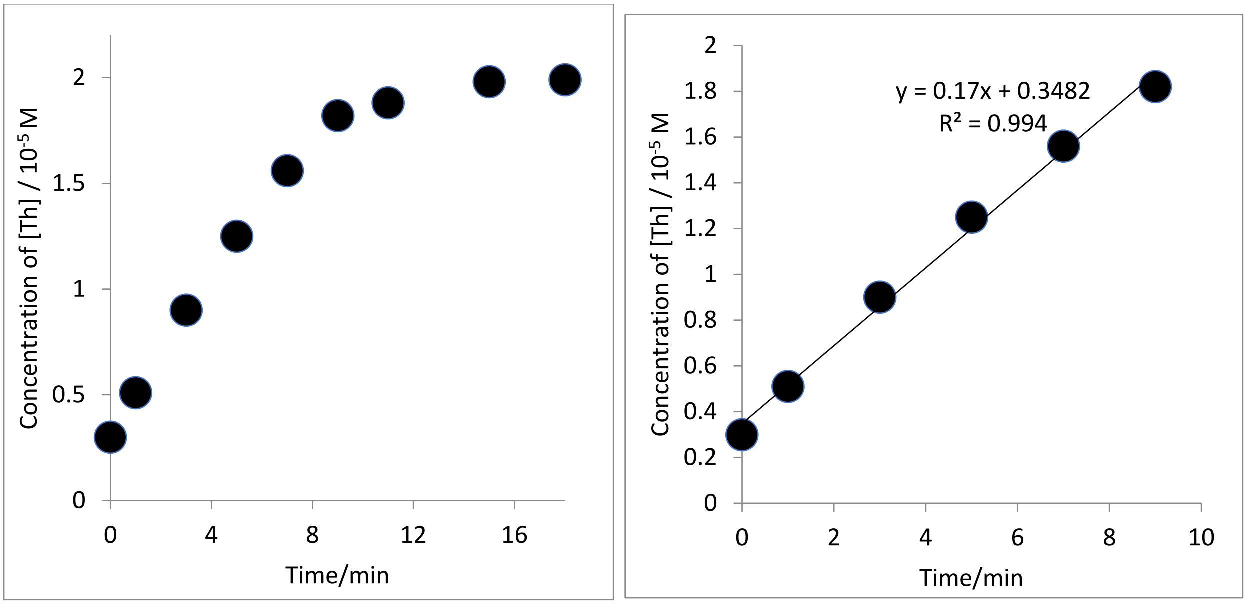

Figure 2.7: Reoxidation of photoreduced Th as a function of time in solutions with 3.8×10^{-2} M SPEEK and 0.82 M PVA.

Figure 2.8 shows the Th absorbance changes in solution during both the reduction and reoxidation processes. Solutions with SPEEK/PVA/Th exhibited a reversible behavior for 9 consecutive cycles of photoreduction and dark reoxidation. Throughout all nine cycles of reduction/reoxidation, the SPEEK/PVA/Th solutions exhibited no shift in the λ_{max} of the dye, or of the shape of the optical signal. The optical density after each cycle remained almost constant providing evidence that the polymer/dye system exhibits a highly reversible behavior.

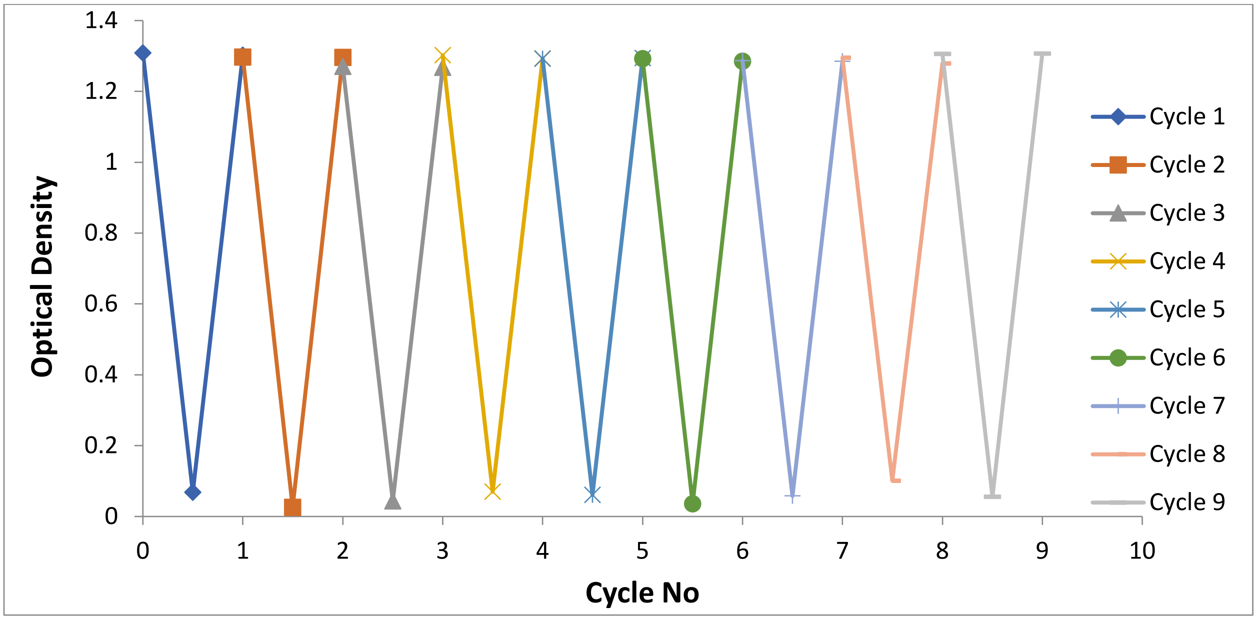

Figure 2.8: Comparison between cycles for photoreduction and reoxidation of 2.0 x 10^{-5} M thionine in 3.8 x 10^{-2} M SPEEK (Solvay) and 0.82 M PVA air free solution at pH=7 with $I_0 = 1.0 \times 10^{-5}$ M (hν)/s.

2.4 Conclusion

Illumination of sulfonated poly(ether etherketone), SPEEK, and polyvinyl alcohol, PVA, in the presence of thionine (Th) results in systems exhibiting reversible redox processes. Efficient reduction of thionine takes place when degassed aqueous mixtures of SPEEK/PVA/Th are exposed to 350 nm photons. This photoreduction process involves radicals of SPEEK (sensitizer) and PVA (H-atom donor), which lead to the formation of semithionine (thionine radical) as an intermediate, and finally leucothionine. The thionine photoreduction proceeds via a zero-order rate law with a rate constant of $k = 1 \times 10^{-6}$ Ms^{-1}. In the presence of air, the reformation of thionine follows a zero-order kinetics with a much slower rate as compared to the reduction process (3.3×10^{-8} Ms^{-1}). The rates of thionine reduction and reformation heavily depend on the pH of the mixture. The quantum yields of photo reduction decreased with decreasing pH and showed highest values for neutral and basic solutions. Detection of the semithionine radical by means of optical measurements was confirmed using electron paramagnetic resonance (EPR) determinations.

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Chapter 3

Light induced reversible reactions in dry SPEEK/PVA films containing thionine

3.1 Introduction

Photo responsive polymers have gained eyeballs in recent past as they initiate reactions using light as energy source. These polymers are interesting as they can transform themselves completely via a photo reaction, which result in many advanced scientific and technological findings.[1,2] Among these, solid state photoreactions show great significant as they are versatile and practically applicable compared to reactions in solutions. However, chemical reactions carried out in solid polymers differ considerably from similar reaction in solutions due to the limitation of rotational and translational possibilities. Even though, studying reactions in solid polymers are fascinating, there are some experimental difficulties that are associated with solid matrices due to these limitations. To overcome this problem, solution studies were carried out first (chapter 2), so it can provide insightful information on understanding the photochemical behavior in solid polymers. Earlier studies of photoreduction of O_2 via blends of sulfonated poly(ether etherketone), SPEEK and poly(vinyl alcohol), PVA solutions were indeed useful to overcome the complications associated with the reduction process of O_2 with crosslinked SPEEK/PVA films.[3,4] Hence, our goal was to use solutions of the same polymer blends to avoid problems associated with reactions taking place in solid films. Some beneficial mechanistic information on dye reduction were obtained via blend of dye doped SPEEK/PVA polymer solutions. In films, PVA acts as the main structural component, however, it also serves as an H-atom donor for SPEEK. Thus, solution experiments were also used to evaluate the importance of PVA as a donor of H atoms.

Solid photosensitive systems proceeding through a free radical mechanism have been described in recent past.[5] Recently, as mentioned earlier, our research group has invented a system to photo-reduce O_2 effectively using a solid polymer matrix, SPEEK and PVA.[4] Moreover, all previous studies with SPEEK/PVA films have proven that photochemical reactions in solid state can be initiated using such polymer combination.[6,7] A significant advantage of SPEEK/PVA blends is that both of their polymeric components are soluble in aqueous solutions enabling production of water-insoluble films using simple solution casting procedures. Thus, their photoreactions can be studied in aqueous solutions as well as cross-linked films of the polymer blends. Crosslinked SPEEK/PVA films are optically transparent, sturdy yet flexible and can be fabricated with thicknesses in the micron range, containing the polyketone as a solute and the polyol as the main component. In this investigation, few dyes were introduced in SPEEK/PVA films to study whether the reversible reduction of the coloring agents was possible. Dyes like methylene blue (MB) and thionine (Th) can easily transformed to the reduced form upon reacting with a SPEEK radical, SPEEK•, that forms under illumination of SPEEK/PVA polymer system (Chapter 2). The reduced form of the dye may then experience oxidation in the presence of air (slow) or H_2O (fast). The result of such process is reforming the original form of the dye, thereby yielding a reversible photochemical system. Numerous studies of the photochemical processes of dye molecules incorporated into solid materials have been carried out in recent years.[8] Thiazine dyes, such as thionine and methylene blue have become important as sensitizers in photochemical, photophysical and photobiological processes.[8] Methylene blue is a very popular dye sensitizer in photochemistry and has been widely used especially in the areas of singlet oxygen production and reductive electron transfer.[9] Reduction of MB by the α-hydroxy radical of D-glucose (a plausible model for the SPEEK radical) occurs with a rate constant of 2.4×10^{10} M^{-1} s^{-1}.[10] Furthermore, rate constants of 3.4×10^9 M^{-1} s^{-1} and 4.4×10^9 M^{-1} s^{-1} were reported for the reduction of methylene blue by the $\bullet CH_2OH$ and $(CH_3)_2C\bullet OH$ radicals.[11] As for Th, the rate of reduction of the dye by these two α-hydroxy radicals (reasonable models for HSPEEK•) were reported to be 2.6×10^9 M^{-1} s^{-1} and 4.2×10^9 M^{-1} s^{-1}, respectively.[11] Further, numerous reports are available on the reversibility of the methylene blue and thionine reduction in various systems.[12] In fact, the rate constant for re-oxidation of the reduced form of methylene blue by oxygen was estimated to be 1.62×10^2 M^{-1} s^{-1} at 25 ^{0}C.[13] Therefore, Th, as well as MB were incorporated into our polymer systems to explore if a reversible redox transformation of these dyes was feasible.

Photochromic properties of SPEEK-based films worth studying include their use as protective barriers in reactive clothing which are chemically inactivate toxic chemicals. Macromolecular systems containing reactive species are proposed to act as protective barriers.[14] Hence, a reactive clothing based on polymeric sensitizers that generate reactive species via exposure to light is an interesting direction. Further, Th-doped films containing SPEEK could find applications as barriers/sensors for O_2 in food packages. Sealed packages might get damaged during transportation hence a simple, inexpensive detection method to monitor these packages can be useful. Oxygen indicators in a form of a film located inside of these food packages may offer a simple solution to the above problem. The indicator should be non-toxic to use with food, hence UV or visible light activated redox indicators seem to be very promising as such indicators. These indicators usually consist of a redox dye, a reducing agent and a solvent.[15] Normally reactive species react with O_2 and change the color of the dye, which enables to monitor packages with damaged/broken seals. Further, for preservation of some food, undesirable oxidation reactions are prevented via active packaging that include oxygen scavengers able to chemically reduce O_2.[16] For instance, presence of oxygen can spoil oxygen-sensitive foods which may lead to change the color and freshness of food products. Therefore, it is necessary to reduce oxygen in the headspace of the package. Even with modified atmosphere packaging (MAP) there are some residual oxygen up to 2%.[17] Thus, additional use of oxygen scavengers inside the packages can be useful to preserve food. Further possibilities of Th dopped SPEEK/PVA films are their use for photo-imaging and photo-patterning by means of UV light. Our investigations tested ways to remove photo-generated patterns using oxidation of the reduced dyes via exposure of films to solvents (H_2O, acetonitrile, and others) containing air.

3.2 Experimental

SPEEK was prepared by sulfonation of poly (ether etherketone), PEEK, supplied by Solvay ($M_n = 4.0 \times 10^4$ g/mol^{-1}). Poly (vinyl alcohol), PVA (99+% hydrolyzed), 2-Hydroxyethyl cellulose, HEC, and Sodium Carboxymethyl cellulose, CMC, with average molar masses of 8.9-9.8 x 10^4 g/mol^{-1}, 9.0 x 10^4 g/mol^{-1} and 9.0 x 10^4 g/mol^{-1} respectively were from Sigma-Aldrich. Further, thiazine dyes; methylene Blue (MB), thionine (Th) and Cresyl Violet (CV) were also from Sigma-Aldrich. All the other chemicals were supplied by VWR. Cross-linked SPEEK/PVA (30/70 wt %) polymer films were prepared using glutaraldehyde as crosslinking agent, followed by a standard procedure.[4] SPEEK and PVA aqueous solutions with concentrations of 3.8 x 10^{-2} M and 0.82 M respectively, together with 0.1 M glutaraldehyde (3.3% by volume) and HCl (0.5 M) yielded films consisting of 30/70 SPEEK/PVA wt%. Higher glutaraldehyde volumes were used for HEC (6.6% by volume) and CMC (10% by volume) films. The lower reactant concentrations were used to prepare films with more reproducible and uniform thickness, while also allowing to prepare films with a wide range of thickness. Typical films dimensions were: 3 cm x 0.8 cm x 0.0075 cm. The dimensions of dry films were measured by means of a meter ruler and a digital micrometer (Mitutoyo 0-1”). To dope SPEEK/PVA films with methylene blue or thionine, first films were washed thoroughly with methanol, then with distilled water. For this purpose, films were immersed in a small petri dish containing 15 ml of methanol and distilled water, each for 30 min. Next the films were immersed in 4 ml of a 10^{-5} M dye solution [consisting of 80 % of methanol and 20 % distilled water (purified water obtained from an ion-exchange resin deionizer) by volume] for 12 h. Figure 3.1 shows the absorption of thionine dye by a SPEEK/PVA film with time.

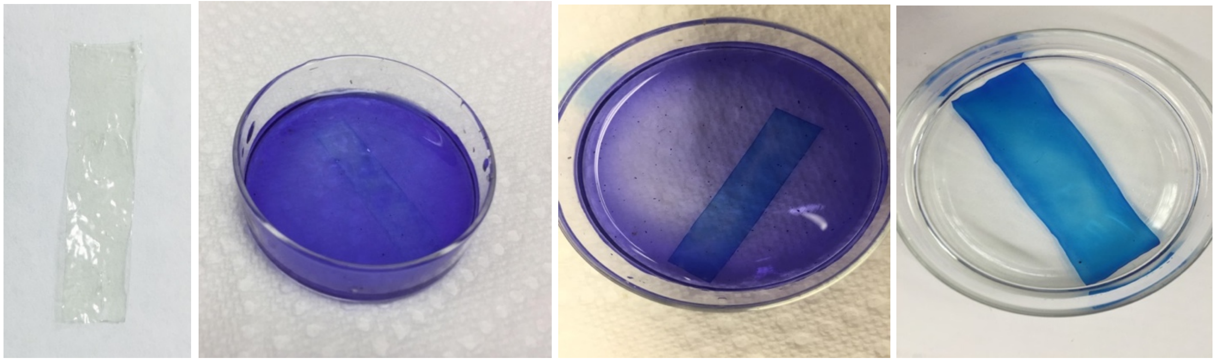

Figure 3.1: a) A washed (with methanol and distilled water) SPEEK/PVA film (30 wt% SPEEK and 70 wt% P VA). Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. SPEEK/PVA film dipped in a 10^{-4} M Th 6 ml solution b) After 1 min c) After 30 min d) After 6+ h. I_0 = 10 μM/s and T = 25 °C. (Higher [Th] concentrations were used for visual purposes only).

Thionine was instantaneously absorbed by SPEEK/PVA films as it is visible in figure 3.1.b) [after 1 min]. However, it took more than 6 hours for the film to absorb the dye completely. Hence, films were dipped inside the dye solution for 12 hrs. Once the dye solution became colorless (after 12hrs), the absorption of the solution was monitored via UV-visible absorption spectra (Shimadzu UV-2450) to confirm the complete absorption of the dye by the film. After that, the Th-dopped films were dried at room temperature for 6+ hrs. Doped films were illuminated inside 1 cm optical cells with λ = 350 ± 15 nm photons generated by a Rayonet, RPR-100 circular illuminator by 16

RPR-3500A lamps with a typical light intensity (I_0) of 10 μM/s. The light intensity (I_0) was determined using the Amberchrome 540 chemical actinometer.[18] Glass optical cell spacers of dimensions, 4.8 cm x 0.75 cm x 0.75 cm were used to hold the films still during the illumination process. Th-dopped SPEEK/PVA films were placed in between the inner surface of the optical cell and the outer surface of glass spacer. The reaction progress was monitored via recording UV-visible absorption spectra (Shimadzu UV-2450) at different illumination times. Figure 3.2 illustrates the color change of the SPEEK/PVA film at different stages of the process.

Figure 3.2: a) A washed SPEEK/PVA film b) Th-dopped SPEEK/PVA film c) After 25 min of illumination of Th-dopped film (30 wt% SPEEK and 70 wt% PVA). Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. I_0 = 10 μM/s and T = 25 °C.

Once the blue color of the dye decayed upon irradiation, the films were placed in 20 ml distilled water for 6-12 h and dried at room temperature for more than 6 hrs. Then, the absorption spectrum was recorded again to check the initial absorption/optical density was achieved or not. The same procedure was employed for numerous cycles to check the reversibility of the system. To study the kinetics of Th reformation in a reasonable time scale, a photolyzed Th/SPEEK/PVA film was placed in an optical cell in contact with 1 ml of distilled water. Afterward, the reaction progress was monitored via recording absorption spectra of the film at different times. Every photochemical experiment was performed at least twice and for the desired exposure time without interruptions, followed by retrieval of samples for chemical analysis. Uniform exposure of the optical tubes was achieved by positioning them at the center and mid height of the cavity inside the Rayonet, where the temperature was 29 °C. All other measurements were conducted at room temperature (25 °C). For the reoxidation measurements at high humidity, illuminated films were placed in a sealed plastic, transparent box (dimensions: 53.5 cm x. 53.5 cm x 51.44 cm) that contained wet sodium chloride (NaCl). About 100 g of wet NaCl (which refreshed in every 2-3 weeks) in a petri dish was placed inside the box to maintain the humidity (75%). A Goabroa mini hydrometer was used to detect any humidity changes inside the box.

3.3 Results and Discussion

First, methylene blue was employed in SPEEK/PVA films as it was a prominently used as an indicator dye in photochemical experiments.[19-21] Upon irradiation, blue MB/SPEEK/PVA films turned colorless due to the formation of leuco methylene blue (LMB). However, MB showed an irreversible transformation in SPEEK/PVA films. Figure 3.3 illustrates the changes in optical spectra, including alterations in the wavelength of maximum absorption (λ_{max}), of a SPEEK/PVA film containing MB after 3 consecutive irradiations. The characteristic shoulder of MB at 620 nm was no longer detected after first illumination. Moreover, the λ_{max} of MB at 670 nm shifted to shorter wavelengths after each illumination, first to 646 nm and then to 654 nm. These are characteristic features of loss of methyl groups from MB forming azure derivatives, indicating an irreversible MB transformation.[22,23] Furthermore, the optical density diminished considerably after each illumination. This further indicates that the MB/SPEEK/PVA system exhibits a nonreversible photochemical behavior. Similar non-reversibility was observed with MB in TiO_2 /tatrate films.[19] It is reported that the original color of MB could not achieved when LMB was exposed to O_2. Even though, using excess tartaric acid in films allowed subsequent rapid recoveries of MB, they were not as complete, indicating a degradation of MB with repeated use.[21]

Since MB was demethylated forming the azure derivatives upon repeated use, the purple cationic dye, thionine (a thiazine dye without attached methyl groups) was subsequently used to avoid the reversibility problems induced by photolysis. The absorption maximum of Th at 600 nm shifts by 15 nm upon binding to SPEEK/PVA polymer system due to the strong electrostatic bond between positively charged thionine and negatively charged sulfonate groups.

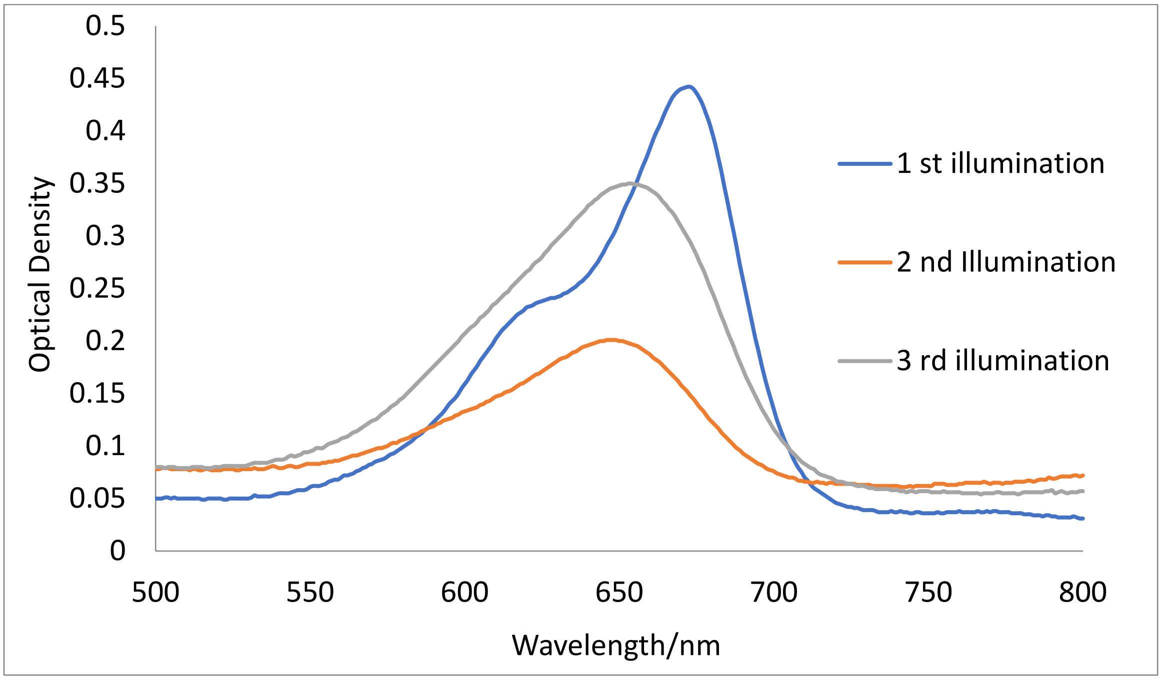

Figure 3.3: Comparison of the optical spectrum after 3 different consecutive illuminations of a MB/SPEEK/PVA film (30 wt% SPEEK and 70 wt% PVA). Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. I_0 = 10 µM/s and T = 29°C during illuminating.

Similar behavior has been reported for solutions highly concentrated (50 - 200 mM) in deoxyadenosine monophosphate (dAMP) or deoxyguanosine monophosphate (dGMP).[24] The molar extinction coefficient (ε) at 615 nm of Th inside SPEEK/PVA polymer films amounted to $4.1 \times 10^4\ M^{-1}\ cm^{-1}$ and was obtained in the range of $2 \times 10^{-4} \leq [Th] \leq 1 \times 10^{-3}$ M where the Lambert-Beer law is obeyed. Despite the shift in λ_{max} and although Th was present in the solid polymer material, the ε value compares well with the extinction coefficient of thionine determined in aqueous solution, $\varepsilon = 5.6 \times 10^4\ M^{-1}\ cm^{-1}$.[25] As in the case of the MB-doped materials, Th/SPEEK/PVA films also turned colorless upon photolysis.

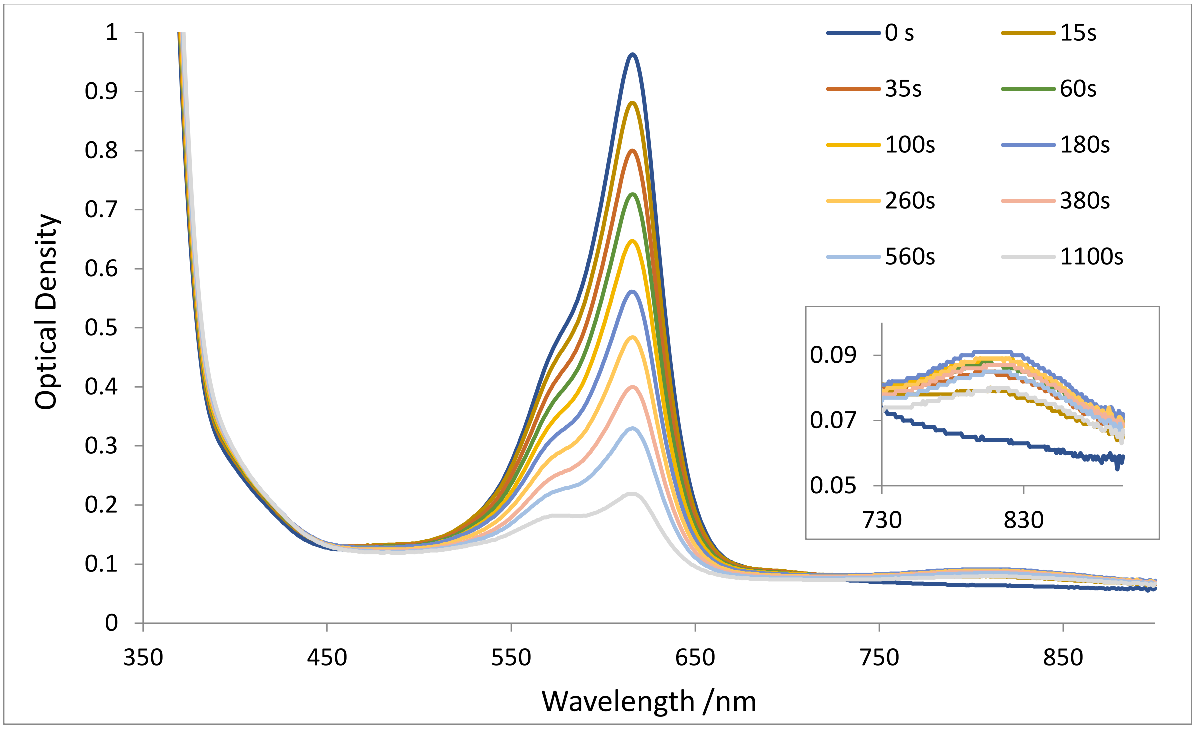

Figure 3.4: Absorption spectrum of a Th/SPEEK/PVA film (30 wt% SPEEK and 70 wt% PVA). Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. $I_0 = 10\ \mu M/s$ and T = 29 °C. Inset: Formation of semithionine intermediate during irradiation.

Presented in Figure 3.4 are the resulting optical changes, consisting of a decrease in intensity across the entire dye spectrum together with formation of a weak signal centered at around 800 nm. Upon irradiation the blue color of the dye decayed due to the formation of the colorless leuco form and also the unstable intermediate semithionine. When Th/SPEEK/PVA films are exposed to UV light, simultaneous formation of SPEEK and PVA radicals is anticipated.[4,26] Earlier solution work has shown that Th is reduced via a two-electron process into the leuco form, leucothionine or LTh (Chapter 2).[27,28] The polymer radicals photogenerated in SPEEK/PVA films were anticipated to reduce Th to the leuco form, which explains the bleaching of the Th spectrum depicted in figure 3.4. In neutral solutions the unstable intermediate semithionine (or thionine radical, Th•) with an absorbance centered at 770 nm ($\varepsilon = 1.72 \times 10^4\ M^{-1}\ cm^{-1}$), also forms. Th• decays via radical-radical combination with $k = 1 \times 10^9\ M^{-1}\ s^{-1}$.[29] However, in the films a broad and weak absorption signal with λ_{max} at around 800 nm - 810 nm, was also noticed (inset of figure 3.4). This signal resembled the optical signal of Th• in solution and was assigned to semithionine. The slight shift in λ_{max} of the radical signal is probably due to the interaction of Th• with the polymer matrix. Interestingly, the Th• signal persisted for several min whereas in solutions the absorbance lasted for 4s. Such a result is understandable as radicals decay much faster in solutions compared to solid systems. Most probably, the unusual stability of the radical originates from strong binding of this species to SPEEK, together with the low solubility of O_2 in the films.[7]

Detection of the LTh absorptions, centered at 310 nm and 262 nm,[28] was not possible due to the strong SPEEK optical absorptions in that range. The overall transformation of Th to LTh involves disproportionation of Th•,[28] a scheme of such transformation is shown in Figure 3.5. Despite the high [Th] present in the films, no shifts in the optical signal shown in Figure 3.4 were detected. In solutions, when high [Th] present, formation of Th dimers and trimers is evident from shifts to shorter wavelengths in the main absorption band.[25]

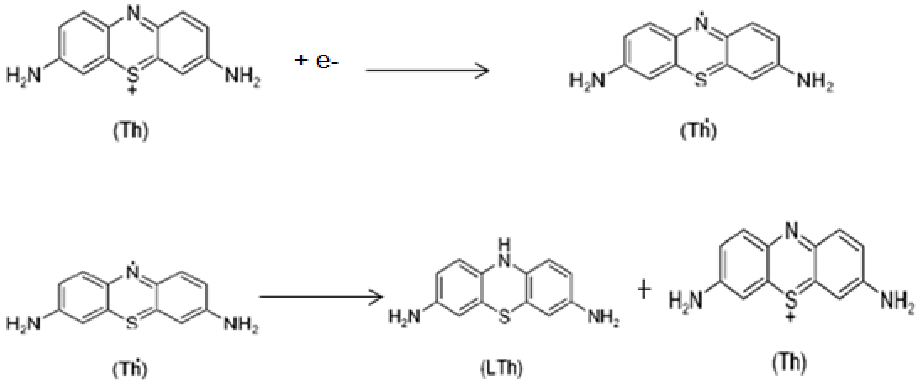

Figure 3.5: Schematic representation for the formation of leucothionine and semithionine.[28]

Spectral changes due to dimerization of Th was anticipated at this [Th], which were indeed noticed in solutions without SPEEK. No evidence of dimer and trimer formation was found in solutions of SPEEK, supporting the notion that association of dye molecules was inhibited due to strong binding of Th to the polyelectrolyte. The fact that no Th aggregation took place in films can be attributed to the strong electrostatic binding of the positively charged thionine with the anionic sulfonic groups of SPEEK, which prevented interactions between dye molecules.

Presented in Figure 3.6 is the decay of [Th] in a SPEEK/PVA film as a function of illumination time; as shown in the inset a fairly linear concentration decrease was noticed initially, followed by a subsequent non-linear change. The Th decay in SPEEK/PVA films during the first 40 s – 50 s of photolysis followed zero-order kinetics with a rate constant of $k = 1 \times 10^{-5}$ M s^{-1}. Figure 3.7 illustrates the evolution of [Th], [LTh] and [Th•] during the thionine photoreduction. The concentration of Th• was calculated directly from the optical signal at 800 nm using the ε value determined previously in solution at 770 nm.[29] However, the maximum [Th•] (≈ 0.15 mM) detected during this reaction is almost negligible as compared to that of LTh. Based on the assumption that Th• dimerizes, in most cases, fast to form LTh, the following equation was used to calculate the concentration of the leuco form,

$$([LTh]_t): [LTh]_t = [Th]_i - [Th]_t - [Th\bullet] \qquad (1)$$

where $[Th]_i$ is the initial thionine concentration and $[Th]_t$ concentration of thionine at time t.

Since radicals can remain trapped in polymeric films, migration of these species can be difficult if not all the trapping sites are equal. In an inhomogeneous system, some sites would reduce the reactive species more easily than others. Electrons can either jump or tunnel from one site to the other, creating deviations from classical rate laws. This is very common for reactions in disordered media and likely to lead to a complex mechanism. In our polymer system, it was assumed that the

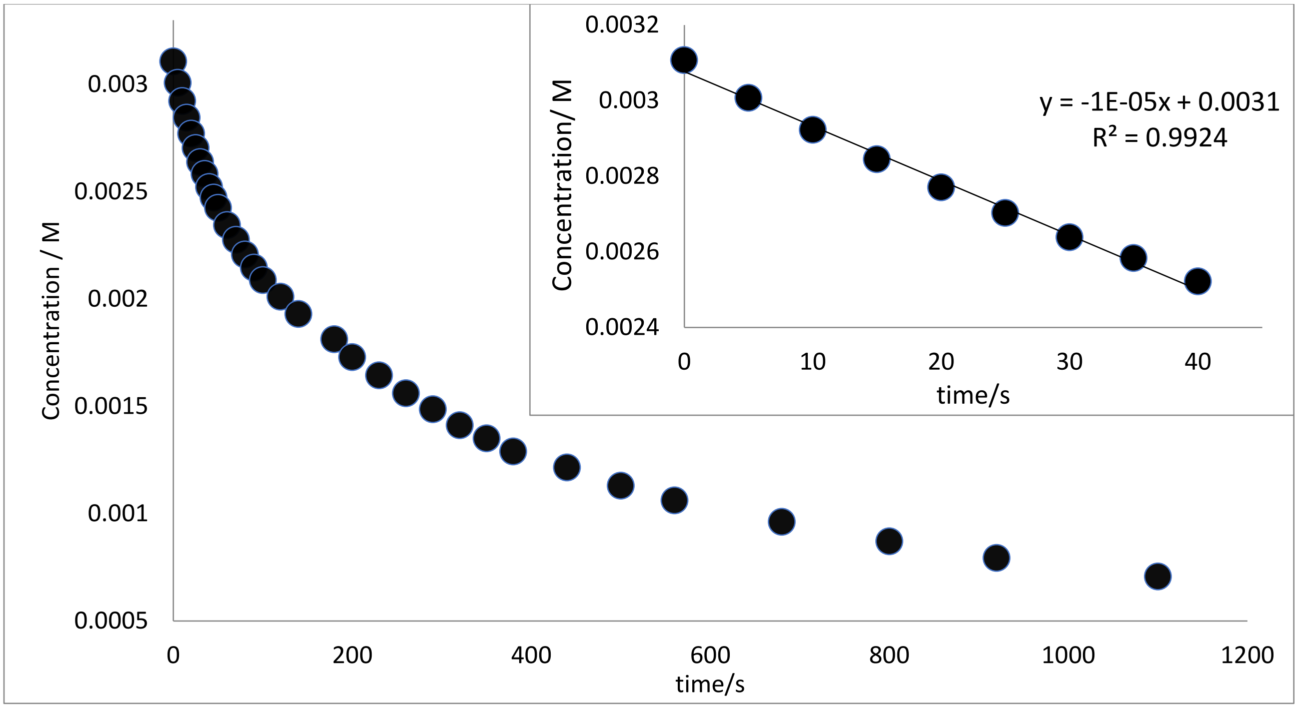

Figure 3.6: Photoreduction of [Th] in a SPEEK/PVA film (30 wt% SPEEK and 70 wt% PVA) with time. Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. I_0 = 10 µM/s and T = 29 °C. Inset: initial linear decay of [Th].

radicals of SPEEK first react with Th molecules that are close by. Once all those Th molecules are reduced, diffusion of radical (or electrons) should either proceed via hoping or tunneling mechanisms. This would enable reduction of Th molecules located further away from sites in the chain where SPEEK• was photogenerated. The initial zero order kinetics can be attributed to reduction of Th bonded to SPEEK monomer units close to those containing SPEEK•. Data collected after the initial zero-order step failed to follow a simple rate law. Chemical reactions proceeding on time-scales comparable to, or shorter than, those of internal rearrangements of the matrix may follow dispersive kinetics.[30] Different dispersive kinetic models were used to test our data, which were fit well with the following rate law:

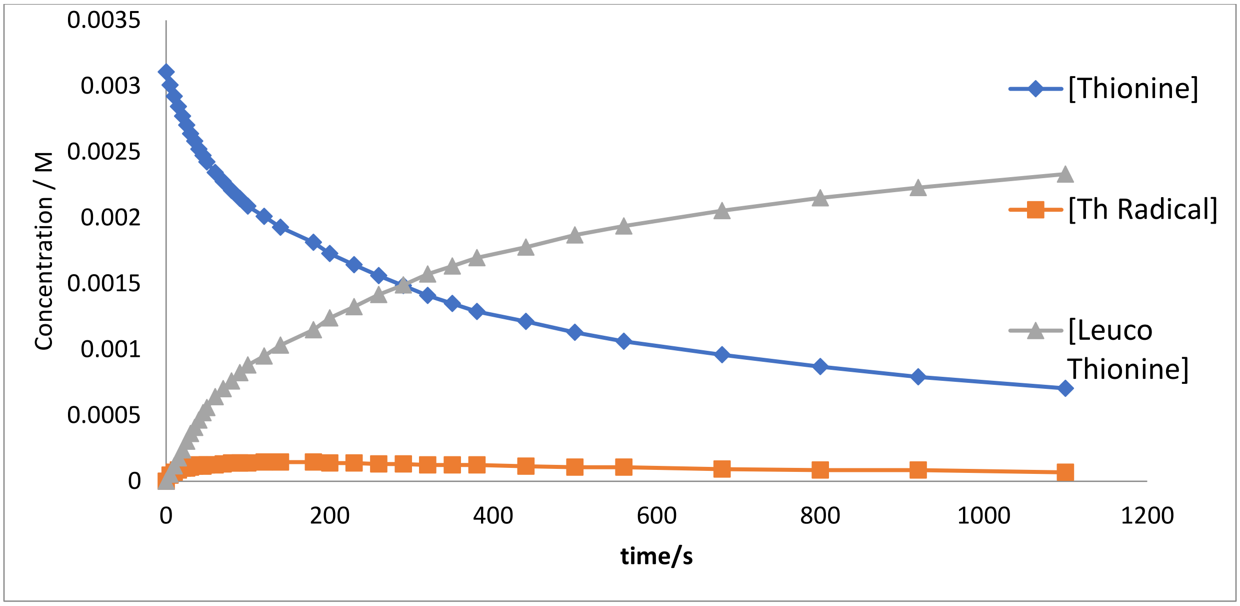

Figure 3.7: Evaluation of thionine, semithionine and leuco-thionine concentrations in a SPEEK/PVA film (30 wt% SPEEK and 70 wt% PVA) with illumination time. Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. I_0 = 10 µM/s and T = 29 °C.

$$[X]_t/[X]_0 = \exp[-(kt)^{\beta}] \qquad (2)$$

where; $[X]_0 = [Th]_0$ is the initial thionine concentration and, $[X]_t = [Th]_t$ is the thionine concentration at time t, k is the rate constant and ß is a constant and $0 < ß < 1$.[31] The tests employed different values for ß; good linear fits of ln $\{[Th]_t/[Th]_0\}$ vs $t^{ß}$ resulted with ß = 0.3-0.5 range, in most cases a value of 0.47 gave the best fit. A representative plot of the data is shown in Figure 3.8. Plots of the data according to equation 2 yielded straight lines and figure 3.8 shows an example supporting the idea that Th was photo reduced in SPEEK/PVA films via dispersive kinetics, unlike Th/SPEEK/PVA solutions which followed zero order kinetics throughout the photoreduction.

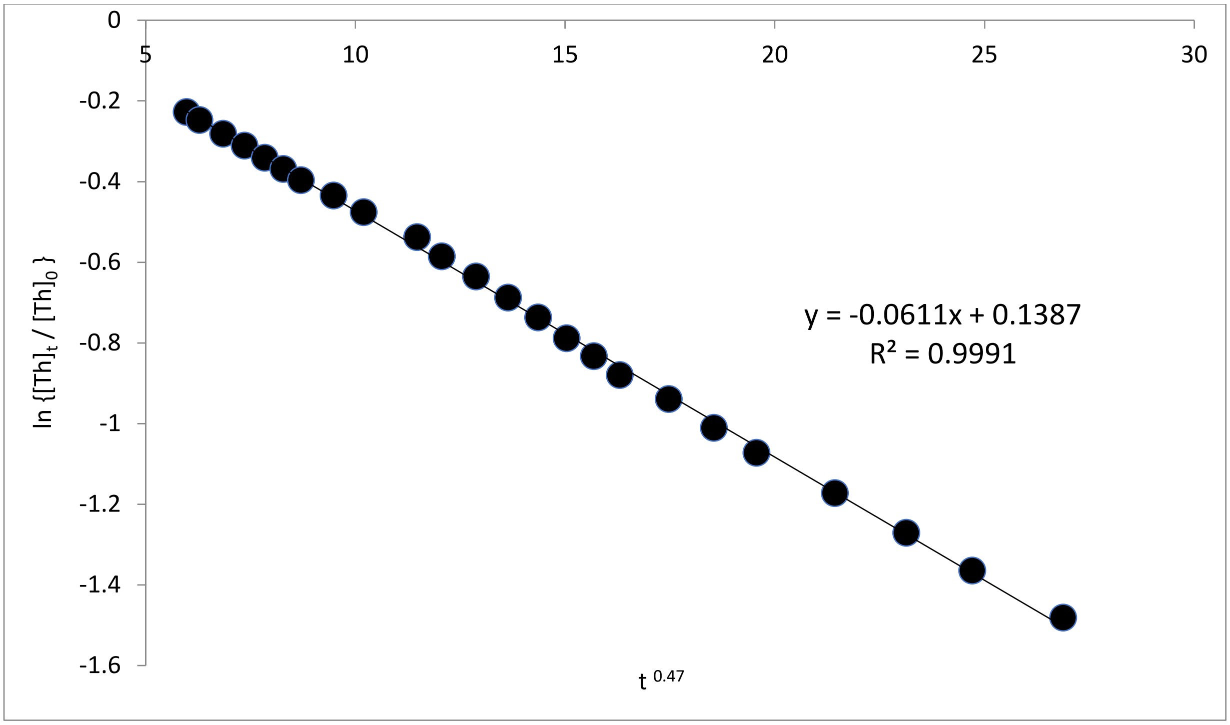

Figure 3.8: Plot of ln $\{[Th]_t/[Th]_0\}$ vs $t^{ß}$ for film Th/SPEEK/PVA film after 40 s of illuminations; ß =0.47. 30 wt% SPEEK and 70 wt% PVA film. Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. I_0 = 10 µM/s and T = 29 °C.

The following mechanism was proposed for the photoreduction of thinone in a SPEEK/PVA system,

$$\text{SPEEK} + h\nu \longrightarrow \text{SPEEK}^{*} \qquad (3)$$

$$\text{SPEEK}^{*} + \text{PVA} \longrightarrow \text{HSPEEK}\bullet + \text{PVA}\bullet \qquad (4)$$

$$\text{PVA}\bullet + \text{SPEEK} \longrightarrow \text{HSPEEK}\bullet + \text{PVA(ox)} \qquad (5)$$

$$\text{HSPEEK}\bullet + \text{Th}^{+} \longrightarrow \text{Th}\bullet + \text{H}^{+} + \text{SPEEK} \qquad (6)$$

$$2\text{Th}\bullet \longrightarrow \text{LTh} + \text{Th}^{+} \qquad (7)$$

SPEEK * represents the triplet excited state of SPEEK, HSPEEK• is the radical of SPEEK after H-atom abstraction from PVA, PVA• represents the radical formed after the loss of a H-atom by the polyol, and PVA(ox) corresponds to a macromolecule in which an alcohol function was oxidized to a ketone group. Because the overall photoreaction is controlled by the initial excitation step (which occurs with an unchanging rate given the constant flux of photons entering the sample) the change in [Th] at short times is linear.

Unlike the Th/SPEEK/PVA solution system, reformation of Th from LTh in films was somewhat complicated and time-consuming. On average, complete recovery of dye color in films took more than 30-45 days. In contrast, recoloration of illuminated solutions required only 15 mins of exposure to air. The very slow oxidation of LTh in dry films exposed to air resulted from the low solubility of O_2 in PVA films. However, exposure of the films to air-saturated H_2O accelerated the reoxidation of LTh. Reformation of thionine by H_2O in SPEEK/PVA films was completed in about 60 min and followed pseudofirst-order kinetics. Figure 3.9 shows a typical plot of the reformation data; the slope of the straight line yielded a rate constant of 0.0395 min^{-1}. This type of rate law probably resulted because in films [LTh] >> [O_2] throughout most of the reaction.

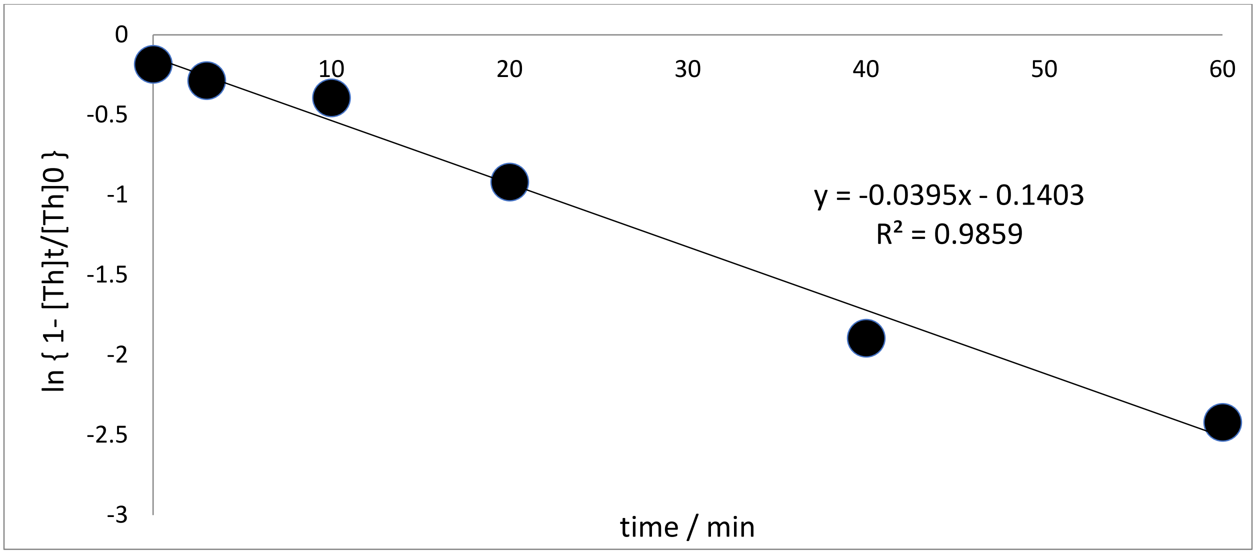

Figure 3.9: First-order kinetics plot for the reformation of thionine in a SPEEK/PVA film, after exposing a photolyzed film to air-saturated water. 30 wt% SPEEK and 70 wt% PVA film. Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. T = 25 °C.

Frequently, reactions occur in the solid state with speeds different than those determined in solution. The reason is that reactants are free to move in solution and their reactivity is usually higher than that in solid matrices. However, Th photoreduction in solutions occurs with a rate constant 5 times lower than the value determined using SPEEK/PVA films, although the same light intensity (10 μM/s) was nominally used in both cases. In solutions, Th is bonded to the SPEEK polymer, hence the whole polymer has to diffuse with Th during the reaction. No dispersive Th photoreduction occurs in solution because diffusion of reactants is not constrained in the fluid medium. However, in films, the polymer and Th molecules are close to each other initially. This explains the apparent faster Th reductions observed initially in films.

Moreover, films were exposed to light via placing them vertically inside a 1 cm cell between two transparent glass spacers. Thus, the photon flux impinging on the films was similar to that entering polymer solutions present in the optical cells. Yet, the average film thickness is only about 7.5 x 10^{-3} cm, implying that the solid polymer matrices were exposed to higher light intensities than solutions. Number of photons per unit of volume is higher in the case of films than solutions. That The employed Aberchrome 540 actinometer measures the photon flux entering a 1 cm optical cell.[32]

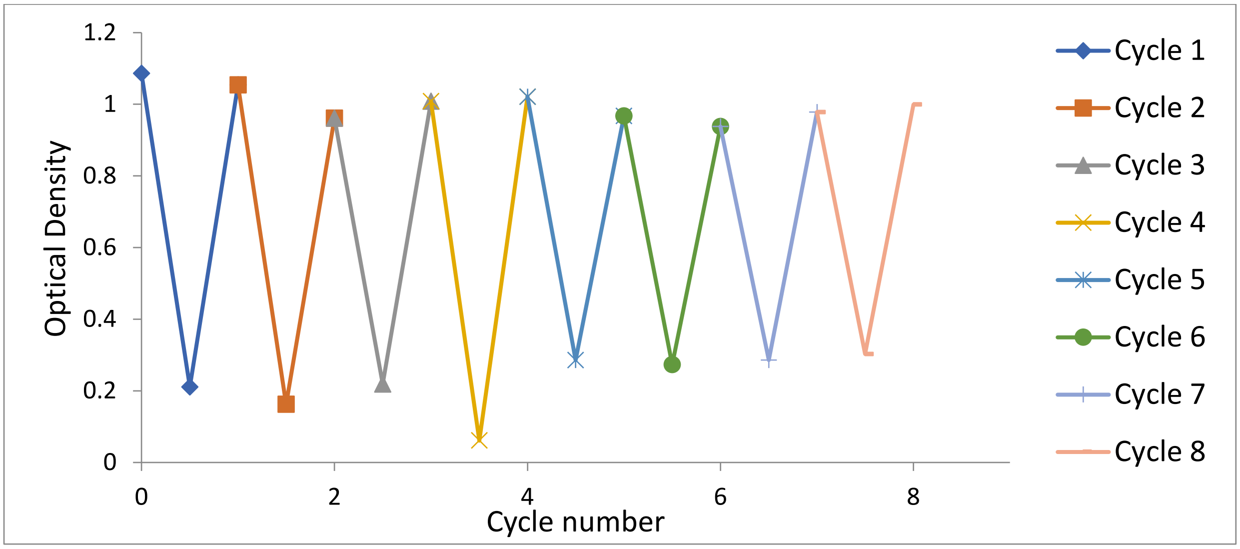

Figure 3.10: Comparison of the optical density changes for eight illumination/oxidation cycles for a Th/SPEEK/PVA film. 30 wt% SPEEK and 70 wt% PVA film. Film dimensions; 3 cm x 0.8 cm x 0.0075 cm. SPEEK from Solvay precursor. I_0 = 10 µM/s and T = 25 °C for oxidation and 29 °C for reduction.

In conclusion, the blue color Th/SPEEK/PVA films form LTh via a semithionine intermediate upon exposure to 350 nm light. After illumination, reoxidation of the reduced dye to blue Th lasted several days, but the process was accelerated by immersion of the films in distilled water for 12 hours, and drying at room temperature for 6 hrs. Hence, consecutive cycles of illumination followed by immersion in H_2O were then repeated eight times. Throughout all eight cycles of illumination/water immersion, the Th/SPEEK/PVA films exhibited no shift in the λ_{max} of the dye, or of the shape of the optical signal, thus confirming the reversibility of the dye in

SPEEK/PVA solid films similar to SPEEK/PVA solutions (Chapter 2). Figure 3.10 illustrates the optical density comparison for all illumination cycles. Interesting observations were made during experiments with Th/SPEEK/PVA films, including evidence that binding of Th to SPEEK was irreversible. Indeed, no migration of Th out of the films was detected when irradiated, or non-exposed, solid polymeric matrices were immersed repeatedly in mixtures of distilled water with methanol, acetonitrile or hexane. As mentioned previously, photochromism is a property that involves a light-induced reversible transformation of color, based on a chemical reaction.[33] Moreover, when photochromic chromophores are incorporate into polymers, exposure to light changes the properties of macromolecular material present in either solutions and solids.[16] An example is to employ photolysis to create patterns on SPEEK/PVA/Th films and then erase them. Patterns were generated within seconds (Figure 3.9), employing photomasks to block different areas of the films exposed to light.

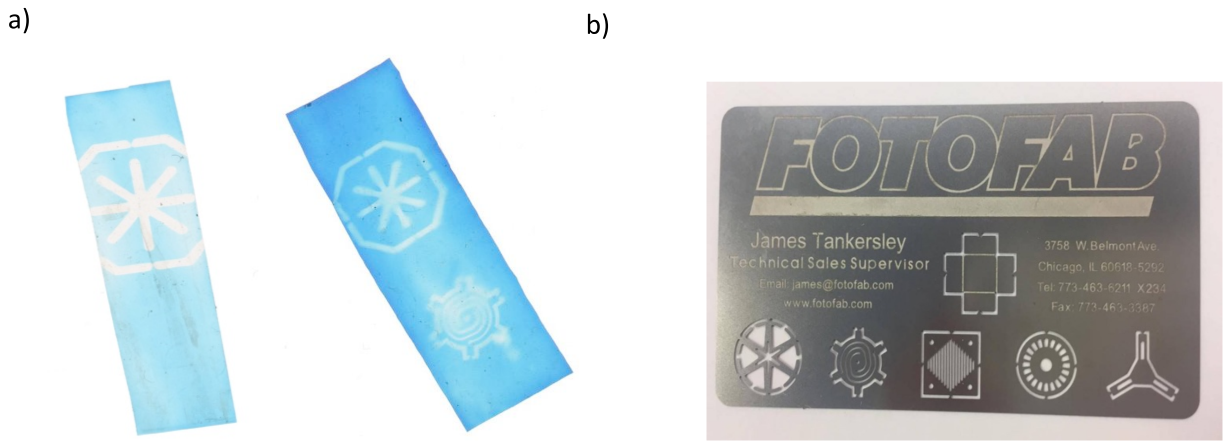

Figure 3.11: a) Images of photogenerated patterns created on Th/ SPEEK/PVA films using the FOTOFAB photo mask b) Image of a FOTOFAB photo mask.

The patterns consisted of colorless areas containing LTh; recoloration occurred within a few days by dipping the exposed films into distilled water, which enabled reaction of LTh with

O_2. However, the slow oxidation of LTh limits the possible applications of Th/SPEEK/PVA films. Th-doped films containing SPEEK could find applications as barriers/sensors for O_2 in food packages. Photolysis of Th/SPEEK/PVA films generates HSPEEK•, LTh and Th• that react with O_2 but a faster oxidation of LTh is needed to achieve useful systems. Because of the low solubility of O_2 in PVA, radicals present in the films are oxidized by oxygen very slow. Our aim was to fabricate and test films that include SPEEK together with macromolecules such as methyl cellulose, hydroxyl methyl cellulose, ethyl cellulose, hydroxyl ethyl cellulose (HEC) and carboxymethylcellulose that may absorb oxygen easily from air and function as H-atom donors alike PVA. Ideal films were optically transparent at around 350 nm to enable SPEEK photochemistry, wrinkle-free when dry and sturdy in the presence of water.

Dye/ Polymer combination	No of days for complete re-oxidation with air (50% humidity)	No of days for the complete re-oxidation at 75% humidity
Th/SPEEK/PVA	40-45	10
CV/SPEEK/PVA	35	10-11
MB/SPEEK/PVA	40-45	11-12
Th/SPEEK/HEC	31	12-13
CV/SPEEK/HEC	29	11-13
Th/SPEEK/CMC	32	16-18
CV/SPEEK/CMC	29	18-20

Table 3.1: Number of days that takes for different dye/polymer combinations for the complete re-oxidation of dye with air and at 75% humidity.

Moreover, the dye Cresyl Violet (CV) was also used instead of Th, as promising re-oxidation results were shown with CV/SPEEK/PVA solutions. Table 1 shows the number of days that took for complete re-oxidation of dye, for different dyes/H atom donor combinations with SPEEK. As previously mentioned, illuminated Th/SPEEK/PVA films took 40-45 days to complete the reoxidation of LTh (colorless) and regain the original color of Th (blue) under normal humidity. (50%). Under the same conditions, complete reoxidation of leuco MB also took 40-45 days and for CV restauration of the original color required 35 days. However, reoxidation rates were higher to some extent when HEC and CMC were used instead of PVA, as complete recovery of the original color required, on average, 10 -15 days less than in films containing the polyol. Apparently both HEC and CMC enable enhanced oxygen permeation as compared to PVA. To clarify that, the stability of photogenerated HSPEEK• was tested in each polymer combination (SPEEK/PVA, SPEEK/HEC, SPEEK/CMC). Under normal conditions (50% humidity, 25^0C), full reoxidation of HSPEEK• in SPEEK/PVA films takes almost 8 hours. However, in SPEEK/HEC and SPEEK/CMC films reoxidation of radical took only 30 mins, thus proving that HEC and CMC enable oxygen permeation to occur more easily compared to PVA. If association of the dyes occurred, reoxidation of photogenerated leuco form was anticipated to occur even slower. All the thiazine dyes used for this experiment (Th, CV and MB) have terminal amine groups on both sides, which could be acting as crosslinkers in the polymer system. If this is true, then the dyes may further restrict the oxygen flow into the films and, thus, delay the oxidation process.

Neither changing the dye nor H atom donor caused a huge improvement in number of days that took for complete re-oxidation at normal humidity (50%). Even though association of HEC and CMC accelerated the reoxidation to some extent, for practical purposes, the improvement is not significant. Since the reoxidation rates increased to a greater extent with addition of water, our next task was to change the humidity of the system to examine any improvements in reoxidation rates. Each and every dye/polymer combination exhibited improved reoxidation rates when they were subjected to higher ambient humidity. Among all the combinations, Th/SPEEK/PVA films showed the highest rate improvement as the number of days to complete the reoxidation process was cut down by almost 30-35 days. Moreover, at 75% humidity, PVA and HEC appear to have similar oxygen permeability as they both took average of 10-13 days for reoxidation of different photoreduced dyes. However, CMC seems to behave differently in the case of oxygen permeability compared to PVA and HEC at high humidity, as CMC films required an average of 16-20 days to complete the reoxidation process. Both PVA and HEC have terminal alcohol groups whereas CMC exhibits terminal carboxylic acid groups, which may restrict swelling of the films at higher humidity levels. Terminal alcohol groups might not hinder film swelling at high humidity levels, thus enabling efficient oxygen permeability at higher humidity levels. At lower humidity levels, CMC seems to behave in a way similar to HEC in terms of oxygen permeability.

On the other hand, the amount of glutaraldehyde added to crosslinked PVA, HEC and CMC films were different from one another. The volume ratio of added glutaraldehyde to crosslink each PVA, HEC and CMC films is 1:2:3 (0.75 ml, 1.5 ml and 2.25 ml) respectively. This could be another reason for the differences between CMC and HEC oxygen permeability at higher humidity levels, as CMC used an additional equivalent of crosslinker during film preparation, thus restricting the flow of oxygen at higher humidity levels. However, even with an additional amount of crosslinker, HEC and PVA seem to be behaving similarly with respect of oxygen permeability at 75% humidity. HEC is a cellulose with more of a loose structure (open ring structure) compared to PVA. Thus, at one equivalent amount of glutaraldehyde (0.75 ml), approximately 25 % of SPEEK migrated out of the films during rinsing steps, as SPEEK/HEC films expand to a greater extent with water due to its loose structure. However, when the same amount of glutaraldehyde was used to crosslink SPEEK/PVA films, no SPEEK migrated out of these films when they were rinsed. The issue was corrected by using an additional equivalent of crosslinking agent for SPEEK/HEC films, which only resulted in 1- 2% of SPEEK loss during the washing process. This could be the reason for the similarities between HEC and PVA at 75% humidity as the swelling of HEC-containing films is quite similar to that of PVA-based films due to the increased crosslinking.

The results of Figure 3.8 indicate that the films transform Th efficiently over numerous cycles of exposure and dark reaction with O_2, and the solid polymer matrices turn colorless when Th transforms into LTh. The average change in [Th] during a reduction step was ≈ 2.4 mM; after 8 steps the total amount of dye reduced was 0.019 M and the total number of electrons transferred corresponded to 0.038 M. Photolysis of SPEEK/PVA films immersed in aqueous solutions induced the reductive dehalogenation of $CHCl_3$ and CCl_4 (Chapter 4). The transformations occurred via chain reactions involving SPEEK• and took place in the presence of air. High quantum yields were determined for these photoreactions, which yielded 0.08 mM and 5 mM Cl^- in the first 2 hours of illumination for $CHCl_3$ and CCl_4, respectively. However, a noticeable yellow coloration of the films occurred during the photoreaction and their efficiency to induce reductions decreased. Repeated experiments with the same film showed that the efficiency dropped by a factor of 2 after every two hours of illumination. Extended irradiation of SPEEK/PVA solutions also induces the yellow coloration,[7] resulting from LAT (light absorbing transient) formation as a by-product of the BP photolysis.[34] LAT results from the cross-reaction of the different radicals generated by the photochemistry of BP chromophores, such as SPEEK• and PVA• in the present polymer system.[35]

Th-doped SPEEK/PVA films as initiators of the photoreduction of $CHCl_3$ and CCl_4, is an interesting investigation. The goal was to utilize Th incorporation in films to prevent LAT formation and the subsequent decrease in photo reactivity that affected films without the dye. In fact, no formation of LAT was detected in Th-doped SPEEK/PVA after 8 cycles of reduction and oxidation (Figure 3.8), although the total number of photogenerated reducing equivalents (0.38 M) was much higher than during the first 2 h of $CHCl_3$ and CCl_4 photoreduction. Hence, assumptions were made that the presence of Th in the films prevented the cross-reaction between SPEEK• and PVA•, thereby suppressing LAT formation. The idea was to eliminate LAT-associated problems, thus enabling the practical use of SPEEK/PVA films for remediation of pollution problems due to the presence of the chloromethanes in aquifers. Preliminary film studies with $CHCl_3$ and CCl_4 showed that photoreductions were most efficient for a SPEEK/PVA film composition of 17/83 wt % (chapter 4), which was different from the one used in the dye experiments. Thus, the first experiments were carried out to optimize the film composition in terms of SPEEK, PVA and Th. Studies on the dependence on the photoreduction on pH were followed in order to ascertain if Th• or LTh participate in the reduction of the halomethanes. Formation of the radical occurs with E°[Th/•Th)] = 0.05 V;[29] since the process also requires participation of a proton the reduction potential decreases by 0.059 V with increasing pH, and the oxidation potential of •Th reaches 0.363 V in neutral solutions.[29] A similar situation occurs for the reduction of Th to LTh but, although the number of protons involved remains unclear, the oxidation potential of the leuco form is about 0.23 V at pH = 9.[36] In contrast, E°[CCl_4/•CCl_3, Cl^-)] = -0.23 V,[37] whereas the potential for the $CHCl_3$ reduction has been estimated to be -0.9 V.[38] Thus, the thermodynamic data predicts that both Th• or LTh will reduce CCl_4 in neutral solutions but not $CHCl_3$. Unfortunately, Th-doped SPEEK/PVA films produced LAT during 2 hrs of illumination. The reason for this formation was the longer illumination time. Normally, Th-dopped SPEEK/PVA film experiments only lasted for 20 min. The amount of Th presented inside the films were enough to prevent cross reactions between SPEEK• and PVA• that generated in 20 mins. However, longer illumination periods produce higher amounts of SPEEK• and PVA•. The amount of Th presented inside films was not enough to prevent those cross reactions, thus the films produced LAT during 2 h illumination. By increasing the Th concentration, films were able to delay LAT production. However, even the highest [Th] employed were not enough to avoid the LAT formation completely.

3.4 Conclusion

Efficient reversible redox processes of thionine (Th) took place when thionine embedded in SPEEK/PVA films were exposed to 350 nm photons. This photoreduction process involved radicals of SPEEK (sensitizer), and induced formation of semithionine (thionine radical) as an intermediate, and finally leucothionine. Thionine was initially photoreduced (first 40 s – 50 s of illumination) via a zero-order rate law with a rate constant of $k = 1 \times 10^{-5}\ Ms^{-1}$. The reaction seemed to follow dispersive kinetics after 40 s - 50 s of photolysis. Reformation of thionine was a very slow process and took 30-45 days for completion, but addition of distilled water (1 ml) to illuminated films accelerated the reaction which then proceeded via first-order kinetics with $k = 2.37\ s^{-1}$. Moreover, the reoxidation rates increased to a greater extend, when the Th dopped SPEEK/PVA films were kept under 75% humidity environment. The reduction and reoxidation of thionine were reversible in Th/SPEEK/PVA films for more than 8 consecutive illumination cycles.

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Chapter 4

Free Radical Chain Photoreduction of CCl_4 and $CHCl_3$ Using Swollen SPEEK/PVA Films in HCO_2H/HCO_2^- buffers

4.1 Introduction

Reduction of halogenated organic compounds offer a straightforward route for an efficient elimination of halide ions. These dehalogenation reactions are attractive, specifically for highly halogenated compound like CCl_4, which shows a considerable resistant to oxidation.[1] Moreover, reductive dechlorination is considered as a feasible method to treat underground contaminant water. [2] The toxicity of chlorinated compounds like CCl_4 and $CHCl_3$ and their frequent presence as a contaminant in underground water[3] have motivated researchers to reduce these chlorinated compounds efficiently into non-toxic chemicals using various methods. [1,4,5] Photochemistry has been using as a simple, less expensive and widely used strategy for degradation of toxic organic pollutants.[6-8] Since environmentally friendly photons serve as the energy source for radical formation, light induced halocarbon reduction has always been a point of interest. Efficient photoreduction of CCl_4 has been investigated in homogeneous solutions of molecular sensitizers to reducing radicals.[9,10] Photoreduction of $CHCl_3$ has also been investigated in recent past.[11] Moreover, our research group has investigated the efficient reductive dechlorination of CCl_4,[1] $CHCl_3$[4] and CCl_3F [5] in air-free aqueous solutions of the sodium salt of sulfonated poly(ether etherketone), SPEEK, and poly(vinyl alcohol), PVA, or HCO_2H/HCO_2^- buffers with detailed mechanism and explanations.

Photolysis of SPEEK/PVA produce α-hydroxy radical (SPEEK•), which acts as a reducing agent for this dechlorination process. Considering the reducing ability of the polyketone radical, the dechlorination of CCl_4 and $CHCl_3$ with this radical seems possible. The oxidation potential for

SPEEK• is about -1.3 V [12] whereas E°(CCl_4/•CCl_3, Cl^-) amounts to be −0.23 V.[13] The potential for $CHCl_3$ has been estimated to be about −0.9 V in ethanol with a similar value anticipated for H_2O as the solvent.[14] Hence, efficient reduction of CCl_4[1] and $CHCl_3$[4] take place upon illuminating aqueous solutions of SPEEK and PVA or HCO_2H/HCO_2^- buffer using 350 nm photons. $CHCl_3$ was photo-reduced to CH_2Cl_2 whereas CCl_4 was reduced to $CHCl_3$ via radical chain reductions in SPEEK solutions. Higher efficiencies were observed when HCO_2^- ions served as H atom donors instead of PVA for both halocarbons.[1,4] The reason for this observation is the participation of the intermediate •CO_2^-, when SPEEK solutions with HCO_2^- photo-reduced using 350 nm photons. Photolysis of benzophenone in the presence of formate forms α-hydroxy radicals of benzophenone and •CO_2^-.[15] Moreover, the chain dechlorination of CCl_4 was 7-10 times more efficient than the reduction of $CHCl_3$ in SPEEK/HCO_2^- solutions.[1,4] The difference in reactivity of these two halocarbons can be attributed to their thermodynamic data. The potential for reduction of CCl_4 is estimated to be -0.23V[13], whereas for $CHCl_3$, the estimated value is about -0.9V in ethanol[16]. Considering that E°[$(CH3)_2C$•$OH/(CH_3)_2C{=}O$, H+] = 1.4 V,[17] the driving force for the reduction of CCl_4 by α-hydroxy radical is about twice as the value calculated in for $CHCl_3$.

However, our research group's main goal was to use this efficient reducing system commercially, as in the likes of fabrics or in optical tubing where the system would be able to degrade the toxic chlorinated compounds either in an aqueous medium or in air. Even though SPEEK/HCO_2^- solution system showed an efficient reduction via free radical chain mechanism, the system is inconvenient for a practical approach, specially using in large scale. Moreover, the solution system is unable to reduce halocarbons in gaseous phase and leaving the system in aqueous solution itself is potentially pollutant to the environment. Hence, this investigation tested ways to use films of SPEEK, combining with the H atom donor, PVA, immerse in an aqueous solution for the dechlorination process. A significant advantage of SPEEK/PVA systems is that their photoreactions can be studied in both aqueous solutions and using cross-linked films of the polymer blends.[18,19] The experiments that were carried in SPEEK/PVA solutions, always provided mechanistic information that were helpful for understanding the photochemical behavior in cross-linked polymer films. Solution studies on H_2O_2 photogeneration provided important insights about reactions occurring in films.[18,19] Moreover, solution experiments that were carried out for photoreduction of dyes like thionine, methylene blue and cresyl violet were helpful in understanding the experimental difficulties that were associated with solid matrices. Thus, our aim is to use the finding from solution tests for photoreduction of CCl_4 and $CHCl_3$ [1,4] to help access the feasibility of SPEEK-based films as protective barriers against toxic compounds. Moreover, photochemical dechlorinations were obtained with both $CHCl_3$ and CCl_4 using poly-(vinyl ferrocene) films.[20] However, performing photoreduction of these halomethanes using solid matrices is not an easy task. The reactants need to diffuse into the films efficiently for the reaction to occur. Then the products need to come out of the films again via diffusion. Such diffusional problems make quantification of the products from reactions that are taking place inside a film, a crucial problem.

Kinetic data on transformation of PVC (Poly vinyl chloride) films was shown to be approachable in a medium of fluid or gas that facilitates the extraction of products from a solid matrix.[21] Moreover, our research group was able to extract H_2O_2 continuously, which produced via photoreduction of O_2 using swollen SPEEK/PVA polymer film immersed in an aqueous solution.[18] It is one of the most recent example for this type of method that used to extract products after reacting with a solid material. Further, qualitative and quantitative analysis of the products were feasible by subjecting photolyzed solution to conventional analytical procedures. Hence, using an analog method to test the ability of SPEEK/PVA films to chemically attack undesirable chemicals like $CHCl_3$ and CCl_4 seems attainable. Our investigation tested a modified version of the method that previously tested to follow the kinetics of above photoreduction. The photogenerated Cl^- ions inside SPEEK/PVA films were extracted into the solution, hence assembling kinetic data via situ potentiometric determination of the product in an aqueous phase. Presented in this chapter is the kinetic data obtained for light induced efficient reductive chain dehalogenation of CCl_4 and $CHCl_3$ by swollen SPEEK/PVA films in an air saturated HCO_2H/HCO_2^- solutions. Under such conditions, the photolysis of SPEEK/PVA films contain HCO_2^- was found to induce dechlorination of CCl_4 and $CHCl_3$ via a chain process. Our goal is to find out the mechanism of the system, optimal conditions for the highest reduction efficiency, to find out a way to reuse the film and finally to use this system for environmental purposes.

4.2 Experimental

Poly(ether etherketone), PEEK, Ketaspire KT-880 FP powder, Mn = 4 x 104 g mol^{-1}, supplied by Solvay, USA, was sulfonated by reacting with sulfuric acid according to a standard procedures.[18] The sulfonated polymer then converted to its Na^+ salt (SPEEK), and characterized accordingly.[12] PVA, poly(vinyl alcohol), 99 % hydrolyzed with an average molar mass of 8.9-9.8 x x 10^4 g/mol^{-1}) was obtained from Sigma-Aldrich. $CHCl_3$ was acquired from Macron, and all the other chemicals including CCl_4 were purchased from Sigma-Aldrich. Crossed linked SPEEK/PVA polymer films were prepared as described in chapter 3. Most photolyzed films contained 17/83 SPEEK/PVA wt %, other compositions were achieved varying the polyketone/polyol molarity ratio. Unless otherwise stated, the dimensions (when dry) of the films were 5 cm X 2.5 cm and the thickness 50 (± 6) μm and each dimension increased by a factor of 1.3 after swelling in H_2O. The thickness was obtained by means of a digital micrometer, Mitutoyo model -1" SFB. The films were cleaned by dipping in a 50:50 CH_3OH/H_2O mixture for 30 mins and then briefly rinsing with distilled water. All films were stored at 4 ^{0}C to ensure the reproducibility of data despite their age.

Photolysis was conducted using a vessel from borosilicate glass, designed with features used in previous potentiometric and photochemical film experiments.[18] Figure 4.1 is an image of the irradiation vessel.

Figure 4.1: a) Image of the vessel including the Ion Selective Electrode (ISE), reference electrode, SPEEK/PVA Film, HCO_2H/HCO_2^- buffer and a magnetic stir. b) Image of inner glass tube, FETFE o-ring and nylon bushing cap with a small opening for a constant circulation of the solution during stirring

Our vessel consists of two cylindrical glass tubes; a small, narrow tube (11cm length, 3 cm diameter) and a large, wider tube (11.5 cm length, 4 cm diameter) that connected by two short vertical tubes. (3.5 cm length, 1.1 cm diameter). Another small tube placed on the top vertical connection tube, enabled the insertion of halomethanes (4 cm length, 1 cm diameter). Inner glass tube (11 cm length, 3 cm diameter) was secured using a combination of FETFE o-ring and nylon bushing cap as shown in Figure 3.1b. The cap was screwed to a glass adaptor fitted on top of the wider glass tube. Swollen SPEEK/PVA films were positioned around the wider the glass tube, in the narrow region between inner surface of the vessel and the outer surface of the inner glass tube. This way the films were held in a fixed, fully extended position without applying excessive pressure on them throughout the experiment. Swollen films are susceptible to rolling on themselves and also to rupturing under mechanical stress. This procedure avoided the extensive manipulation of somewhat fragile swollen films.

An ion selective electrode (ISE) from Thermo Scientific, Orion 9417BN, together with a Radiometer K601 mercurous sulfate reference electrode was used to monitor the Cl^- during photolysis A Radiometer PHM 95 instrument was connected to these electrodes to determine the concentration of the chloride potentiometrically. The electrodes were inserted into two glass cylindrical tubes; ion selective electrode (ISE, 3 cm diameter, 11 cm height) into the wider cylindrical tube and the reference electrode (2 cm diameter, 11 cm height) into small narrower tube. Since the reference electrode is light sensitive, the small glass tube was darkened using spray paint to prevent any exposure to the photon flux during illumination. The two electrodes were tightly fit via perforated septa (which also served to close the vessel) and immersed into the solutions. The solution is an electrolyte solution (mostly HCO_2H/HCO_2^-) as the kinetics were determined potentiometrically. The illumination vessel was filled with 54 ml of the electrolyte. Chloromethanes (CCl_4 = 1 ml, $CHCl_3$ = 2 ml) were added through insertion tube using a gas tight syringe to the electrolyte solution. Before the insertion, the chloromethanes were washed several times to with distilled water to remove the stabilizer. To ensure the efficient circulation of the solution through the connecting tubes, constant and fast stirring rate was used between two glass cylindrical tubes. A large fraction of injected chloromethanes was phase separated due to their low solubilities in water. Solubility of CCl_4 is 5.1 x 10^{-3} M (or 37.5 μl CCl_4 in 75 ml of aqueous solution)[23] whereas the solubility of $CHCl_3$ is 6.6 x 10^{-2} M (or 0.3 ml of chloroform in 54 ml of H_2O at 20 ^{0}C).[23] To establish an equilibrium of the mixture with films, the solution was stirred for 5 -10 min prior to the illumination, hence excess CCl_4 and $CHCl_3$ mostly appeared as dispersed small droplets. For degas experiments, the solution mixture was bubbled with $Ar_{(g)}$ for 30 mins under constant stirring (sealed the vessel with rubber septa) prior to the illuminations. Calibrations for ISE were performed daily to reduce the experimental errors.

Irradiations were carried out inside Rayonet, RPR-100 circular-illuminator that generated photons with $\lambda = 350 \pm 15$ nm by means of 16 RPR-3500A lamps. Amberchrome 540 was employed as a chemical actinometer to determine the experimental light intensity (I0).[19, 22] By placing the samples at the center and mid height position within the cavity of the illuminator where the temperature was 29 °C, a uniform exposure of the samples was achieved. All the solutions were prepared with purified water obtained from a Millipore Milli-Q Biocel system. Necessary pH adjustments were done by adding small aliquot of 0.1 M NaOH and 0.001M HCOOH to the HCO_2H/HCO_2^- buffer. Determinations of [H+] employed a Mettler Toledo Seven Multi S80 meter in conjunction with an acumen electrode. Optical spectra were recorded on a Shimadzu UV−Vis 2501PC spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) determinations utilized a Hewlett-Packard 5890 Series II gas chromatograph coupled to a Trio 2000-1133 quadrupole mass spectrometer.

4.3 Results and Discussion

Illumination of swollen SPEEK/PVA films in contact with aqueous solutions with electrolytes such as HCO_2^- buffer containing CCl_4 and $CHCl_3$, produced a significant amount of Cl^-. However, illumination of swollen films failed to generate the Cl^- without in contact with any electrolyte solutions. Moreover, the lack of Cl^- photogeneration in the absence of formate buffers was notable given the quenching of ketones by chloromethane solvents, producing HCl and radicals.[24] Further, the control experiments performed in the dark, as well as in the absence of SPEEK/PVA film, formate buffer or other H atom donors (as electrolyte solution), CCl_4 or $CHCl_3$, failed to produce Cl^- ions (with or without air). Photolysis of SPEEK/PVA films that contained HCO_2^- yielded an optical signal with a wavelength of maximum absorbance (λ_{max}) at 565 nm due to the formation of SPEEK•.[12] Illumination of SPEEK/PVA films also detected this absorbance maximum (that persisted for several minutes) as well as systems containing HCO_2^-, however the signal was not observed in the presence of CCl_4 or $CHCl_3$, indicating the reduction of SPEEK• by these chlorocarbons.

Illustrated in Figure 4.2 is a plot depicting the amount of chloride ion concentration ($[Cl^-]$) produced as a function of illumination time for air saturated 0.36 M HCO_2^- buffers at pH 7.3 containing swollen 17 wt% SPEEK and 83 wt% PVA films. All photoreductions of CCl_4 (air saturated) consisted of two linear steps; a short, somewhat slow initial step where the concentration of chloride ions increased linearly as a function of time, which lasts for 30 to 33 min, followed by another liner step in which the concentration of chloride ions increased rapidly compared to the initial step. The preliminary slow process is known as the induction period. The rate of photoreduction of Cl^-, $r(Cl^-) = d[Cl^-]/dt$, was calculated from the slops of the second linear step and then employed to evaluate quantum yield of the Cl^- formation, $\phi(Cl-) = r(Cl^-)/I_0$.

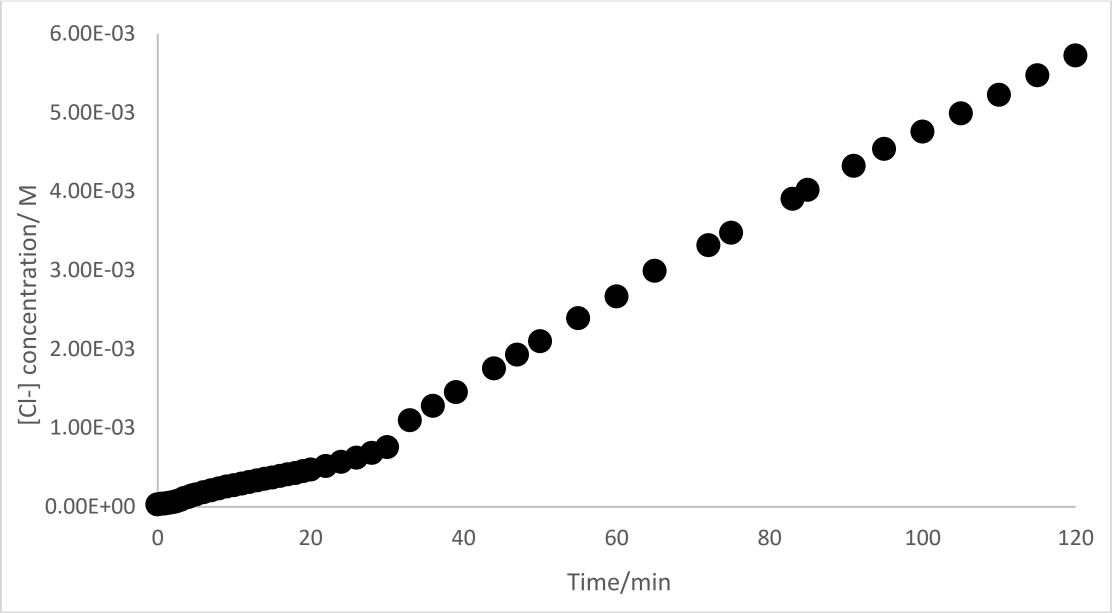

Figure 4.2: Evaluation of Chloride ion concentration during photolysis of air saturated 0.36 M formate buffer containing swollen 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm) and 1 ml of CCl_4 at pH 7.3. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(h*ν*)/s and T = 29 °C.

However, these evaluations required some corrections. The linear dependency of Cl^- formation with time is an indication that the photon flux absorbed by the SPEEK/PVA film controlled the CCl_4 reduction process. The reaction rate is directly depended on the photo process took place in the film which generated reducing radicals. Even though the Cl^- ions were generated inside swollen films, they migrated into the solution due to the continuous extraction method, a method employed in previous experiments[18], thus allowing to detect chloride using a potentiometric method. Therefore, the above plotted data were resulted from the dilution of Cl^- by the solution in contact with swollen films. This dilution of Cl- is corrected by using the equation, D_f = V(solution)/V(film), where V(solution) is the solution volume and V(film) corresponds to the volume of the swollen film. Only length and width of swollen films were attainable by direct determinations as the thickness of the wet film was difficult to get by the micrometer. According to our research group's previous investigation, each of the dimension of a SPEEK/PVA film is increased by a factor of 1.3 during swelling.[18] By applying that and calculating V of the swollen film and D_f, the rate of photogenerated Cl^- corrected for its dilution, $r_c(Cl^-) = D_f\, r(Cl^-)$.[18] A further correction was needed for the light intensity as the polymer film only captures a fraction of photons entering the vessel. This was corrected by using the ratios of surface areas between the irradiation vessel and the swollen polymer film. The light intensities were determined via actinometery.[18] The amount of photons absorbed by the polymer film (I_c) can be calculated from the equation; $I_c = I_o$ x S_Af, where S_Af is the ratio of surface area of swollen film and vessel.[18] Thus, the corrected quantum yield for the formation of Cl^- ions $\phi(Cl-)$, was then calculated using corrected rate and the photon flux absorbed by the polymer film; $\phi(Cl-)= r_c(Cl\text{-})/I_c$. Potentiometric quantification of $[Cl^-]$, typically exhibited an error of 5% however deviations about 20% were observed with SPEEK/PVA polymer films. Similar deviations were noted during the photoreduction of CCl_4, $CHCl_3$ in SPEEK/HCO_2^- solutions and O_2 induced by both SPEEK/HCO_2^- solutions and SPEEK/PVA films.[1,4,18,19] A contributor to the above deviations of $\phi(Cl-)$ was the light scattering from CCl_4 droplets that formed upon stirring the solutions with excess chloromethane. Given that the fraction of scattered photons was not accounted for, the derived $\phi(Cl-)$ values corresponded to lower limits of the quantum efficiencies of Cl− formation. Also, the large deviations in quantum yields probably reflect the heterogenous nature of the polymeric photochemical systems, especially in solid systems. However, the deviations observed in the present study were lower (by about 10%) than those encountered during the O_2 photoreduction using SPEEK/PVA films,[18] presumably due to the fact that the SPEEK synthesized from solvay PEEK was significantly more photoactive than the sulfonated polyketones prepared from other precursors.[1,4]

The Cl^- formation was controlled by the photogenerated reducing radicals which only depends on the light intensity I_0, thus followed zero order rate law. Large $\phi(Cl^-)$ values at low photon fluxes are an indication of a chain reaction. Earlier investigation of photoreduction of CCl_4 via SPEEK/HCO_2^- solutions were concluded to follow chain reaction mechanism and the calculated $\phi(Cl^-)$ for the photoreduction in 0.36 M HCO_2^- at pH 7.3 was 1.4.[1] Under same conditions, swollen SPEEK/PVA films showed a significantly high quantum yield, almost 200 times higher ($\phi(Cl^-) = 264$) compared to the values from solution experiments. Such high efficiencies are not frequently found when reducing chlorocarbons, particularly with systems that contain air. This indicates that the CCl_4 photoreduction via films also follows a similar chain reaction pathway.

More often, the length of the induction period was reproducible and independent of reaction conditions. During this period, the reduction was slow but formation of Cl^- occurred occasionally. The increment of Cl^- ions were liner hence followed zero order kinetics. Similar induction periods were observed during the photoreduction of CCl_4 and $CHCl_3$ initiated by degassed SPEEK/HCO_2^- solutions and CCl_3F induced by TiO_2 particles.[1,4,25] However, the length of the induction period was irreproducible, short and scaled in a non-linear behavior compared to above results from air-saturated swollen SPEEK/PVA films. The reason for this deviation could account for the presence of oxygen in film system. The irreproducible nature for the previously carried experiments were due to the interference of trace amounts of oxygen left after degassing, because small amounts of O_2 can scavenge some of the photogenerated radicals and interfere the photoreduction process. Moreover, the presence of air increased the induction period.[25,26] The film system wasn't degassed initially, hence the induction period continued until all the oxygen is reduced. Another contributor for the shorter induction periods in solution experiments can be attributed to the differences in irradiation vessels that were used for the experiments. The headspace of the vessel employed in the film experiments were about 1/3 larger than the vessel used for the solution system. An obvious consequence was that a larger O_2 amount needed to be reduced in the film system, yielding a longer induction period. According to the findings from our research group, O_2 was reduced to H_2O_2 by photogenerated SPEEK• in both solutions and films.[18,19] This confirms that the induction period is related to the O_2 concentration of the system and at high concentrations of O_2, oxygen competes with chloromethanes to generate reducing radicals. α- Hydroxy radical of 2-propanol, $(CH_3)_2C{\bullet}OH$, can be a model compound for HSPEEK• as the rate constants between HSPEEK• with CCl_4 and $CHCl_3$ are unknown. The rate constant for the reduction of CH_2Cl_2 and O_2 by $(CH_3)_2C{\bullet}OH$ are ~ 1 x10^6 M^{-1} s^{-1} and 4 x 10^9 M^{-1} s^{-1} respectively.[27] For air-saturated SPEEK/PVA solutions, $[O_2]$ = 0.26 mM[19], and the water solubility of CCl_4 and $CHCl_3$ are 5.1 mM and 66 mM respectively.[23] If HSPEEK• reduce O_2 and CCl_4 / $CHCl_3$ with similar rate constants to those of $(CH_3)_2C{\bullet}OH$, then the resulting pseudofirst-order rate constants are 1 x10^6 s^{-1} and 6.6 x 10^4 s^{-1} , thus proving that the reduction of O_2 by HSPEEK• is the dominating step during the induction period. Initially, HSPEEK• reacts with oxygen predominantly to form H_2O_2, hence generate a very small amount of Cl^- compared to the second step. The consumption of oxygen during the induction period enables CCl_4 and $CHCl_3$ to increasingly compete for the HSPEEK•, resulting a rapid formation of Cl^- formation at the end of the induction period. Longer induction periods were expected for the systems that contain oxygen hence, the effects of O_2 on photoreduction of CCl_4 were tested by constantly bubbling oxygen throughout the experiment and the results are shown in figure 4.3. Clearly the presence of oxygen further lengthened the induction period such that there was no second step as the induction period continues to hold on till end. Moreover, introduction of O_2 decrease the efficiency of photoreduction CCl_4 significantly. As shown in figure 4.3, an increase in $[O_2]$, substantially decrease the photoreduction, lowering the quantum yield of formation of Cl^-, $\phi(Cl-)$ to 38.8. On the other hand, no induction period was noticed in degassed systems and the

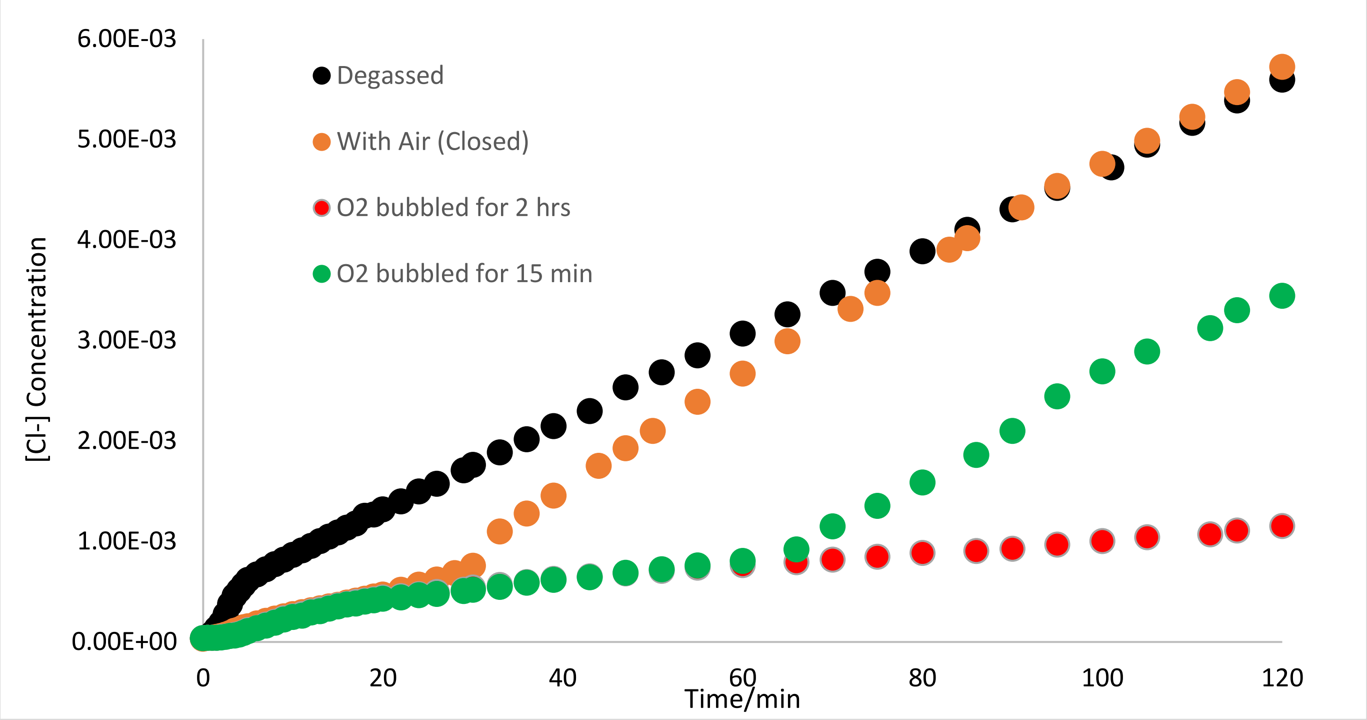

Figure 4.3: Formation of chloride ions during photolysis of 0.36 M formate buffer containing swollen 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm) and 1 ml of CCl_4 at pH =7.3. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(hν)/s and T = 29 °C. Data obtained with air (●), without air /degassed (●), data obtained with constant bubbling of oxygen (●) and data obtained with bubbling of oxygen for 15 min (●).

rate of Cl^- formation was relatively high initially, compared to the system when air was present. This demonstrates that at low oxygen concentrations, O_2 is unable to compete with CCl_4 and becomes reduced by a slow process involving $\bullet CCl_3$.[27] Similar effects on reduction efficiencies were noted in photoreduction of $CHCl_3$ via SPEEK/HCO_2^- .[4]

Figure 4.4 shows that significant amounts of Cl^- ions were formed upon exposing formate buffers containing SPEEK/PVA films with $CHCl_3$ to light. Similar to CCl_4, photoreduction of air-free $CHCl_3$ also exhibited a short and somewhat reproducible induction step.

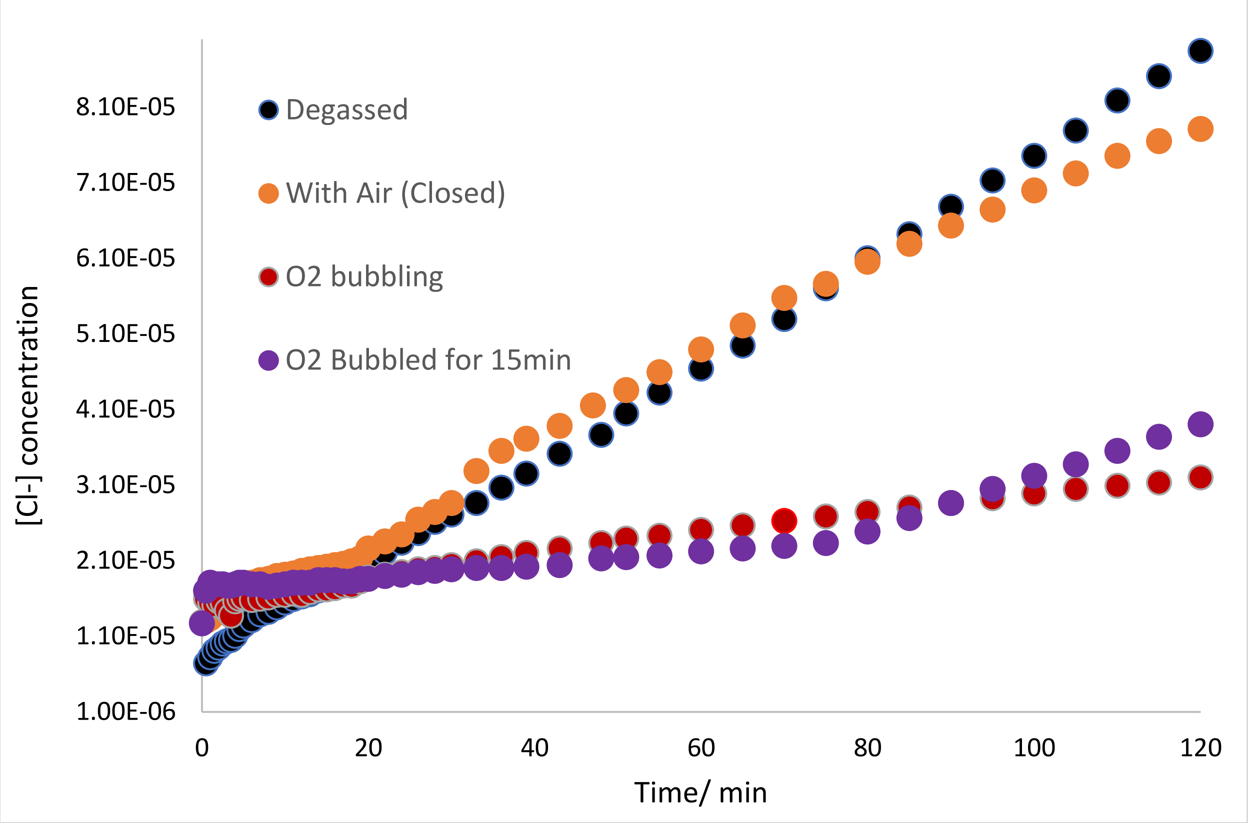

Figure 4.4: Formation of chloride ions during photolysis of 0.36 M formate buffer containing swollen 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm) and 2 ml of $CHCl_3$ at pH =7.3. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(hν)/s and T = 29 °C. Data obtained with air (●), without air /degassed (●), data obtained with constant bubbling of oxygen (●) and data obtained with after bubbling oxygen for 15 min (●).

Most of the induction periods detected during the photoreduction lasted only for about 16-20 min (CCl_4 = 30 -33 min) and the formation of Cl^- was almost negligible compared to the data obtained for CCl_4. Even for the second step, the quantum yield determined with $CHCl_3$ was about

100 times smaller than the values detremined for CCl_4 under similar conditions. A somewhat similar kind of difference between CCl_4 and $CHCl_3$ (10 times) in reduction efficiencies was observed in solution experiments as well.[1,4] Thus, the analogies found between the radical reductions of CCl_4 and $CHCl_3$ suggested that the dehalogenation of chloromethanes initiated by SPEEK/PVA films also proceeded via chain transformation. Moreover, photoreduction of $CHCl_3$ induced by SPEEK/PVA films were 10 times higher than the reduction induced by SPEEK/HCO_2^- solutions. These observations also hinted the possibility of a chain process involved in photoreduction. Chloride ions moderately quenches the triplet state of benzophenone with a quenching rate constant of $k_q = 2.2 \times 10^5$ M^{-1} s^{-1}.[29] This explains the initial slow growth (with CCl_4)/ almost no growth (with $CHCl_3$) of chloride ions as an analogous quenching of the SPEEK excited state was anticipated. Given the high reduction efficiencies, quenching seems not to be a significant factor for the photoreduction of CCl_4. However, quenching becomes significant during the photoreduction of $CHCl_3$, which was less effective. Thus, from two chloromethanes CCl_4 was selected in efforts to optimize the experimental conditions for the photoreductions.

Fast photoreduction of CCl_4 took place in the presence of formate buffer, compared to the rates obtained in solutions containing phosphate (K_2HPO_4), perchlorate ($NaClO_4$), HEC (2-hydroxyethyl cellulose) and CMC (sodium carboxymethyl cellulose) as H-atom donors. This was confirmed by using the same concentration of each of the H-atom donors (4×10^{-3} M) for quantum yield determinations. An exception was HEC; the much higher viscosity of this polymer forced us to use a lower concentration. The quantum yield observed for 4×10^{-3} M formate buffer was 23, whereas for others, it ranged from 3-11. Moreover, comparison of photoreduction efficiencies in the presence of formate and phosphate at higher concentrations (5×10^{-2} M), resulted similar results. The analysis of data showed that the quantum yield was 7 times higher with formate, $\phi(Cl^-)$

= 49.9, than that of phosphate, $\phi(Cl^{-})$ = 7.2. Such findings indicated that formate ions act more efficiently as a H-atom donor than the other compounds.

Previous investigations of SPEEK/PVA films with a polyketone/polyol weight percentage of 30/70 w/w% resulted in optimized Ag^{+} [12,30,31] and Th^{+} (chapter 3) photoreductions. Hence, experiments were carried out to find out if such compositions yielded efficient photoreductions of the chloromethanes as well. The efficiencies were analyzed using different SPEEK compositions. Even though changing the SPEEK concentration altered the amount of PVA in the film as well, all the films utilized contained a large excess of polyol over the polyketone. Thus, the changes in the photoreactivity of the resulting films were attributed mainly to effects originated from changing the SPEEK composition. Illustrated in figure 4.5 is the evaluation of $\phi(Cl^{-})$ during the photoreduction of CCl_4, as a function of w/w% composition of SPEEK in SPEEK/PVA films in both induction step and second step. The speed of the photoreduction increased rapidly with increasing weight percentage of SPEEK until maximum quantum yields of 111.2 and 264.97 were reached at 17% polyketone for the induction period and the second step respectively. After this maximum, $\phi(Cl^{-})$ decreased gradually upon further increases in the polyketone concentration. A similar behavior was noticed during the CCl_4 photoreduction in SPEEK/HCO_2^{-} solutions.[1] As previously noted, these quantum yields are much higher than the maximum yields for Ag^{+} and O_2 reduction (0.07 and 0.02 respectively)[12,18,19] as well as for the CCl_4 and $CHCl_3$ photoreductions in SPEEK/HCO_2^{-} solutions (1.4 and 0.2 respectively).[1,4] Such findings support the notion that chain processes were involved in the dehalogenations induced by SPEEK/PVA films.

SPEEK absorbs photons and generate HSPEEK• which is the photo-initiator for the reactions that involve SPEEK. At low SPEEK concentrations, less photons are absorbed thus reducing the ability of films to effectively photoreduce chloromethanes. The initial rise of $\phi(Cl^{-})$

in figure 4.5 can be understood since increasing SPEEK composition increases the amount of photogenerated SPEEK• thus increasing reduction efficiencies.

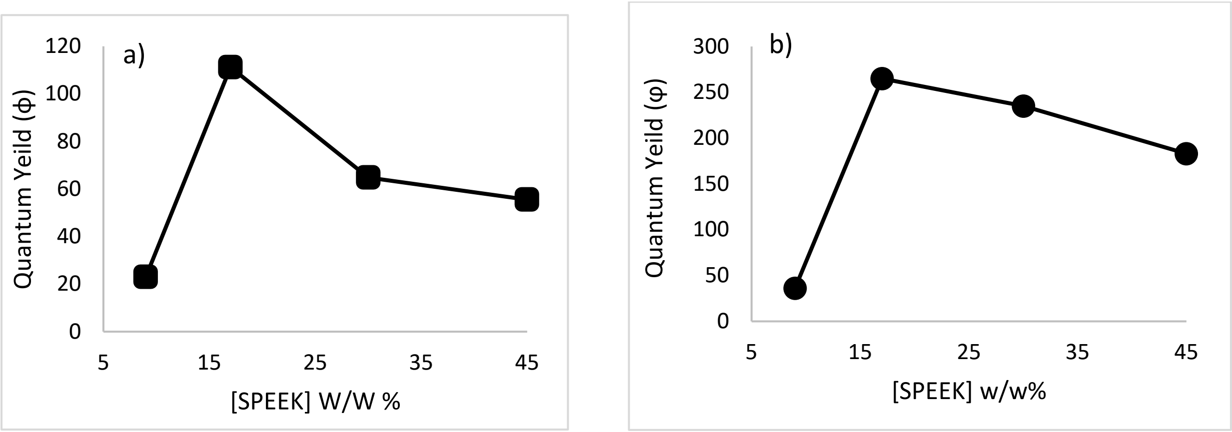

Figure 4.5: Evaluation of the $\phi(Cl^-)$; a) during the induction period, b) during the second step, as a function weight% of SPEEK in dry SPEEK/PVA films (average thickness, 50 μm) that contains 0.36 M formate buffer (average thickness, 50 μm) and 1 ml of CCl_4 at pH =7.3. SPEEK from solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(hν)/s and T = 29 °C.

On the other hand, quenching of BP triplet excited state by benzophenone molecules is a fast reaction in aqueous solutions with $k_q = 1.8 \times 10^8 \ M^{-1} \ s^{-1}$.[32] Moreover, intramolecular self-quenching of triplet excited states from carbonyl groups of pVBP (p-vinylbenzophenone) is known to take place .[33] However, in the case of SPEEK, formation of two or more triplet excited state per chain seems unlikely considering the concentration and the light intensity used for the experiments. Assuming that only intermolecular quenching of the triplet state by benzophenone groups from other SPEEK molecules took place, the data of figure 4.5 can be explained if such process becomes significant at higher SPEEK compositions and decreases the efficiency of HSPEEK• photogeneration. Higher SPEEK compositions induce closer packing of the polyketone chains, which force a closer proximity between benzophenone groups from different SPEEK chains, thus increasing the intermolecular quenching.

Presented in figure 4.6 is the quantum yield of formation of Cl^-, with varying HCO_2^- concentrations for the second step of CCl_4 photoreduction. The quantum yield increased with increasing formate concentration resulting the highest $\phi(Cl^-)$ value of 464.23 at 0.5 M formate. Increasing the concentration of H atom donor can induce a fast quenching of the triplet excited state, thus

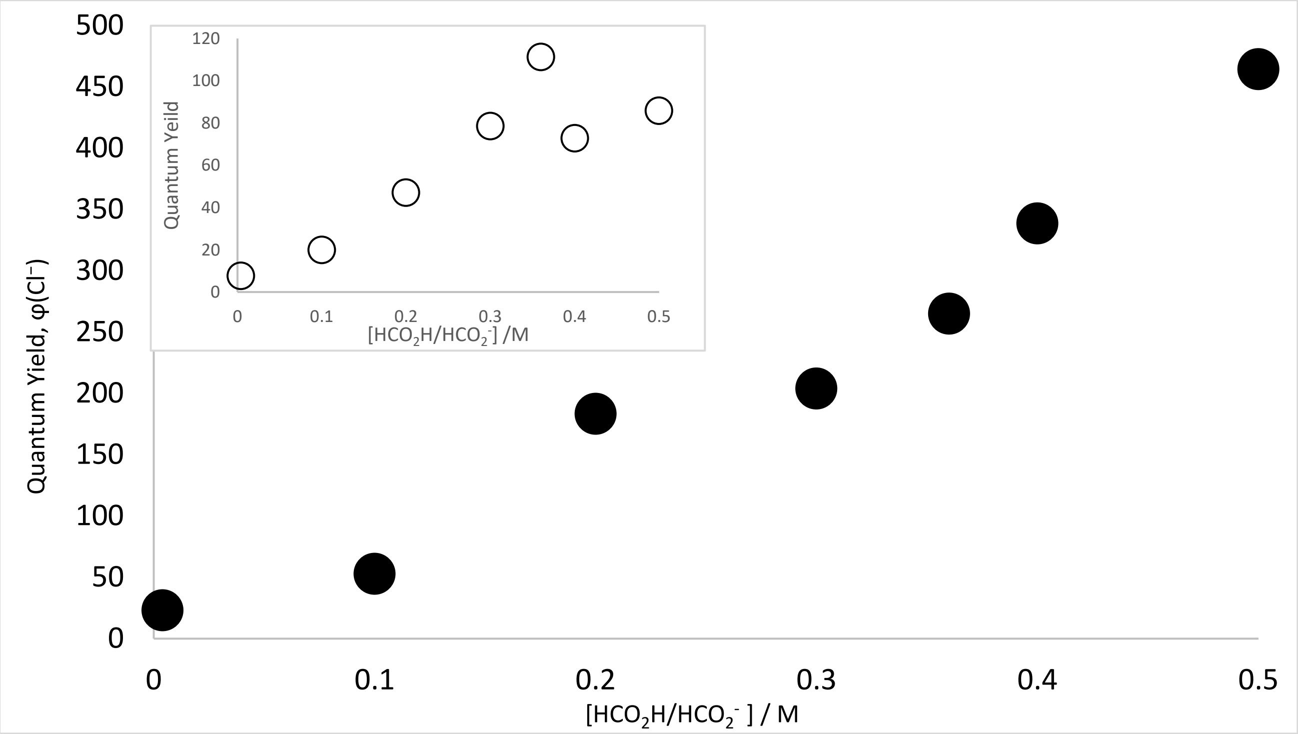

Figure 4.6: Quantum yield of formation of Cl^- as a function of HCO_2H/HCO_2^- concentration during the second step of the CCl_4 photoreduction. The swollen films contained 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm); solutions contained 1 ml of CCl_4 at pH =7.3. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(hν)/s and T = 29 °C. Inset: Data obtained during the induction period.

producing HSPEEK• more efficiently leading to faster reduction of chloromethane. However, as illustrated in figure 4.6 inset, during the induction period, ϕ(Cl^-) also increased with increasing formate concentration but reached a maximum efficiency at [HCO_2^-] = 0.36 M and decreased thereafter. A possible explanation for this unusual behavior involves a possible quenching of the SPEEK triplet excited state by HCO_2^-. If energy transfer between excited BP groups of SPEEK and the carbonyl groups of HCO_2^- is slow, the effects of such transitions will be noticeable only at the highest formate concentrations resulting in lower quantum yields. However, there is

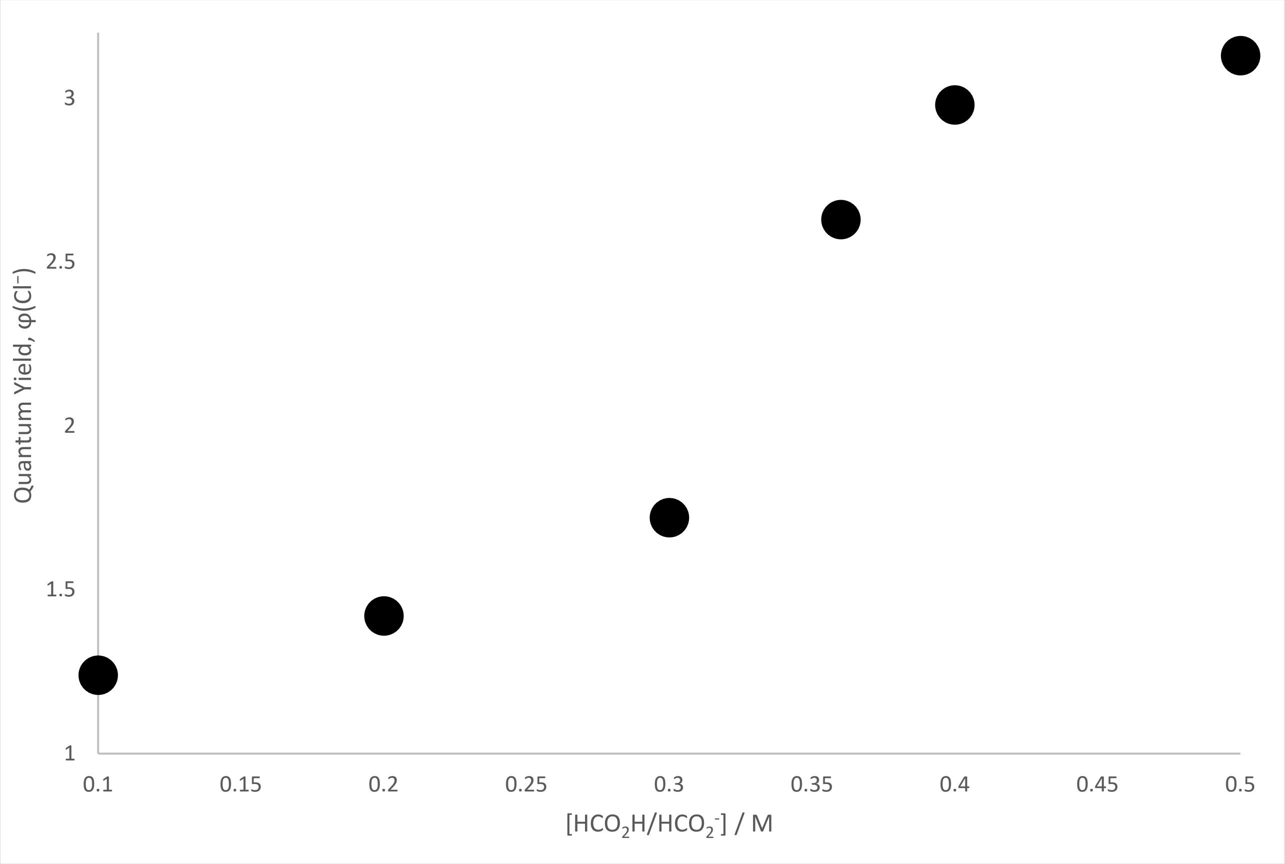

Figure 4.7: Quantum yield of formation of Cl^- as a function of HCO_2H/HCO_2^- concentration during the second step. The system comprised of swollen 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm) and 2 ml of $CHCl_3$ at pH =7.3. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(hν)/s and T = 29 °C.

still no straightforward explanation for the two different behaviors noticed during the two steps (induction period and second step) with respect to formate concentration. Similar behavior of quantum yields with varying HCO_2^- concentrations were observed for the photoreduction of $CHCl_3$ as well (Figure 4.7). Like CCl_4, $\phi(Cl^-)$ increased with increasing formate concentration and the increase followed the same pattern as that of CCl_4. The quantum yield augmented slowly until $[HCO_2^-]$ reached 0.3M but increased rapidly thereafter. However, as noted before, the observed $\phi(Cl^-)$ values were 50-150 times lower as compared to those found during the CCl_4 reduction. Moreover, formation of Cl^- was almost negligible during the induction period, hence no variation of $\phi(Cl^-)$ with $[HCO_2^-]$ was noticed.

Substantial support that a chain mechanism operated during the photoreduction of CCl_4, $CHCl_3$ and CCl_3F was obtained from post-irradiation experiments. The supporting evidence consisted of $[Cl^-]$ increases after photolysis was terminated due to a dark chain propagation process.[1,4,5,34,35] Figure 4.8 illustrates the changes of $[Cl^-]$ in an experiment with CCl_4 during cycles of alternating illumination and dark periods lasting 10 mins and 25 mins, respectively. While the formation of $[Cl^-]$ was obvious during illumination, a substantial amount of $[Cl^-]$ was generated during the dark periods even though the rates was 20 times smaller than the values obtained with light. The increases in $[Cl^-]$ were fairly linear initially during both illumination and dark periods but turned sublinear at longer dark times. Although the photolytic rates decreased with each cycle, the rates for the dark reactions increased with a rising number of cycles (inset of figure 4.8). These results demonstrated that the photoreduction of CCl_4 continued even after termination of photolysis, thus providing strong support that a chain process was involved.

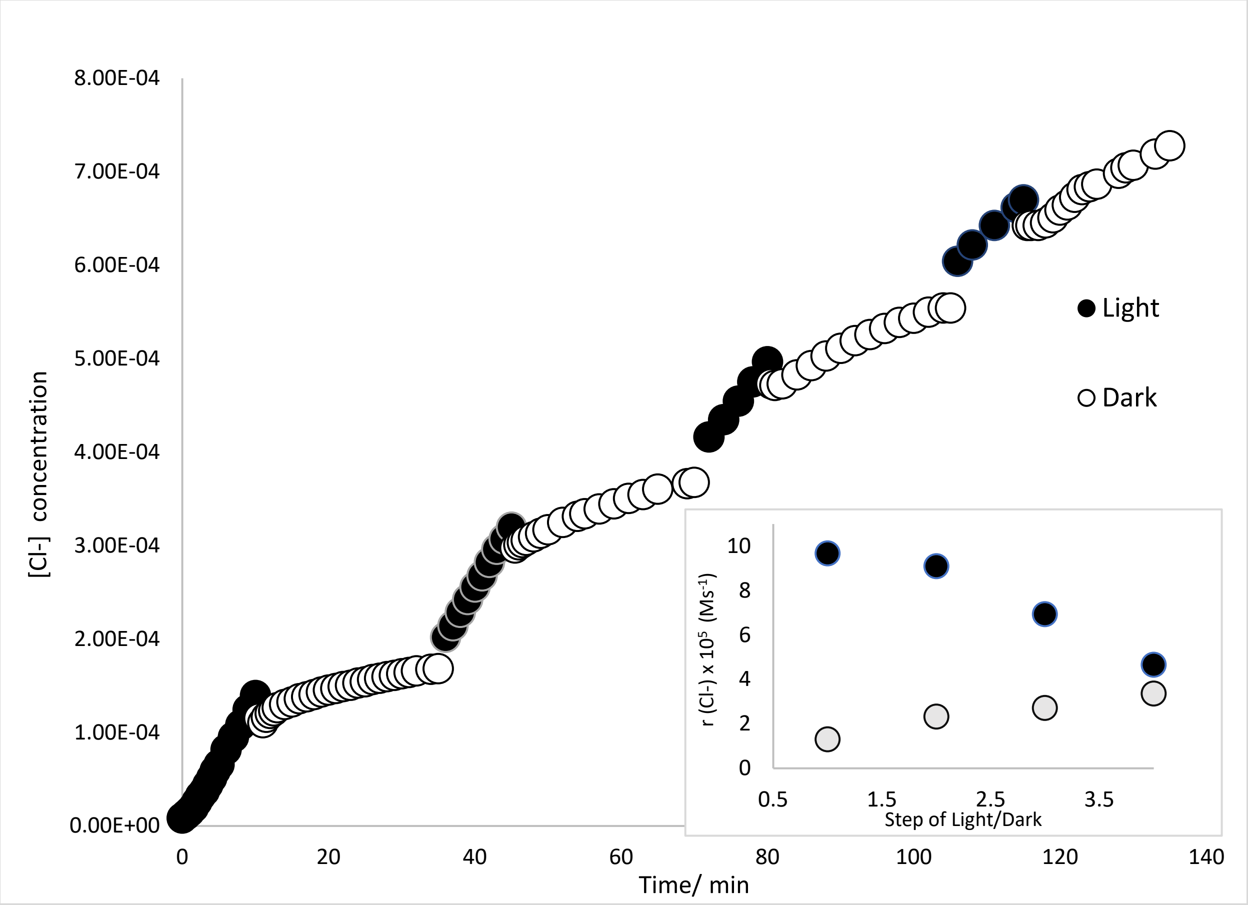

Figure 4.8: Change of [Cl$^-$] during cycles of alternating illumination (●) and dark (○) periods lasting 10 mins and 25 mins separately, during the photolysis of 0.36 M formate buffer containing 1 ml of CCl_4 at pH =7.3 in contact with swollen 17 wt% SPEEK and 83 wt% PVA film. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(h*v*)/s and T = 29 °C during illumination, T= 25^0 C during the dark periods. Inset: Rates of [Cl$^-$] formation during illumination (●) and in the dark (○).

Presented in Figure 4.9 is the data obtained for the formation of [Cl$^-$] during alteration of illumination and dark periods with $CHCl_3$. The initial induction period was avoided as the formation of [Cl$^-$] was negligible during that time.

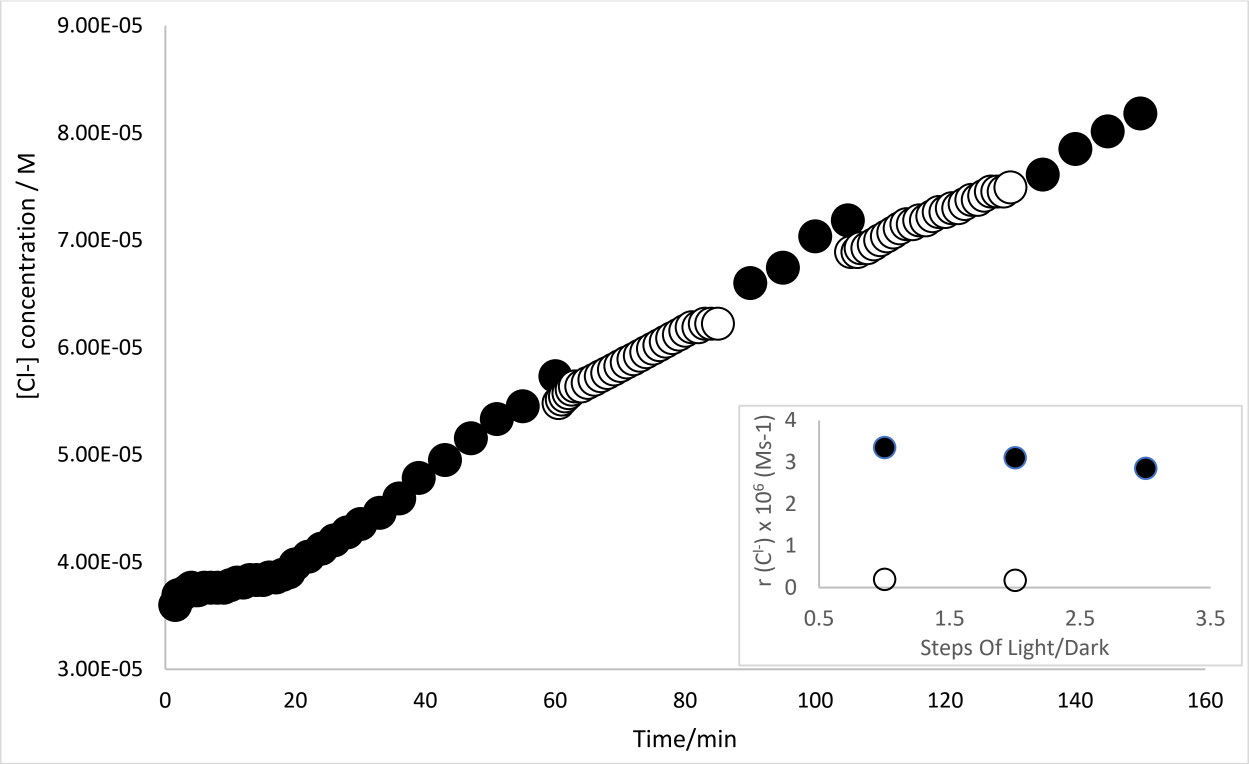

Figure 4.9: Change of [Cl$^-$] during cycles of alternating illumination (●) and dark (○) periods, photolysis of 0.36 M formate buffer containing 2 ml of $CHCl_3$ at pH =7.3 in contact with a swollen 17 wt% SPEEK and 83 wt% PVA film (average thickness, 50 μm). SPEEK from Solvay precursor; $I_0 = 2.2 \times 10^{-6}$ M(h*v*)/s and T = 29 °C upon photolysis, T= 25^0 C during dark periods. Inset: Rates of [Cl$^-$] formation during photolytic (●) and dark (○) periods.

Moreover, a longer exposure was used to prevent artifacts, given the lower rates associated with the photoreduction of $CHCl_3$. The formation of [Cl$^-$] even during the dark period supported an involvement of a chain process during the photoreduction of $CHCl_3$, which resembled the findings noticed when CCl_4 was reduced.

Figure 4.10 depicts the comparison of initial and final quantum yields of [Cl$^-$] formation during CCl_4 photoreduction as a function of pH in the range of $4 \leq pH \leq 9$. Experiments in highly acidic and basic solutions were not conducted as high [H_3O^+] and [OH^-] can interfere with the potentiometric [Cl$^-$] determinations. Both initial and final $\phi(Cl^-)$ increased smoothly as the acidity decreased in the range of $4 \leq pH \leq 7$ to a maximum of 111.2 and 265 at pH =7.3 and exhibited a linear and steep decrease thereafter. This evolution of $\phi(Cl^-)$ with pH also matched that of $\phi(Cl^-)$ determined during the photoreductions of CCl_4 and $CHCl_3$ in SPEEK/HCO_2^- solutions.[1,4] In fact, almost all the experiments with SPEEK, the yield of photogenerated HSPEEK• increased smoothly with decreasing acidity, reached a maximum value in neutral solutions and dropped at pH >8.[1,4,18,19] Such behavior can be explained in terms of photoprocess of generating HSPEEK•, which is expected to be similar to the formation of the reducing α-hydroxy radical of BP, $(Ph)_2C{\bullet}OH$, involving the photogenerated triplet excited state ($^3BP^*$) of benzophenone.[36]

The low quantum yields in acidic solutions can be explained on the basis of the quenching of the BP triplet excited state by H_3O^+. Efficient quenching of $^3BP^*$ by H_3O^+ via energy transfer occurs with a rate constant of k_q = (3.8−6.4) Å~ 10^8 M^{-1} s^{-1}, thereby inhibiting formation of $(Ph)_2C{\bullet}OH$.[32,37] Thus, at the lower pH values, an analogous quenching of the triplet excited state of SPEEK by hydronium ions limited the quantum yields of formation of radicals, $\phi(SPEEK{\bullet})$[1,4]. This resulted in decreasing efficiencies with increasing acidity to yield the lowest $\phi(Cl^-)$ at pH = 4. Support for such explanation was provided by determinations of the broad SPEEK phosphorescence centered at λ_{max}= 470 nm, which resembled the emission of poly(p-vinylbenzophenone), a compound frequently used as a model of polymeric benzophenones. The SPEEK phosphorescence at pH = 3.5 decreased by about 30% as compared with the intensity determined at neutral or weakly basic solutions.[38] Quenching of the SPEEK excited state by OH^- could be one of the contributing factors for the $\phi(Cl^-)$ decline at pH > 7.3 as energy transfer from $^3BP^*$ to OH^- takes place with a value of 5 x 10^6 M^{-1} s^{-1}.[29] The overall trend of figure 4.10, including a maximum efficient at pH = 7.3, matched closely with the photoreduction efficiencies determined for CCl_4 chain reduction in SPEEK/HCO_2^- solutions.

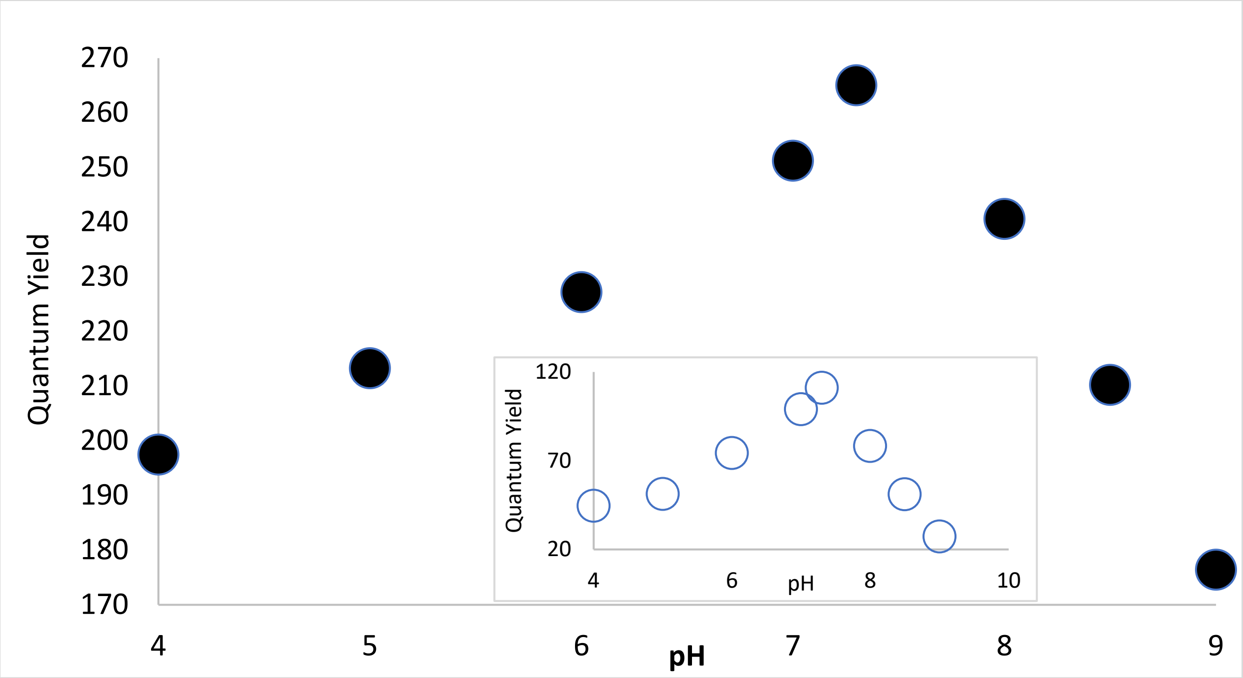

Figure 4.10: Evolution of $\phi(Cl^-)$ as a function of pH in illuminated solutions of 0.36 M formate buffer with 1 ml of CCl_4 at pH = 7.3 in contact with swollen 17 wt% SPEEK and 83 wt% PVA films (average thickness, 50 μm) and. SPEEK from Solvay precursor. $I_0 = 2.2 \times 10^{-6}$ M(hν)/s and T = 29 °C. Inset: $\phi(Cl^-)$ vs pH data obtained during the first step.

On the basis of that finding, an obvious conclusion was that CCl_4 was also photoreduced by swollen SPEEK/PVA films in HCO_2^- solutions via a similar mechanism but with significantly higher efficiencies than those determined in solutions.

4.4 Conclusion

Reduction of CCl_4 and $CHCl_3$ induced by the photolysis of SPEEK/PVA films were shown to occur in air-saturated aqueous solutions containing HCO_2H/HCO_2^- as H atom donors. Swollen

SPEEK/PVA films systems showed significantly higher quantum yields for both CCl_4 and $CHCl_3$ reductions compared to the SPEEK/HCO_2^- solution systems. These high quantum yields hinted the possibility of a chain process involve in photoreduction of these chloromethanes. Both photoreductions consisted of two linear steps; a short initial step (induction period), followed by another linear step (second step) where [Cl^-] increased rapidly compared to initial step. The induction period is directly related to the O_2 concentration of the system. This was confirmed by performing degassed experiments, which exhibited no induction period. Further, longer induction periods were observed when the solutions were bubbled with O_2 was throughout the illumination. Between two chloromethanes, CCl_4 photoreduction efficiency is 100 times higher compared to the $CHCl_3$ reduction efficiency. Fast photoreduction of chloromethanes took place in the presence of formate buffer compared to other H atom donors. The composition of the films also effects the efficiency of the photoreduction. A maximum quantum yield of 265 was obtained for the photoreduction of CCl_4 with films containing 17/83 w/w/% of SPEEK/PVA. Substantial evidence for a chain mechanism was obtained during post-irradiation experiments with both CCl_4 and $CHCl_3$ as generation of Cl^- continued even after exposure to light was interrupted due to a dark chain propagation process

The solution pH affects heavily the photoreduction rate of CCl_4 since $\phi(Cl^-)$ increased smoothly as the acidity decreased in the range of $4 \leq pH \leq 7$ to a maximum at pH =7.3, exhibiting a linear and steep decrease thereafter.

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