Photoreduction of Chlorinated Organic Pollutants Using Solutions or Films of a Polymeric System via a Free Radical Mechanism

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Abstract

Efficient reduction of chlorinated organics took place upon exposure to 350 nm photons in aqueous solutions containing sulfonated poly(ether etherketone), SPEEK, and either poly(vinyl alcohol), PVA, or HCO_2H/HCO_2^- buffers. Chloride ions together with H^+ were photogenerated and the rate of Cl^- formation, $r(Cl^-)$, was a linear function of time. The efficiency of the photoreaction increased in air-free solutions, since oxygen is a scavenger of the reducing species, SPEEK•. Using formate buffers as H-atom donors not only generated Cl^- as a reaction product but also induced reductions at least 10 times faster than in the presence of PVA. Differences in obtained quantum yield, $\Phi(Cl^-)$, were also noticed when SPEEK samples were prepared from poly(ether etherketone) precursors supplied by Evonik (called E-SPEEK) or Victrex (known as V-SPEEK) or Solvay (known as S-SPEEK). Efficiency for the reduction of the chlorinated organics increases more than 20 fold using SPEEK/PVA film as a reducing system instead of aqueous SPEEK/PVA solution. Drastic $\Phi(Cl^-)$ increases were noticed in neutral solutions and at pH = 7.3 the quantum yield reached maximum values exceeding one irrespective of the nature of SPEEK. The dependence of $r(Cl^-)$ on $(I_0)^{1/2}$, I_0 = light intensity, and the occurrence of post-irradiation formation of Cl^- via reduction of $CCl_4/CHCl_3$ in the dark are further evidence that the photoreaction proceeded via a chain process.

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List of Abbreviations

BP	benzophenone
BPK	benzophenylketyl
PEEK	poly(ether ether ketone)
SPEEK	sulfonated poly(ether ether ketone)
PVA	poly(vinyl alcohol)
^{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
r_c	corrected rate
r_i	initial rate
UV	ultraviolet
Vis	visible
E^0	energy potential
I_0	light intensity

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Chapter I

Photoreduction of chlorinated organic pollutants using solutions or films of a photosensitive polymeric system

1.1 Introduction

Macromolecular materials are somewhat unique in that their properties can be manipulated to achieve multiple purposes. For instance, alteration of the properties of non-ionic polymers can easily be achieved by binding ionic groups to their macromolecular chains, or via blending such materials with another that is ionic. Advanced polymers exhibiting a variety of new properties may be helpful to solve environmental problems that are hard to tackle with conventional technologies. Some chemicals frequently used, or even produced in the natural environment have been eventually found to be toxic. Remediation of places contaminated with toxic chemicals is not always straightforward given that different sites can exhibit various levels of complexity. Thus, remediation methodologies that can be adapted to the requirements of a specific site are bound to be more successful. Presented in this dissertation is an investigation that aimed at producing materials able to utilize electromagnetic energy for degrading some unwanted chemicals. These desired polymeric materials, the way they were prepared and their properties and reaction mechanisms, together with the selected environmental contaminants and the way they were degraded will be presented and discussed in the subsequent sections.

Macromolecular materials able to respond in a desired fashion that specific changes of the surroundings have been called smart polymers. Numerous studies have been devoted to identify and characterize such materials, which can be present in solution, gel or film states. Successful utilization of smart polymers have been envisioned for a wide range of areas such as: fuel cell development and batteries,[1-3] optical devices,[4] environmental applications,[5] nanotechnology,[6-11] and others including drug delivery systems.[12-14] Smart or stimuli responsive polymers (SRPs) are high-performance (or technological advanced) macromolecular materials which respond to a small changes in the environment that can be physical, chemical or biochemical stimuli. Three commonly stimuli and their responses are presented in figure 1.1.[15]

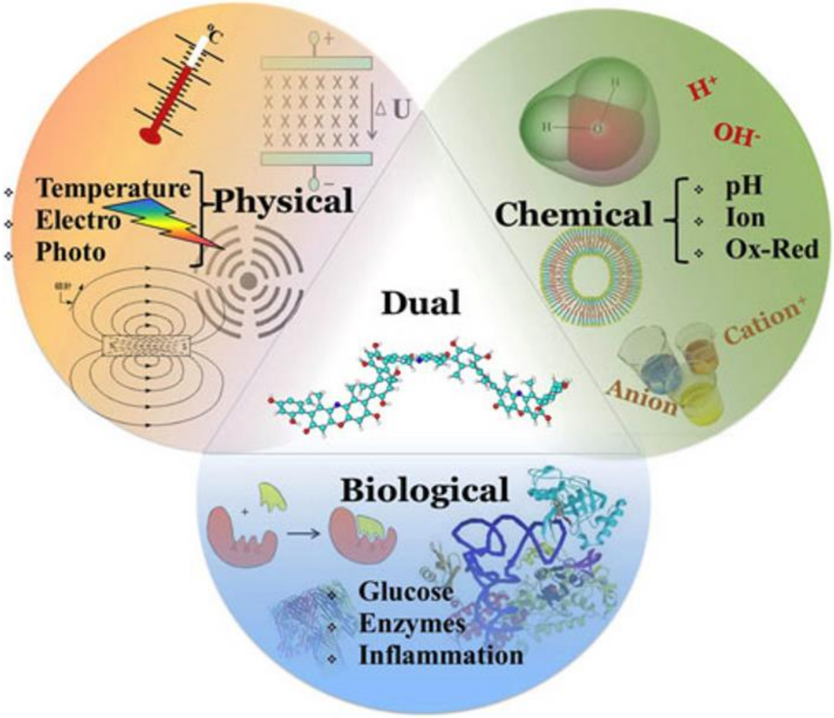


Figure 1.1 Adopted figure for stimuli and stimuli responsive polymers.[15]

Physical stimuli that dependent on temperature, light, ultrasound, as well as magnetic, mechanical or electric effects can modify the dynamics of macromolecular chains. Chemical stimuli can be induced by the solvent, ionic strength, electrochemical potential and pH, which may modulate molecular interactions between polymer and solvent molecules, or between polymer chains. Biochemical stimuli depend on effects due to receptors, enzymes and metabolites.[15] The potential abilities and flexible behavior of polymers have encouraged researchers to further develop smart materials with the aim of achieving self-regulated structures and characteristics.

Various techniques are available for modulating polymers at the molecular level to achieve desired functionalities Among such techniques are grafting, blending, interpenetration of polymer networks and preparation of polymer complexes.[16] Blending is a moderately simplistic process in which two or more polymers are mixed mechanically to form a mixture that exhibits characteristics not found in any of the original constituents. This method has produced materials able to exhibit wound monitoring and skin-care capabilities, moisture/temperature management and also aesthetic appeal simply by incorporating SRPs into fabrics.[17]

1.2 Photo-responsive Polymers

Among SRPs, light-sensitive, or photo-responsive, polymers has attracted great attention for their ability of utilizing light as an energy source that is cheap, renewable and readily available. Compounds that contain chromophores, that is groups consisting of conjugated π bonds, or heteroatoms having non-bonding and valence shell electron pairs, are known to be light sensitive.[18] Photo-responsive polymers endure a variety of transformations such as isomerization, ionization, homolytic fragmentation, hydrogen abstraction, and also redox reactions. Light-sensitive macromolecules that quialify as SRPs are only those in which the chomophoric group is not consumed during the photochemical transformation. In other words, SRPs are photoreponsive polymers that return to their initial state after experiencing a reversible change upon absorption of photons. In electrochemistry, there have been huge number of studies based on polymers, such as polyimide, polyaniline, poly(vinylcarbazol), that exhibit light-induced redox properties.[19] Light- sensitive polyelectrolytes are useful in nanotechnology and surface engineering since they experience specific changes as a response from to pH, ionic strength, and solvent changes.[20] Light-responsive polymers are highly advantageous for applications in drug delivery and nanomedicine as light can be applied instantaneously and under specific conditions with high accuracy.[14,16] Furthermore, light-responsive polymers that can generate reducing species have attractive interest for a variety of applications.[5-8,21,22] Since light can be focused on polymer surfaces, and can be delivered to distant locations using optical fibers, an intriguing possibility is to guide photons into films of light-responsive polymers immersed in contaminated waters. Redox reactions induced by exposure to such photons may be then induce pollutant decontamination within the aquatic system. Identification of appropriate photoresponsive polymeric systems and elucidation of their reaction mechanisms are important objectives of this investigation. The main goal of this dissertation was to figure out possible uses of a SPR photochemical system for the elimination of contaminants in aquatic environments.

1.3 Halogenated organic pollutants in environments and point of interests

Due to their low chemical reactivity, halogenated hydrocarbons and their substituted derivatives can be stable and non-biodegradable to the natural environment. Pollution of aquatic environments by these toxic chemicals can result from manufacturing processes and also due to their use as solvents, pesticides, dyes, drugs and explosives.[23] Additionally, these chemicals can circulate through the environment through the food chain as illustrated in Figure 1.2.

Halo-organic compounds are not only important industrial solvents, but are used in the manufacture of petrochemicals, dyes, resins, pharmaceuticals, synthetic fibers, explosives and cosmetics. Chloroform, carbon tetrachloride, dichloromethane and chlorinated benzenes are the major solvents that migrate into the environment in various ways, thereby creating environmental issues.[23] Hence, protection against the presence of these toxic chemicals in the environment has always been a point of concern in areas of healthcare, agriculture production, emergency response and military personnel. Scientists have investigated several remediation strategies for the degradation of halogenated organic pollutants including biological or microbial,[24] chemical,[25-32] photochemical,[33-37] thermal[38] and electro-reductive techniques.[39-40] Although microbial degradation is considered a "green" technique, this methodology is very slow, time-consuming and expensive to afford at a large scale. Chemical methods can be used in large scales but require large volumes of reactive compounds and solvents, which may be toxic as well. On the other hand, enormous amounts of energy are ususally needed for the thermal degradation of pollutants since such processes occur only at high temperatures. While the electro-reductive technique requires a relatively lower consumption of

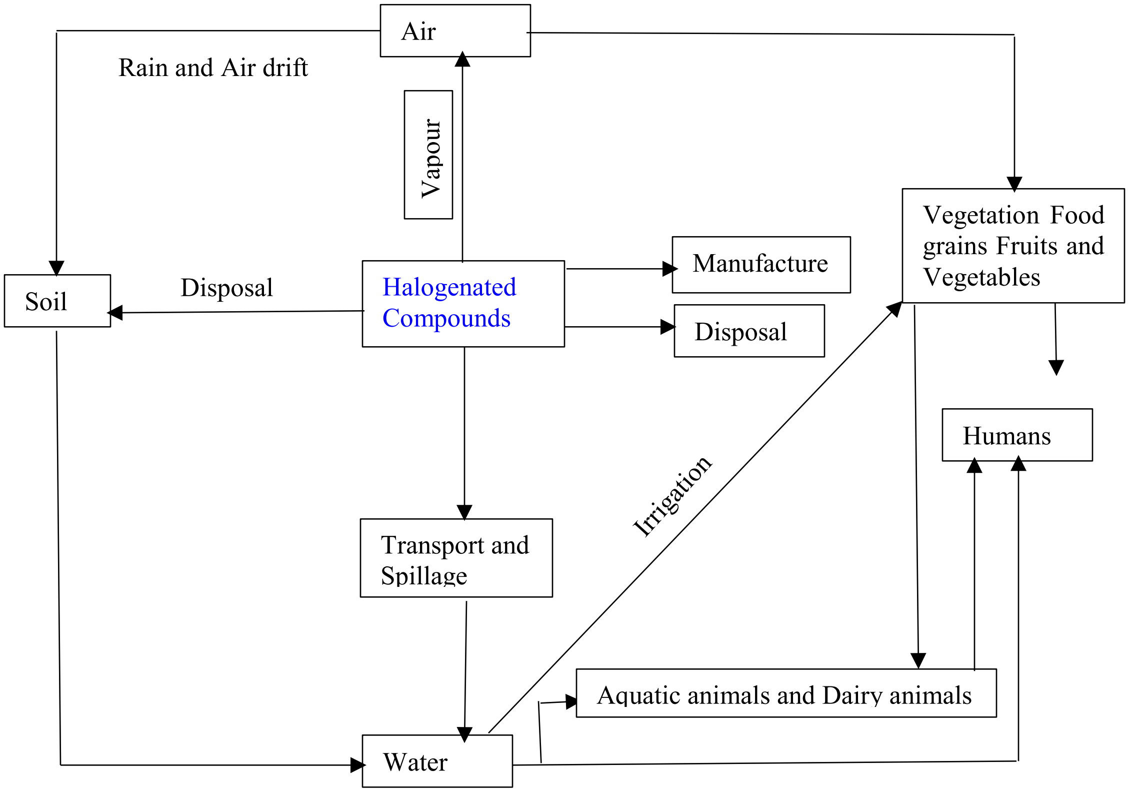


Figure 1.2. Adopted schematic depiction of halogenated chemicals circulation in the environment through the food chain.[23]

energy and less time, the design and construction of suitable installations is very difficult and complex, as the selection of electrodes and solvents. On the other hand, photocatalytic methods have been claimed to be relatively simple, cost effective and greener techniques if the suitable "photocatalyst" can be found.[23-26]

There have been reports on the photodecomposition of chlorinated organic pollutants using UV/H_2O_2 where about 100% degradation/removal of the pollutants has been claimed. Several reports have claimed efficient photo-removal of toxins such as CCl_4, $CHCl_3$, trichlorophenol (TCP) and pentachlorophenol (PCP) using H_2O_2 activated by UV light.[23] Possible drawbacks of this method is that the degradation of the pollutants can yield new toxic species as intermediates or products. In addition, hard UV light is expensive and very large amounts of costly peroxide are required. A very large number of studies have documented the use of oxidation processes based on the Fenton (Fe^{2+} + H_2O_2) and photo-Fenton reactions, as well as utilization of semiconducting oxide particles dispersed in water for remediation of chlorinated compounds.[23,33,34,41-44] The semiconductor particles were either pure or doped, with TiO_2 being the most extensively used "photocatalyst." Although numerous claims have been made that such remediation procedures are fast, cost effective and efficient, no successful large-scale utilization of these methods is known. In the case of the Fenton-based processes the cost of the peroxide has been a detrimental factor for treatment of large volumes of contaminated water. Another disadvantage of oxidations is that they are quite slow, as they usually generate harmful toxic byproducts that take a long time to completely degrade. In the case of TiO_2 systems keeping the particles suspended is not always easy and subsequent separation of them from the treated solutions can be also problematic.

Another area of interest, is the realization of self-decontaminating materials for chemical & biological protective clothing.[45-47] The idea is to creative protective barriers in garments through incorporation into fabrics of reactive compounds. or filters, films, membranes and fibers that inhibit diffusion of toxins or microorganisms. Current military protective garments include carbon black particles that immobilize toxins and pathogens. This method provides excellent protection but over a limited time only (until the C particles become saturated with adsorbed material), and the users can be subjected to heat problems under continuous use. Utilization of SPRs systems for degradation of pollutants is a relatively new approach that can be promising since these materials may be modulated into different forms useful for a variety of applications. For instance, incorporation of light-sensitive polymers into garments seems straightforward, as macromolecular materials can frequently be cross-linked to fabrics.

The polymeric system investigated in this dissertation exhibits a number of positive features for the treatment of water contaminated with halogenated organic pollutants. Initially, the investigation was carried out using aqueous solutions with the aim to figure out the basic photochemicall properties and reaction efficiency of the selected photosensitive SPR system. Further goals involved elucidation of the reaction mechanism and the scope of the photoreactions including a survey of chemicals that can be transformed with the polymeric system. For instance, utilization of thin films of the polymeric system indicated that the solid materials exhibit a potentially interesting self-decontaminating ability since they photogenerate hydrogen peroxide, which can inactivate toxins and pathogens.[21]

The selected polymeric system contains benzophenone (BP) moieties, which are excited upon illumination with UV light.[18] Excitation of the BP carbonyl group induces a (n → π*) electronic transition that yields a triplet excited state, $^3(BP)^*$, through a 100% efficient intersystem crossing. Presented in Figure 1.3 is a detailed mechanism of the BP excitation process followed by formation of a α-hydroxy radical of the ketone via H-atom abstraction from a neighboring donor molecule. In the presence of oxygen, the BP α-hydroxy radical can reduce O_2 and produce a superoxide radical ($O_2^{\bullet-}$), or the protonated form (the hydroperoxyl radical, $HO_2^{\bullet}$). These species disproportionate forming H_2O_2,, which can oxidize a variety of pollutants. Hydrogen peroxide is used as a biocide for disinfection, sterilization, and antisepsis, and generation of H_2O_2 via O_2 reduction was demonstrated to occur when a polymer containing BP groups was illuminated in the presence of air.[21] Subsequent (unpublished) work from our lab has shown that incorporation of such a polyketone into fabrics can be accomplished via polymer cross-linking, forming the basis for simple self-cleaning materials. A somewhat similar strategy for achieving systems with those properties has been recently presented and involves chemical bonding of BP molecules to fabric fibers.[45] Instead of focusing on the oxidizing properties of systems that generate H_2O_2, the present dissertation is centered on the reducing characteristics of macromolecular materials able to form α-hydroxy radicals with light.

1.4 Benzophenone as a photosensitizer:

The presence of a carbonyl group in benzophenone provides this molecule with the ability to function as a chromophore. Furthermore, BP can also act, as a highly efficient photosensitizer, and a numerous photochemical reactions initiated by this molecule have been extensively studied.[48-51] Excitation of the BP ground state, (S_0) to the first singlet excited state, (S_1) occurs as the carbonyl group absorbs photons of $250 \leq \lambda \leq 380$ nm. The excited BP singlet state (S_1) promptly undergoes intersystem crossing to yield the lowest energy BP triplet state, T_1.[51,52] As indicated in Figure 1.3, the T_1 BP state behaves somewhat as a di-radical, prone to undergo H-atom abstraction. Such reaction proceeds efficiently if a H-atom donor is present in the system yielding an α-hydroxy (benzophenyl ketyl or BPK), radical of benzophenone. BPK radicals are highly reactive is an reducing species with a half-life in solution of about 10^{-8} seconds.[52,53]

Aliphatic hydrocarbons containing hydrogen atoms at the alpha position an the electron donating heteroatoms (such as O, N or S) are the most common H-atom donors, and isopropanol is the most studied compound with donating abilities.[54,55]

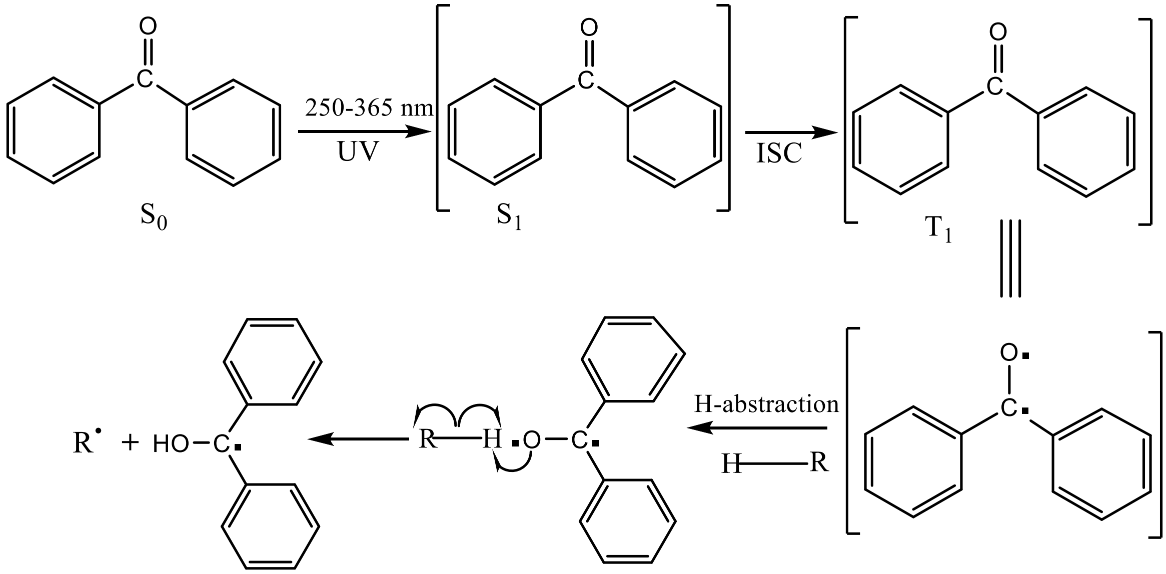


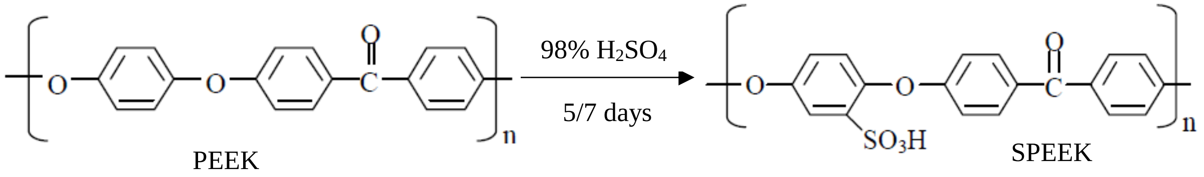
Figure 1.3. Photoreaction of benzophenone.

In the case of benzophenone derivatives, their reactivity depends largely upon the nature of the substituent groups attached to the aromatic rings and also on and solvent properties. For unsubstituted BP the triplet excited state of lowest energy is highly reactive, while substitution with numerous functionalities lowers the energy of the triplets as well as their reactivity.[56] For instance, BP molecules with with an electron donating species (amino, dimethylamino, hydroxy, methoxy) at the meta or para positions of the aromatic ring exhibits less reactivity than the parent compund while substitution with electron withdrawing groups are more reactive.[57-59] The reactivity of benzophenone derivatives is also affected by the nature of the surrounding solvent molecules since their polarity affects the relative energies of the substituted ketones. Modified macromolecules containing BP functions in their chains have been used in this investigation for generating reducing α-hydroxyl radicals.

1.5 SPEEK/PVA reducing system

Considering the combination of benzophenone and isopropanol as a model for the efficient photogeneration of reducing α-hydroxy radicals upon illumination, researchers from our lab designed a polymer mixture (blend) that emulated the BP/$(CH_3)_2CHOH$ system. Poly(ether etherketone), PEEK, is a commercially available polymer containing BP moieties that exhibits high chemical, thermal, and mechanical stabilities.[60]

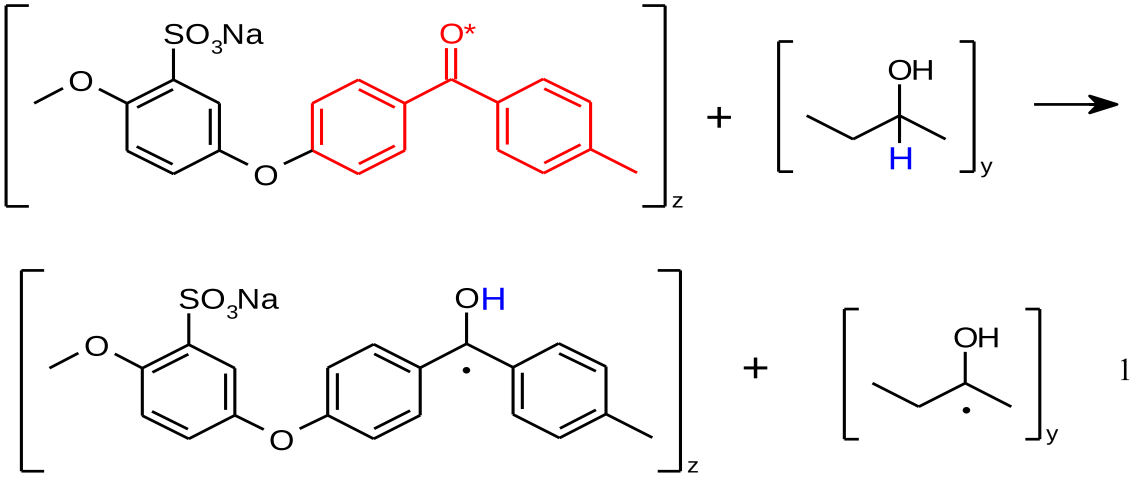
PEEK is insoluble in nearly all liquids at room temperature, whereas treatment of PEEK with concentrated H_2SO_4 produces water-soluble sulfonated poly(ether etherketone), SPEEK, according to reaction 1.1.[60]



1.1

Although SPEEK macromolecules are well-known for their high proton conductivities that are relevant to fuel cell applications, only few studies have been centered on the light-induced reactivity of these polymers.[61-63]

SPEEK was selected by researchers in our group because the presence of BP functions in the macromolecular chains was anticipated to provide the polymer with interesting photochemical properties similar to those of benzophenone. In addition, SPEEK is water-soluble, which enables the study of the photochemical properties of the polymer in the liquid state, and also allows a facile incorporation of the polyketone in films prepared via casting techniques. While SPEEK was anticipated to act as a sensitizer, poly(vinyl alcohol), PVA, was selected to function as the H-atom donor given that the structure of the monomers in this polymer is somewhat analogous to that of 2-propanol. Furthermore, the water solubility of PVA allowes the use of solution-casting methods followed by chemical crosslinking for the preparation of thin, optically transparent films that are insoluble in solvents and also sturdy yet flexible.[6] Optical and ESR results have confirmed that illumination with 350 nm photons yield an SPEEK excited state that reacts with PVA to generate a reducing α-hydroxy radical (BPK radical) together with a carbon-centered radical of PVA.[6-9]



1.2

The proposed transformation is summarized by reaction 1.2 and involves formation of a triplet excited triplet SPEEK, {^{3}SPEEK*}, upon exposure to 350 nm light. Subsequently {^{3}SPEEK*} abstracts an H-atom from PVA producing a α-hydroxy radical of the polyketone denoted as SPEEK•. The concurrently formed carbon-centered radical from PVA (PVA•) can reduce a second polymeric BP functionality, resulting in up to two SPEEK• radicals per absorbed photon. Further experiments have shown that SPEEK• is able to reduce O_2 forming H_2O_2 in air saturated aqueous SPEK/PVA solutions or in swollen cross-linked films of the polymer blends,.[21,22] The estimated oxidation potential of SPEEK• amounts to about 1.3 V, similar to that the value of the BP radical.[7] Hence, the strong reducing ability of the polyketone radical enabled this species to reduce several metal ions, such as Ag^+, Au^{3+} and Cu^{2+}, to metallic crystallites in the absence of air.[7] This means that illuminated SPEEK/PVA systems can be useful for the synthesis of metal nanoparticles. Recently, the successful reduction of CCl_4 induced by with SPEEK• have been demonstrated in aqueous solutions.[5] Presented in this dissertation are some of these results together with further data on the reductive dechlorination of some halogenated organic pollutants, such as CCl_4, $CHCl_3$, induced by photolysis of SPEEK/PVA solutions and films.

1.6 SPEEK/HCO_2^- system as a source of reducing radicals

Efficient reduction of halogenated organic compounds including chlorofluorocarbons (CFCs) have been reported earlier using illuminated suspension of titania particles also containing HCO_2^- .[64-66] Oxidation of HCO_2^- by the suspended TiO_2 particles generated $•CO_2^-$ which is an effective reducing radical that can participate as a carrier in chain dehalogenations.[64] The idea of using HCO_2^- is because the $•CO_2^-$ radical exhibits a higher reducing power, $E_0[•CO_2^-/CO_2] = 1.8$ V than that of the α-hydroxy radical from 2-propanol, $E_0[(CH_3)_2C•OH/(CH_3)_2C{=}O, H^+] = 1.4$ V.[67] The triplet excited state of BP is known to react with HCO_2^- via H-atom abstraction , to form BPK and pressumably $•CO_2^-$ radicals.[68] Hence, an analogous reaction was anticipated to take place between ^{3}(SPEEK)* and HCO_2^- ions to yield SPEEK• and $•CO_2^-$ radicals. A logical expectation was that generation of $•CO_2^-$ in SPEEK systems would facilitate the occurrence of chain processes by taking part in propagation steps or by accelerating that reduction of the halogenated compounds present in the system.[64]

In principle, the $\cdot CO_2^-$ radical can reduce a carbonyl group from SPEEK forming a second polyketone radical. Alternatively, the $\cdot CO_2^-$ radical could also participate in the reduction of the halogenated compounds if their concentrations were high enough. However, the available evidence indicated that SPEEK• is the only reactive species that reduces the halogenated compounds.

One of the purposes of the present studies was to establish the efficiency and mechanism through which halogenated organic compounds are reduced in aqueous SPEEK/HCO_2^- solutions. That initial knowledge was expected to be very useful for unraveling the processes involved during the photoreductions occurring when SPEEK/PVA films were employed as sensitizers. As mentioned before, ideal photosensitive macromolecules are only those exhibiting SRPs properties, that is, polymers able to remain unchanged during the reactions they initiate. Hence, another goal was to determine possible changes in reactivity suffered by SPEEK/PVA polymer blends during the photoreductions. If alterations were noticed, then another aim was to determine ways to restore the reactivity of the polymer blends. Finally,, the data gathered in these investigations was expected to help assessing the viability of using SPEEK/PVA films for detoxification of contaminated waters, and also the possibility of using them as reactive barriers in protective clothing.

1.7 Goals and prospects of the dissertation

The widespread presence of toxic halogenated toxic organic chemicals constitutes an environmental issue all over the world. Finding simple, cost efficient and effective techniques to solve this problem is not an easy task. Phtotochemical transformations are among the simplest, potentially cost efficient and greener approaches for remediation of the toxic chemicals. Further advantages of these methods are their ability to generate nontoxic products, and to inactivate viruses and bacteria.[23,69]

Achievement of a successful method seems to depend mainly on finding appropriate sensitizers (or "photocatalysts") able to initiate efficient the degradation processes. The photoactivity of TiO_2 and ZnO toward degradation of environmental contaminants has been investigating extensively.[69] Upon illumination with UV light, these sensitizers generate oxidizing species, including •OH radicals, that oxidize toxic chemicals. However, •OH is a very indiscriminate oxidizer that attacks all species present in the system resulting in slow oxidations.

Molecules containing carbonyl groups can generate singlet oxygen, $^1O_2$, that oxidize organic compounds and also generate $O_2^{\bullet -}$, followed by formation of H_2O_2 that is able to oxidize some toxic chemicals.[18] However, $^1O_2$ decays fast in water via energy transfer to solvent molecules and is not an effective oxidizer in aqueous systems. Ketones also produce ketyl radicals with a high quantum yields as their triplet excited states are able to abstract a H-atom from neighboring alcohol molecules.[70,71] Ketyl radicals can function as reductants toward toxic chemicals specially halogenated organic pollutants. The SPEEK/PVA belnds can mimic the radical reactions initiated by the BP/alcohol system by generating SPEEK•, which much alike ketyl radicals should be able to reduce chlorinated organic compounds.

Replacing PVA with HCO_2^- as H-atom donor may result in a better efficiency of SPEEK• formation. The reason for such assumption is that reduction of BP groups from SPEEK by PVA• (formed through reaction 1.2) is anticipated to be somewhat inefficient as this process involves motion of 2 different macromolecular species. In addition, entanglement of the polymer chains seems to have limited somewhat the reactions of the polymer radicals.[5] In contrast, higher yields of SPEEK• formation were anticipated when HCO_2^- served as H-atom donor because the resulting $\bullet CO_2^-$ is highly mobile, permitting efficient reduction of the BP functions present in SPEEK. A significant difference is that SPEEK/PVA blends can be used in the form of films, or via crosslinking them onto other solid materials such as fabrics. In contrast, combinations of SPEEK and HCO_2^- can only be employed in aqueous medium. The following reactions will represent the mechanism of forming oxidizing and reducing radicals from SPEEK/PVA or SPEEK/ HCO_2^- system.[5,21]

$$\{R'RC{=}O\}_z + h\nu \rightarrow {}^3\{R'RC{=}O\}_z^* \qquad (1.3)$$

$$^3\{R'RC{=}O\}_z^* + \{CH_2CHOH\}_y \rightarrow \{R'RC\bullet OH\}_z + \{CH_2C\bullet OH\}_y \qquad (1.4)$$

$$\{CH_2C\bullet OH\}_y + \{R'RC{=}O\}_z \rightarrow 2\{R'RC\bullet OH\}_z + \{CH_2C{=}O\}_y \qquad (1.5)$$

$$^3\{R'RC{=}O\}_z^* + HCO_2^- \rightarrow \bullet CO_2^- + \{R'RC\bullet OH\}_z \qquad (1.6)$$

$$\{R'RC\bullet OH\}_z/\{CH_2C\bullet OH\}_y + O_2 \rightarrow \{R'RC(OH)OO\bullet\}_z/\{CH_2C(OH)OO\bullet\}_y \qquad (1.7)$$

$$\{R'RC(OH)OO\bullet\}_z/\{CH_2C(OH)OO\bullet\}_y \rightarrow \{R'RC = O\}_z/\{CH_2C = O\}_y + HO_2\bullet \qquad (1.8)$$

$$HO_2\bullet \rightleftharpoons H^+ + \bullet O_2^- \qquad (1.9)$$

$$HO_2\bullet + H^+ + \bullet O_2^- \rightarrow H_2O_2 + O_2 \qquad (1.10)$$

where $\{R'RC{=}O\}_z$ represents SPEEK, $\{CH_2CHOH\}_y$ corresponds to PVA, $^3\{R'RC{=}O\}_z^*$ represents $\{^3SPEEK^*\}$, $\{R'RC\bullet OH\}_z$ corresponds to SPEEK• and $\{CH_2C{=}O\}_y$ represents an oxidized PVA molecule.

An important hurdle in the photogeneration of SPEEK• is the presence of even small amounts of O_2 as oxygen is an efficient scavenger of reducing radicals. Interestingly and unlike the case of the BP excited triplet state, quenching of $\{^3SPEEK^*\}$ by O_2 was not found to be important.[21,22] Other quenchers that could exert an effect on the efficiency of some photorecations were H^+, OH^- and Cl^- ions generated as reaction products. As anticipated, the presence of O_2 partially inhibited the photoreactions which were, therefore, studied initially in the absence of oxygen. While air-free systems were useful to establish reduction mechanisms, they were not suitable for studies of barrier properties and potential practical applications. Nevertheless, the mechanistic knowledge gained in air-free systems was crucial for enabling to define reaction conditions that allowed investigations relevant to potential applications.

One of the expected challenges was to find suitable methods for studying reactions initiated by SPEEK/PVA films. SPEEK/PVA solutions required a high PVA concentration (0.36M) to ensure an efficient H-atom abstraction (step 1.4) in order to generate enough SPEEK• so as to obtain high reduction efficiencies. However, using solutions of high PVA concentrations hinders the diffusion of the reactants. Hence, PVA was replaced with HCO_2^- ions, which acts as a H-atom donor as like PVA, resulting in higher rate of SPEEK• formation and increased reduction efficiencies. Given that incorporation of HCO_2^- ions into the films was not possible, the performance of the solid sensitizers was explored in solutions containing formate ions as an additional source of H-atom donors. SPEEK/PVA films swell in water because of the presence of the polyol in them.[21, 72] Although the amount of swelling is a function of film dimensions, incorporation of water in the solid matrices was not a factor that controlled the photoreductions. Surprisingly, the reduction efficiency of the films was a function of their thicknesses, suggesting that chain processes were able to propagate from films into solutions that contained formate ions.

Many studies have been reported on reduction of halogenated organic pollutants using various sensitizers.[23-37] However, a thorough review of the literature revealed that no investigations on reduction of halogenated organic pollutants have been carried out using SPRs material was found to be able to photogenerate reducing radicals either in solutions of films.[7-10,23-29] Therefore, this investigation has established a new avenue for the potential remediation of halogenated pollutants in the environment via chain reactions, as well as for exploration of novel materials as light-activated barriers in protective clothings.

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Chapter II

Photoreduction of $CHCl_3$ in Aqueous SPEEK/HCO_2^- System Involving Free Radicals

2.1 Introduction

Reductions of halogenated organic compounds offer a straightforward route for the efficient eliminations of halide ions. These reactions are appealing for highly halogenated compounds, which exhibit significant resistance to oxidations. In fact, reductive dechlorinations are considered as possible means to treat underground contaminations involving stable and persistent chlorinated fluids.[1] A typical example is CCl_4 and mechanistic investigations have shown that reduction of this chlorocarbon by α-hydroxy radicals of simple alcohols or $\bullet CO_2^-$ produced $CHCl_3$ via efficient chain reactions.[2-8] Since $CHCl_3$ is a toxic and recurrent contaminant of groundwater,[9,10] efforts have also been made to identify procedures for the degradation of this chemical. Photochemical strategies have been explored in efforts to drive the degradations using light as the energy source. However, photoreductions of $CHCl_3$ have been investigated mainly in organic solvents.[11,12] In contrast, studies in aqueous systems have been centered on $CHCl_3$ oxidations using dispersions of semiconducting or clay particles as sensitizers (or "photocatalysts").[13,14] Oxidations have also been performed in liquid chloroform containing heterogeneous as well as homogeneous sensitizers in efforts to improve the efficiencies of the photoreactions.[15,16]

Although photosensitive macromolecules have been studied extensively, only few of them are known to induce reductive dehalogenations. Photochemical dechlorinations were achieved with sensitizers such as sodium poly(styrenesulfonate), PSS, containing carbazol chromophores,[17,18] and also using poly(vinylferrocene) films.[19] Recently, the reductive dechlorination of CCl_4 was photoinitiated in air-free aqueous solutions of the sodium salt of sulfonated poly(ether etherketone), SPEEK, that also contained poly(vinyl alcohol), PVA, or HCO_2H/HCO_2^- buffers.[20] The conceptual basis for selecting SPEEK/PVA mixtures (or blends) was the well-studied system comprising of benzophenone (BP or $(Ph)_2C{=}O$) and 2-propanol.[21] In the macromolecular systems, SPEEK served as the sensitizer whereas PVA acted as a H-atom donor. Photolysis of SPEEK/PVA blends in solutions, or as solid films, produced α-hydroxy radicals of the polyketone (SPEEK•), and these species acted as reducing agents that transformed several metal ions to metallic crystallites as well as oxygen to H_2O_2.[22-24]

CCl_4 was reduced via radical chain reductions in SPEEK solutions, but higher efficiencies occurred when HCO_2^- ions served as H-atom donors instead of PVA.[20] Photolysis of benzophenone in the presence of formate was proposed to yield BP α-hydroxy radicals and $\bullet CO_2^-$.[25] Thus, the faster dechlorination of CCl_4 in SPEEK solutions containing HCO_2^- was attributed to participation of $\bullet CO_2^-$ in the transformation. Such interpretation seemed consistent with the selective and efficient reductions of CCl_3F (CFC 11) and CCl_2FCClF_2 (CFC 113) occurring in systems able to photogenerate $\bullet CO_2^-$ as a reductant.[26,27] Optimum experimental conditions in the SPEEK system included utilization of CCl_4-saturated solutions with high $[HCO_2^-]$ and ensured efficient conversions of carbon tetrachloride to $CHCl_3$.[20] Although the chosen experimental conditions favored the CCl_4 reduction over the dechlorination of $CHCl_3$, the resulting selectivity may have also reflected a rather inefficient chloroform phototransformation. In fact, the chain dechlorinations of CCl_4 were 6 - 10 times more efficient than the reductions experienced by $CHCl_3$ when $(CH_3)_2C\bullet OH$ was employed as a reductant.[3,5,7,8]

The differences in reactivity of the two halomethanes can be rationalized employing available thermodynamic data. Reduction of CCl_4 occurs with $E°[CCl_4/\bullet CCl_3, Cl^-)] = -0.23$ V,[28] whereas the potential for $CHCl_3$ has been estimated at about -0.9 V in ethanol with a similar value anticipated for H_2O as the solvent.[29] Considering that E°[$(CH_3)_2C{\bullet}OH/(CH_3)_2C{=}O, H^+$] = 1.4 V,[30] the driving force for the CCl_4 reduction by the α-hydroxy radical is about twice the value calculated in the $CHCl_3$ case. A considerable driving force is also expected for the $CHCl_3$ photoreduction in SPEEK/HCO_2^- solutions since the estimated oxidation potential of SPEEK• was ≈ 1.3 V,[22] whereas E°[$\bullet CO_2^-/CO_2$] = 1.9 V.[30] Testing the feasibility of photodehalogenating chloroform with SPEEK systems seems worth pursuing because the CCl_4 reduction yielded $CHCl_3$.[20] Findings from these tests were also expected to help assessing the viability of SPEEK-based films as protective barriers against toxic compounds.[31] In fact, solution studies on the H_2O_2 photogeneration provided mechanistic insight about the reactions occurring in films, thereby bypassing experimental hurdles associated with solid matrices.[24] Presented in this report are kinetic results obtained with $CHCl_3$ under conditions identified previously to optimize the CCl_4 photoreduction.[20] Under such conditions, the photolysis of aqueous SPEEK solutions containing HCO_2^- ions was found to induce dechlorination of $CHCl_3$ via a chain process.

2.2 Experimental Section

Samples of poly(ether etherketone), PEEK, were received as gifts from Evonik (VESTAKEEP L4000G film and VESTAKEEP L4000P powder, average molar mass of $M_n = 5 \times 10^4$ g mol^{-1}) and Solvay (Ketaspire KT-880 FP powder, $M_n = 4 \times 10^4$ g mol^{-1}). Powders of these materials were reacted with H_2SO_4 to yield the acid from of SPEEK, which was subsequently converted into the Na^+ salt according to a previously described method.[31] $CHCl_3$ was from Macron, all other chemicals including PVA (99 % hydrolyzed, $M_n = 8.9\text{-}9.8 \times 10^4$ g mol^{-1}) were purchased from Sigma-Aldrich or Fisher. Aqueous solutions were prepared with water purified using a Millipore Milli-Q Biocel system; they contained 0.018 M SPEEK (per monomer units) together with buffers consisting of [HCO_2H] + [HCO_2^-] = 0.36 M, where $NaCO_2H$ also maintained a high ionic strength. When PVA was used instead of the formate buffers, the solutions contained 0.36 M of the polyol (per monomer units) and 0.1 M $NaClO_4$ as an inert electrolyte. All experiments employed the Na^+ salt of sulfonated PEEK referred to as SPEEK; procedures for the preparation of the polymer solutions and a description of the glass photoreactor used in illumination experiments have been provided before.[20]

Prior to photolysis, the solutions were bubbled with Ar for 20 min under continuous stirring in sealed photochemical reactors. Samples of the as-received $CHCl_3$ were washed several times with H_2O to remove the stabilizer and the resulting liquid was degassed as indicated previously,[26] followed by injecting 2 mL (by means of gas-tight syringes) into a sealed photoreactor containing 80 mL of the SPEEK solutions saturated with Ar. Given that the solubility of $CHCl_3$ in water is only 6.6 x 10^{-2} M (or 0.43 mL of chloroform in 80 mL of H_2O at 20 ^{0}C),[32] a large fraction of the injected chloroform remained phase-separated from the aqueous phase. Illuminations were conducted by means of 350 (± 15 nm) photons generated from a Rayonet 100 source; the temperature inside the cavity of the circular illuminator was 29 °C. Variations of light intensity were achieved by changing the number of lamps present in the illuminator. Unless otherwise stated all other determinations were performed at room temperature of 22 °C.

Description of the photolytic procedures, including light intensity (I_0) determination, as well as of analytical methods employed for product identification and quantification were provided previously.[20] All photochemical experiments were performed under continuous stirring and, at least, twice. Illuminations conducted with air-saturated solutions yielded the same results when the photochemical reactor was open or sealed with septa. GC-MS analysis of liquid and headspace samples was performed on solutions photolyzed extensively. 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: 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 min of Ar-saturated SPEEK solutions in EPR tubes. Photolysis of the tubes occurred inside 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

Blank experiments performed in the absence of light, $CHCl_3$, SPEEK, or of H-atom donors failed to yield products associated with a reduction process. The lack of Cl^- photogeneration in the absence of PVA or formate buffers was significant given that chloromethane solvents can quench the fluorescence of ketones generating HCl and radicals.[33] In those cases association of an excited state of the ketone with a solvent molecule produced an exciplex. Fluorescence quenching originated from a reactive process since the exciplex subsequently decayed to the observed products. Figure 2.1 shows that Cl^- ions were formed upon exposure to light of SPEEK solutions containing PVA or formate buffers, indicating that H-atom donors were required to induce reduction of $CHCl_3$. Obviously, formation of exciplexes involving excited SPEEK and $CHCl_3$ was not feasible presumably because association between highly charged polyelectrolyte chains and chloroform molecules was energetically unfavorable.

Plots depicting the amount of Cl^- produced as a function of illumination time, such as those presented in Figure 2.1, exhibited a short and somewhat irreproducible initial step. This preliminary process is known as the induction period during which the reduction is frequently slow but bursts of Cl^- formation occur occasionally. Analogous observations were made in photoreduction experiments with CCl_4, CCl_3F and CCl_2FCClF_2.[20,26,27] Induction periods typically originate from traces of air remaining in the solutions after degassing because small amounts of O_2 can scavenge some of the photogenerated radicals and interfere with the reduction process. While most of the induction periods observed during the $CHCl_3$ reduction in degassed SPEEK solutions lasting 1-2 min, their length increased for slow photoreactions and also when irradiations were conducted at low I_0 values or in the presence of higher $[O_2]$, as will be shown later. Considering that only minor and sometimes erratic $[Cl^-]$ changes occurred during the induction periods, further analysis of these results was not warranted.

Immediately after the induction period $[Cl^-]$ increased linearly for about 7-10 min of illumination, followed by a non-linear rise thereafter. The slope of this linear process served to derive the reaction rate, $r(Cl^-) = d[Cl^-]/dt$, which was the basis for the subsequent calculation of the quantum yield of chloride ion formation, $\phi(Cl^-) = r(Cl^-)/I_0$. Such evaluations resulted in systematic $\phi(Cl^-)$ deviations of about 20% that were similar to those determined for the photoreductions of CCl_4 and O_2.[20,24] They probably originated from the rather heterogeneous nature of the polymer systems, where association of the polyelectrolyte chains was facilitated by their high concentration.[22] Another contributor to the deviations of $\phi(Cl^-)$ was scattering of light induced by small $CHCl_3$ droplets formed upon stirring the solutions containing excess halomethane. Given that the fraction of scattered photons was not accounted for, the derived $\phi(Cl^-)$ values corresponded only to lower limits of the quantum efficiencies of Cl^- formation.

Photoreactions were conducted under conditions identified previously to yield the most efficient reductions of CCl_4, namely: 0.018 M of the polymeric photosensitizer and 0.36 M of the formate buffer or PVA.[20] Illustrated in Figure 1 are the evolutions of $[Cl^-]$ as a function of irradiation time for solutions at pH = 7.3 containing SPEEK derived from the Evonik precursor and either of the H-atom donors. A fast photodechlorination took place in the presence of the formate buffer with $\phi(Cl^-)$ = 0.2 whereas the quantum yield was only 0.006 when PVA served as H-atom donor. Comparison of the photoreduction efficiencies in the presence of the formate buffer and PVA resulted in a $\phi(Cl^-)$ ratio of 33. The CCl_4 photoreduction yielded a very similar $\phi(Cl^-)$ ratio of 55 since efficiencies of 1.37 and 0.025 were determined for solutions with HCO_2^- and the polyol, respectively.[20] Further analysis of these results showed that the CCl_4 photoreduction in formate solutions was between 7-11 times more efficient than that of $CHCl_3$. An analogous ratio of reaction efficiency, 6 to 10, was determined for the chain reductions of CCl_4 and $CHCl_3$ induced by $(CH_3)_2C{\bullet}OH$.[3,5,7,8] Consequently, the analogies found between the radical reductions of $CHCl_3$ and CCl_4 suggested that the photodehalogenation of chloroform initiated by SPEEK also proceeded via a chain transformation.

SPEEK prepared using either film or powder PEEK samples from Evonik resulted in identical rates of $CHCl_3$ photodehalogenation. Photolysis of these sensitizers in air-free solutions containing PVA or HCO_2^- yielded a small amount of polyketone radicals that decayed via a slow second-order process.[20,22,24] Optical detection of the photogenerated SPEEK• was feasible because this species exhibited an optical signal with a wavelength of maximum absorbance (λ_{max}) at 565 nm that persisted for several min. The radical signal was not observed in the presence of $CHCl_3$, indicating that SPEEK• reacted with chloroform in a shorter time scale. Several experiments were conducted with SPEEK made from the Solvay precursor; photolysis in the presence of HCO_2^- but without $CHCl_3$ failed to yield the SPEEK• optical signal. However, the data of Figure 2.1 demonstrates that a faster reduction of $CHCl_3$, with $\phi(Cl^-)$ = 0.6, took place upon illumination of this polymeric sensitizer. These results mean that although SPEEK• generated by the Solvay polymer decayed fast in the absence of $CHCl_3$, this radical was still able to reduce the halomethane with an improved efficiency. Obviously, the polymer radicals generated via photolysis of the Solvay-derived polyketone were at least 3 times more reactive than those produced using the sensitizer made from the Evonik precursor.

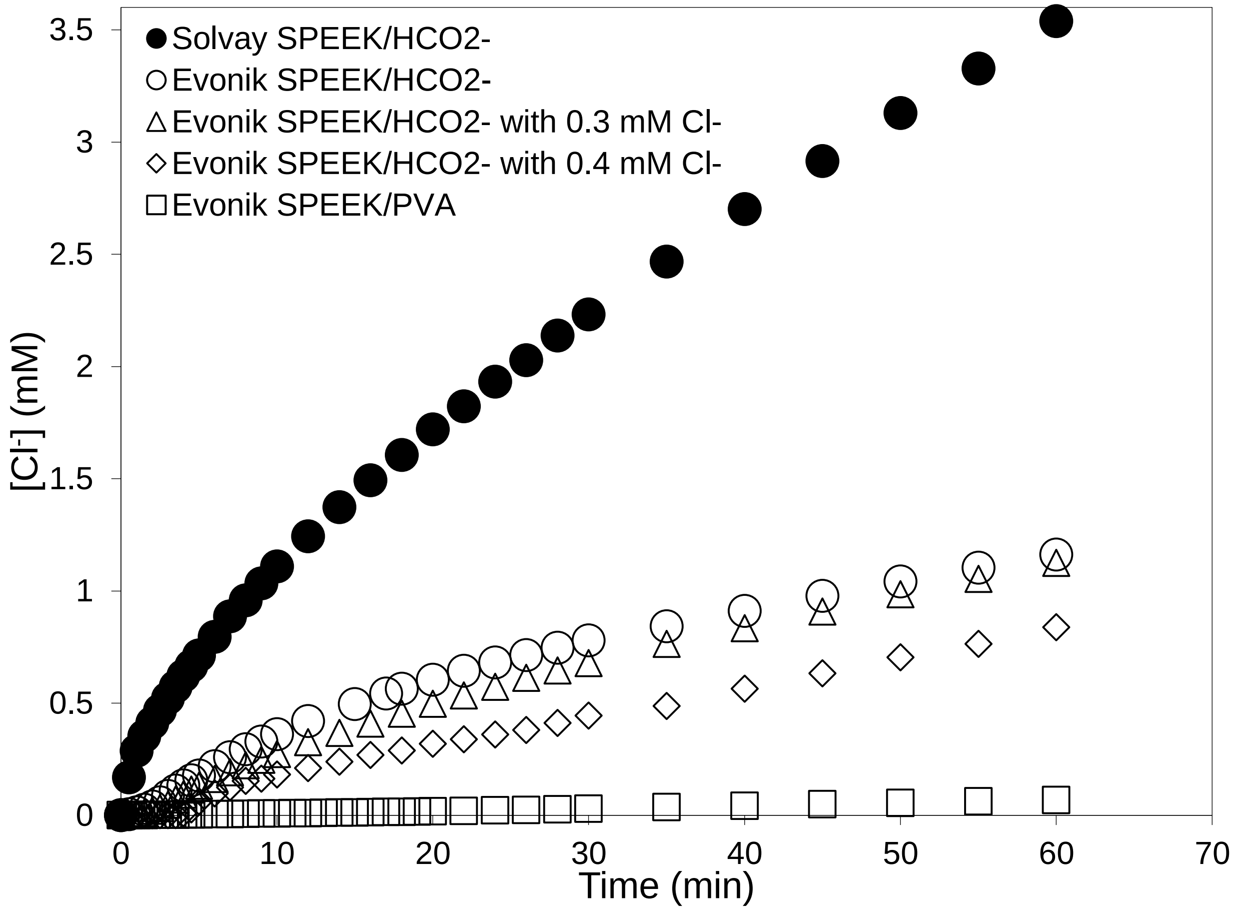

Figure 2.1. Formation of chloride ions during photolysis of degassed solutions of 0.018 M SPEEK from Evonik PEEK containing 2 mL $CHCl_3$ at pH = 7.3 with (□) 0.36 M PVA and 0.1 M $NaClO_4$ ($I_0 = 3.8 \times 10^{-6}$ M (hν)/s), or 0.36 M formate buffer and initial [Cl^-]: (○) 0 mM ($I_0 = 3.8 \times 10^{-6}$ M (hν)/s), (△) 0.3 mM and (◇) 0.4 mM ($I_0 = 2.2 \times 10^{-6}$ M (hν)/s). (●) Air-free solution containing 0.018 M SPEEK from Solvay PEEK, 0.36 M formate buffer, 2 mL $CHCl_3$ at pH = 7.3 with $I_0 = 2.2 \times 10^{-6}$ M (hν)/s.

The kinetic data from numerous $CHCl_3$ reduction experiments revealed that Cl^- formation deviated from linearity once $[Cl^-]$ reached between 0.2-0.4 mM. Chloride ions are moderate quenchers of the triplet state of BP with a quenching rate constant of $k_q = 2.2 \times 10^5$ M^{-1} s^{-1},[34] and a plausible explanation for the nonlinear growth of $[Cl^-]$ involved an analogous quenching occurring for excited SPEEK. To test this possibility, illuminations were carried out with solutions that initially contained chloride ions. Included in Figure 2.1 are the results obtained with 0.3 and 0.4 mM Cl^-. Introduction of increasing halide ion concentrations decreased the length of the linear $[Cl^-]$ change without altering the $\phi(Cl^-)$ value. However, more significant changes occurred at longer irradiation times where solutions with added $[Cl^-]$ above 0.2 mM exhibited an increasing retardation of the photoreaction. Furthermore, an inhibiting Cl^- effect intensified at higher initial halide ion concentrations. In contrast, the photoreduction of CCl_4 yielded linear increases in $[Cl^-]$ over long irradiation periods.[20] Both sets of results can be reconciled if quenching of excited SPEEK by Cl^- was not an efficient process. For CCl_4 quenching was not perceptible given that chain propagation took place efficiently during the photoreduction of this compound. On the other hand, quenching became increasingly significant for $CHCl_3$ because chain propagation was less effective. Evidence supporting such interpretation will be presented later in conjunction with post-irradiation results.

Presented in Figure 2.2 is the evolution of the rate of Cl^- formation correlated with the change in light intensity indicating that the reaction speed increased only slightly (by ~ 2) upon a 4.5 fold increase in I_0. In analogy to the chain photoreduction of CCl_4,[20] $\phi(Cl^-)$ decreased with increasing light intensity from 0.3 to 0.14 when I_0 varied from 8.2×10^{-7} to 3.8×10^{-6} M(hν)/s. Included in the inset is a plot showing that the $\phi(Cl^-)$ variation was nearly linear with $I_0^{-1/2}$. Similar dependencies were noticed for the photoreductions of CCl_4, CCl_3F and CCl_2FCClF_2,[5,20,26,27] and are typical of what is seen in chain transformations involving radical-radical termination reactions.[35] As for CFC 113,[27] the $CHCl_3$ dehalogenation was characterized by low quantum efficiencies at all photon fluxes. Unlike the case of CCl_4, where $\phi(Cl^-) > 1$ at low I_0 values,[20] no significant advantage resulted from using small intensities of light. Hence, most experiments with $CHCl_3$ employed moderate light intensities thereby avoiding the long induction periods and slow dehalogenations typically encountered at low I_0.

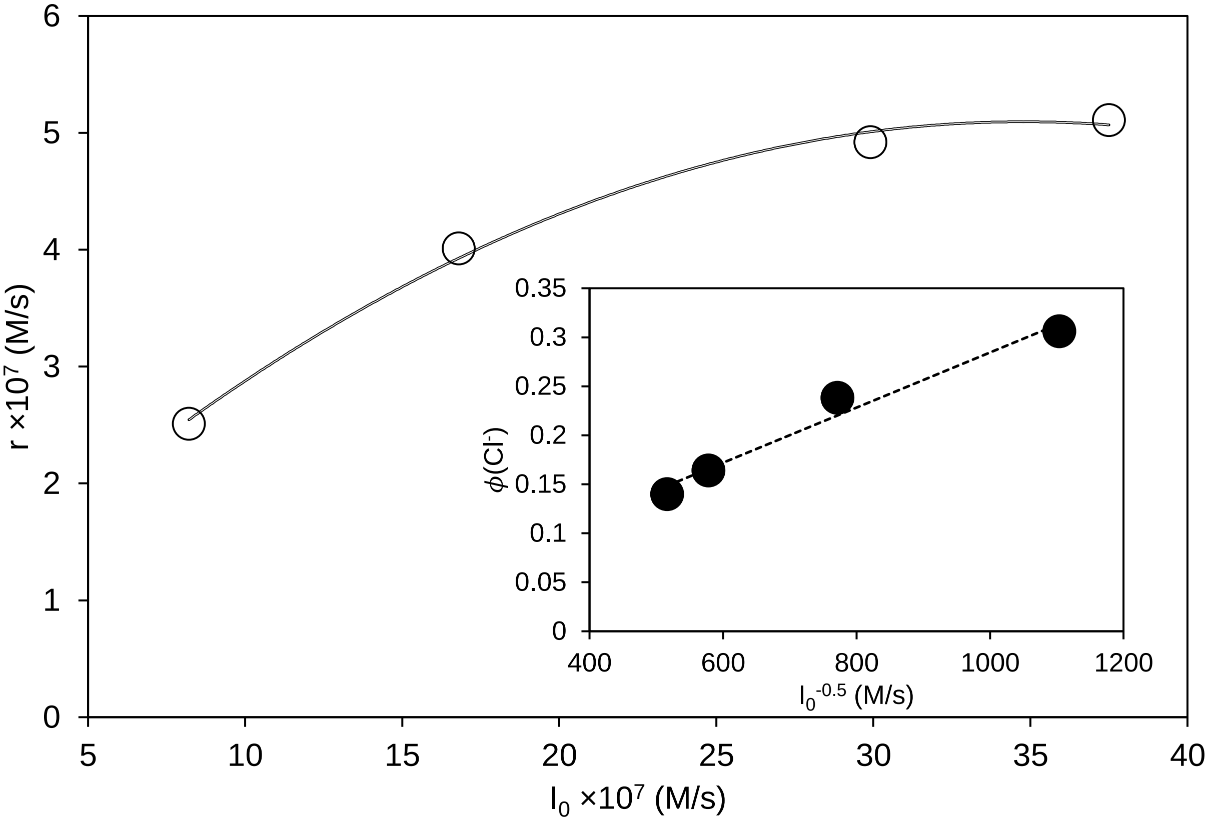

Figure 2.2. Dependence of the photoreduction rate on light intensity for degassed solutions with 0.018 M SPEEK, 0.36 M formate buffer at pH = 7 containing 2 mL $CHCl_3$. Inset depicts the near linear dependence of $ø(Cl^-)$ with the inverse of the square root of I_0.

Illustrated in Figure 2.3 is the variation of $\phi(Cl^-)$ as a function of the volume of chloroform added to the aqueous SPEEK solutions. The photoreaction became faster with increasing chloromethane volume, followed by a less pronounced rise in $\phi(Cl^-)$ above the $CHCl_3$ solubility limit of 6.6×10^{-2} M. As shown in the inset, $\phi(Cl^-)$ increased linearly with chloroform concentration in the range where the halomethane was soluble; under these conditions the photoreaction obeyed a first-order rate law with respect to $[CHCl_3]$. The additional $\phi(Cl^-)$ increases noticed above the solubility limit similar to those observed when CFC 11 was photoreduced,[36] implying that the phase-separated $CHCl_3$ also contributed to the reduction process. Transformations of reactants located in different phases have been explained in terms of a model that envisions partially miscible liquids as separated by a thin interfacial region.[37] In analogy to the photodechlorination of CCl_3F,[36] the model implies that the higher $\phi(Cl^-)$ values found above the $CHCl_3$ solubility limit resulted from additional processes made possible by the thin interfacial film located between the aqueous and organic phases.

According to this model, a gradient of $[CHCl_3]$ existed across the film with the highest concentration (12.2 M) at the organic phase and the lowest (the H_2O solubility limit) at the border with the aqueous solution.[37] The interfacial region aided the photoreduction via enabling a fast $CHCl_3$ transport between organic and aqueous phases. This permitted an efficient replenishment of consumed chloromethane, ensuring that $[CHCl_3]$ remained at the solubility limit in H_2O. While migration of $\bullet CO_2^-$ and SPEEK• into the $CHCl_3$ phase seems unrealistic, the reducing radicals migrated into the water-containing interfacial film where they reduced $CHCl_3$. The higher $[CHCl_3]$ present in the film opened an additional fast reduction channel, which operated in conjunction with the $CHCl_3$ reduction that took place in the aqueous solution. Because each $CHCl_3$ droplet possessed a thin film, stirring fragmented the liquid chloroform into small droplets thereby increased the total interfacial region. Adding larger $CHCl_3$ volumes induced further droplet formation, which explains the data of Figure 2.3 above the solubility limit. According to these results the interfacial reduction contributed with about 24% of the total transformation at the highest $CHCl_3$ volume added, but this is probably a lower limit as an unknown fraction of I_0 was lost due of light scattering induced by the droplets.

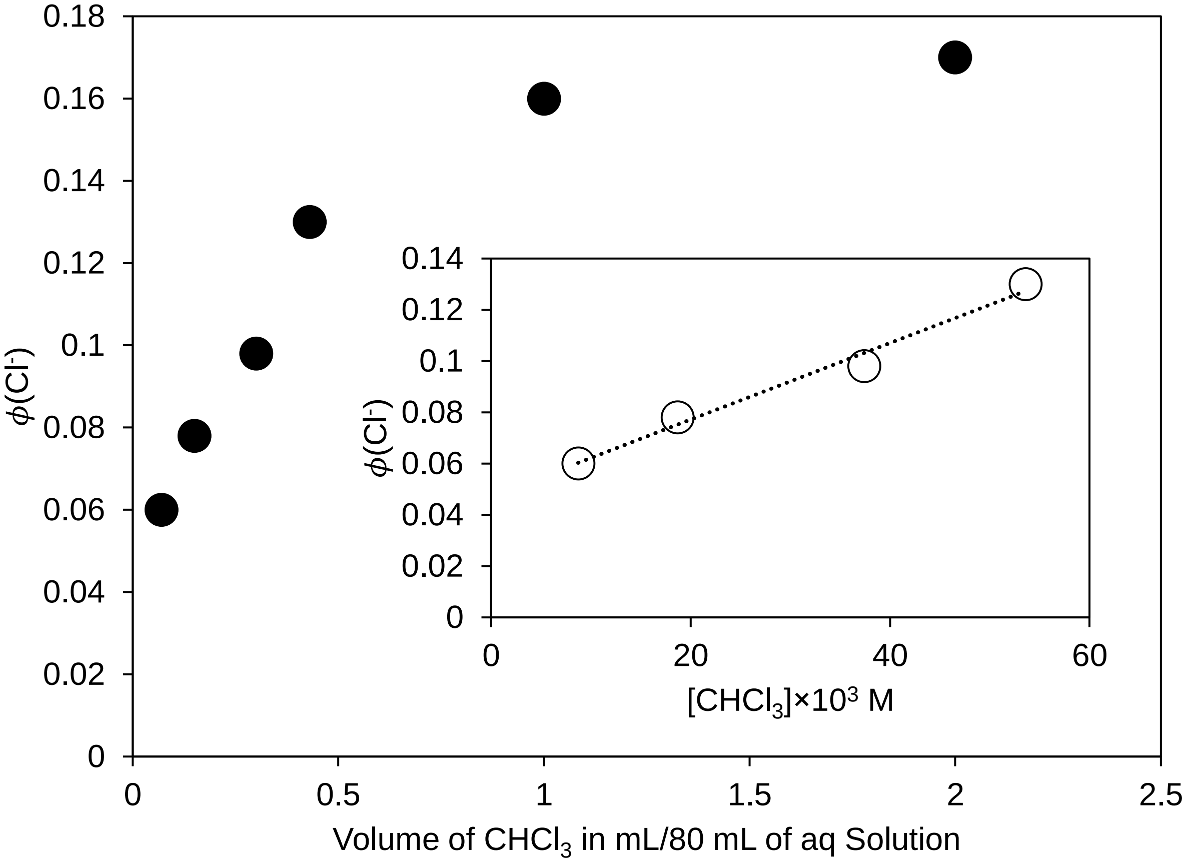

Figure 2.3. Evolution of ø(Cl^-) as a function of $CHCl_3$ volume added to degassed solutions with 0.018 M SPEEK, 0.36 M formate buffer at pH = 7.3 with $I_0 = 3.8 \times 10^{-6}$ M (hν)/s. The inset shows the linear variation of ø(Cl^-) with [$CHCl_3$] below the solubility limit (6.6×10^{-2} M) in H_2O.

Displayed in Figure 2.4 is the evolution of $\phi(Cl^-)$ with decreasing acidity in the range of $4 \leq pH \leq 9$; experiments in highly basic solutions were not conducted since OH^- can interfere with the potentiometric Cl^- determinations. Starting from a very low yield at pH = 4, the reaction efficiency increased sharply as the acidity decreased. Such behavior is explained in terms of the photoprocess leading to SPEEK•, which is akin to the formation of the reducing α-hydroxy radical of BP, $(Ph)_2C•OH$, by the photogenerated triplet excited state ($^3BP^*$) of benzophenone.[21] H_3O^+ quench $^3BP^*$ via energy transfer ($k_q = 7 \times 10^8$ M^{-1} s^{-1}), thereby inhibiting radical formation.[38] An analogous quenching of the SPEEK triplet excited state by hydronium ions explained the low $\phi(Cl^-)$ value at pH = 4, and also the swift increase in efficiency with decreasing $[H_3O^+]$. This rationalization was support by preliminary examinations of the broad SPEEK phosphorescence centered at $\lambda_{max} = 470$ nm that resembled the emission of poly(p-vinylbenzophenone), a compound frequently used as a model of polymeric benzophenones.[39] Indeed, the SPEEK phosphorescence at pH = 3.5 decreased by about 30% as compared with the intensity determined in neutral or weakly basic solutions.

The large increase of $\phi(Cl^-)$ with declining $[H_3O^+]$ culminated with a maximum of 0.2 at pH = 7.3, followed by a drop in efficiency thereafter. Earlier studies have shown that the yield of photogenerated SPEEK• increased smoothly with decreasing acidity, remaining nearly constant in neutral solutions before dropping at pH > 8.[20,24] Hence, the sharp $\phi(Cl^-)$ increase and sudden drop shown in Figure 2.4 was not due to changes in the SPEEK• yield. Quenching of the SPEEK excited state by hydroxide ions only partially contributed the $\phi(Cl^-)$ decline at pH > 7.3 as energy transfer from $^3BP^*$ to OH^- takes place with a low k value, 5×10^6 M^{-1} s^{-1}.[34] An important observation is that the overall trend of Figure 2.4, including a $\phi(Cl^-)$ maximum at pH = 7.3, matched very closely the dependence of reaction efficiency on $[H_3O^+]$ determined for the CCl_4 chain reduction.[20] Based on such findings one obvious conclusion was that both chloromethanes were photoreduced through a similar mechanism. In general, the $CHCl_3$ photodechlorination was 10 times less efficient than in the case of CCl_4, but 5 times more efficient at $pH < 8$ than the non-chain photoreduction of O_2.[24] The differences between these photodehalogenations can be rationalized if the chloroform reduction also proceeded via a chain process but with propagation steps significantly less efficient than those for CCl_4.

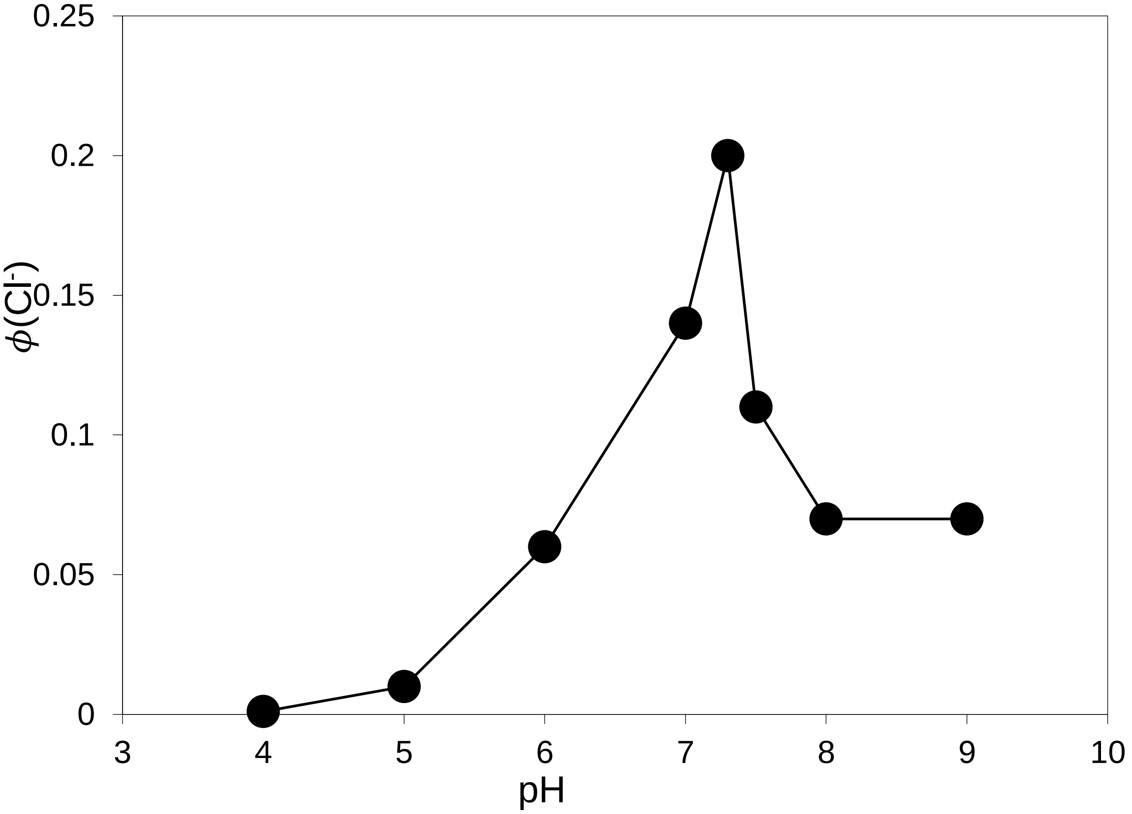

Figure 2.4. Efficiency of Cl^- formation as a function of pH determined via illumination of air-free solutions containing 0.018 M SPEEK, 0.36 M formate buffer and 2 mL $CHCl_3$; $I_0 = 3.8 \times 10^{-6}$ M (hν)/s.

Post-irradiation experiments provided convincing evidence that the radical photoreduction of CCl_4 and CCl_3F proceeded via chain mechanisms.[20,36,40] Figure 2.5 depicts the [Cl^-] changes induced by cycles of alternating illumination and dark periods lasting 3 min each obtained in an experiment with $CHCl_3$. Linear increases in [Cl^-] occurred during both illumination and dark periods, which turned sub-linear at longer times. These results clearly demonstrated that reduction of $CHCl_3$ continued after photolysis ended, but with slower [Cl^-] increases in the dark. Values of r(Cl^-) derived from the linear [Cl^-] changes are shown in the inset of Figure 2.5 for both photochemical and dark reactions; which indicate that the rates decreased with rising number of cycles. The photolytic rate dropped smoothly from 4.7×10^{-7} M/s to ~ 1/2 of this value after 10 cycles, whereas r(Cl^-) remained constant for CCl_4 at 8×10^{-7} M/s over numerous cycles.[20] Also, r(Cl^-) for the dark reduction of $CHCl_3$ (6.3×10^{-8} M/s) declined by a factor of 2 after 6 cycles (inset in Figure 2.5); in the CCl_4 case the rate remained constant at 2×10^{-7} M/s. The results of Figure 2.5 clearly showed that the $CHCl_3$ photodehalogenation proceeded via a chain transformation. At the same time, the continuous drop in r(Cl^-) for both photolytic and post-illumination reductions of chloroform, together with the 3 times lower r(Cl^-) values in the dark, demonstrated that the propagation process was less efficient than for CCl_4.

An important observation was that no post-irradiation formation of Cl^- occurred for solutions containing [$CHCl_3$] lower or equal than the solubility limit in water. This means that the dark reaction required the presence of excess $CHCl_3$ because this transformation originated mainly from the interfacial region existing between the chloroform droplets and the aqueous solution. Efficient chain processes require fast propagations given that these steps generate the main products. Utilization of solutions with high concentrations of reactants are needed to achieve long chains when propagations occur with low rate constants.[35] Previous photoreduction studies in water identified high [HCO_2^-] as necessary to induce chain reactions but reaching similarly large [halomethanes] was restricted by their limited solubility in water.[20,36] In the chloroform case, the interfacial film seemed best suited to enable efficient chain reactions given the higher [$CHCl_3$] present in this region. While propagations occurred both in the aqueous phase and within the film, the dark reactions originated from the longer chains taking place in the interfacial region. However, increases of [Cl^-] photogenerated within the film eventually decreased [$CHCl_3$] in that region, affecting negatively chain propagation and diminishing r(Cl^-) as shown in the inset of Figure 2.5. High [Cl^-] present in the aqueous phase also affected the $CHCl_3$ amounts present in the interfacial layer thereby decreasing r(Cl^-) as depicted in Figure 2.1.

As mentioned previously, $^3BP^*$ was quenched efficiently by HCO_2^- ($k_q = 1 \times 10^8\ M^{-1}\ s^{-1}$) presumably with formation of $(Ph)_2C{\bullet}OH$ and ${\bullet}CO_2$.[25] An analogous reaction was proposed for illuminated SPEEK solutions containing the formate buffer.[20] EPR experiments were, therefore, conducted to assess if SPEEK• and ${\bullet}CO_2^-$ were involved in the photodehalogenation of $CHCl_3$. Figure 2.6 shows a spectrum collected from an air-free SPEEK/formate solution at pH = 7, without $CHCl_3$, that was photolyzed inside an optically transparent glass Dewar at room temperature, followed by rapid freezing (still under illumination) with liquid N_2. A single broad and intense signal with g = 2.003 was observed at 77 K that remained unchanged after heating the sample to about 100 K. Such signal was previously generated during photolysis of SPEEK/PVA solutions or polymer films and corresponds to SPEEK•.[23] Illumination at 77 K of solutions with SPEEK derived from the Solvay precursor yielded an identical spectrum but the radical disappeared upon heating the sample to 100 K. This observation further confirmed that SPEEK• generated from the Solvay-derived SPEEK was more reactive than the radical formed using the polymeric sensitizer made from the Evonik precursor.

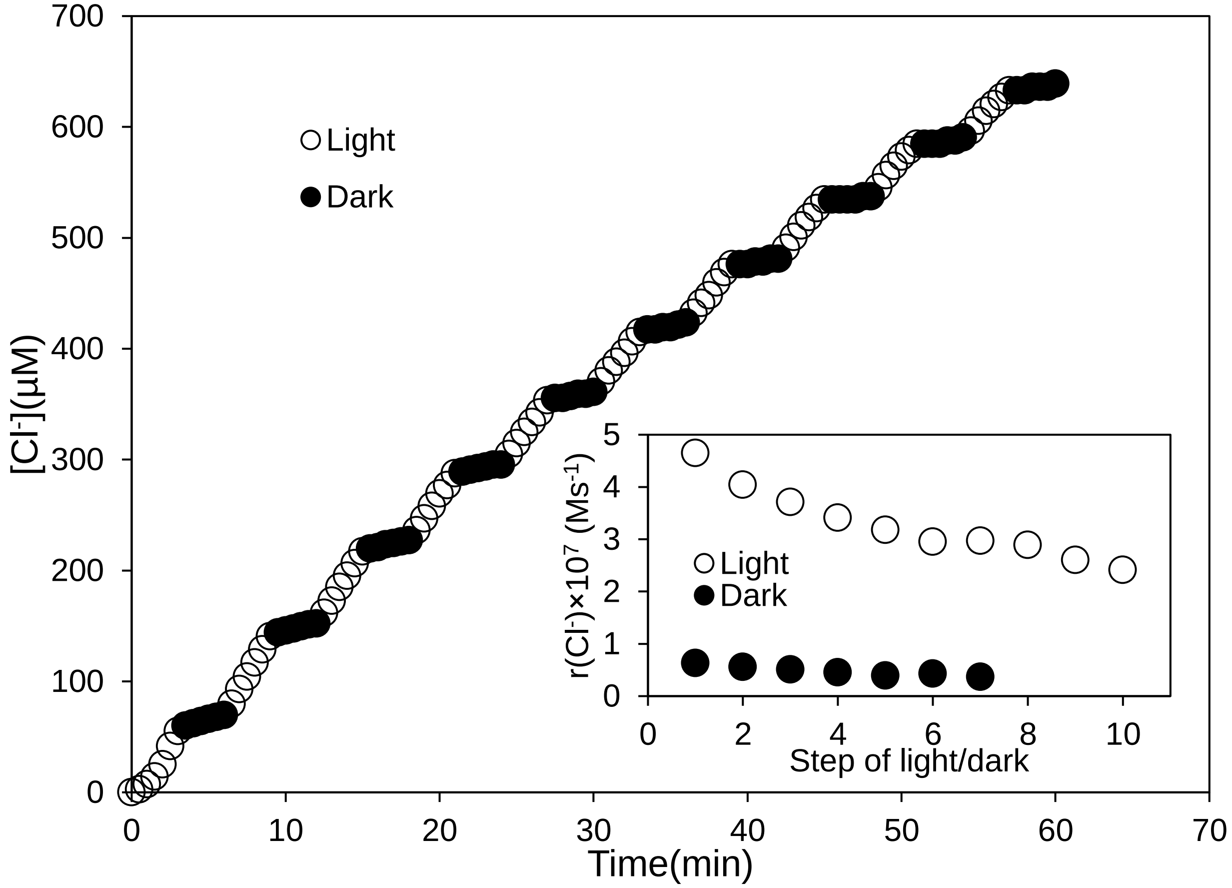

Figure 2.5. Change of [Cl$^-$] during cycles of alternating illumination (○) and dark (●) periods lasting 3 min each in a degassed solution of 0.018 M SPEEK and 0.36 M HCO_2^- at pH = 7.3 containing 2 mL $CHCl_3$ with $I_0 = 3.8 \times 10^{-6}$ M (hν)/s. Presented in the inset are the rates of Cl$^-$ formation during the illumination (○) and dark (●) periods.

While the spectrum of $\bullet CO_2^-$ has been reported,[41] efforts to detect this radical via irradiation at 77K of degassed, neutral solutions of SPEEK/HCO_2^- free of $CHCl_3$ generated only the SPEEK• signals. Previous EPR attempts to detect the PVA radical (PVA•) expected to form from photolysis of SPEEK/PVA blends also failed.[23] Such outcome was unsurprising as the high [SPEEK] used in the experiments facilitated a fast scavenging of PVA• by the polyketone; a similar reaction between •CO_2^- and SPEEK can account for the failure to detect the carboxylate anion radical directly. Experiments using slightly acidic solutions yielded different results as displayed in Figure 2.6. A complex spectrum was recorded consisting of very broad and weak signal at low magnetic fields together with a doublet flanking the SPEEK• peaks. In addition, a broadening of the low-field SPEEK• peak suggested the presence of another signal partially overlapping with that of the polymer radical. Spectral simulation involving subtraction of the signal from the polymer radical confirmed that an intense singlet overlapped with the SPEEK• peak. No changes resulted upon variation of the pH between 4.5 and 5 or substitution of water by D_2O. The signals were only detected in slightly acidic medium and vanished after heating the samples to 100 K, implying that they originated from reactive species.

H-atom abstraction from HCO_2H by •OH forms •CO_2H and HCO_2• and an earlier EPR study on this reaction reported signals from two different species.[42] While a broad doublet detected at low fields was attributed to •CO_2H, an additional sharp singlet was assigned to a complex of this radical with HCO_2H. However, •CO_2H is the protonated form of •CO_2^- ($pK_a = 1.4$) exhibiting an oxidation potential only 0.08 V less positive than that of the radical anion.[30] Hence, detection of •CO_2H was unlikely since this strong reducing radical was expected to react equally fast as •CO_2^- with SPEEK. Furthermore, the H-D exchange reaction of HCO_2H in D_2O yields HCO_2D, which upon H-atom abstraction was anticipated to form •CO_2D instead of •CO_2H and result in significant spectral changes.[43] The lack of any such alterations when photolysis was carried out in D_2O indicated that •CO_2H was not the detected species. In the formate buffer, [HCO_2H] amounted to 1.9×10^{-2} M at pH = 5, but this was observed to decrease by two orders of magnitude upon neutralization of the solutions. Thus, H-atom abstraction from HCO_2H by excited SPEEK seemed improbable due to the negligible [acid] under such conditions, which would be one explanation for the lack of EPR signals as observed in neutral solutions. Some of the signals displayed in Figure 2.6 seemed to have originated from HCO_2• because formation of this radical was not affected by the presence of D_2O or H_2O.

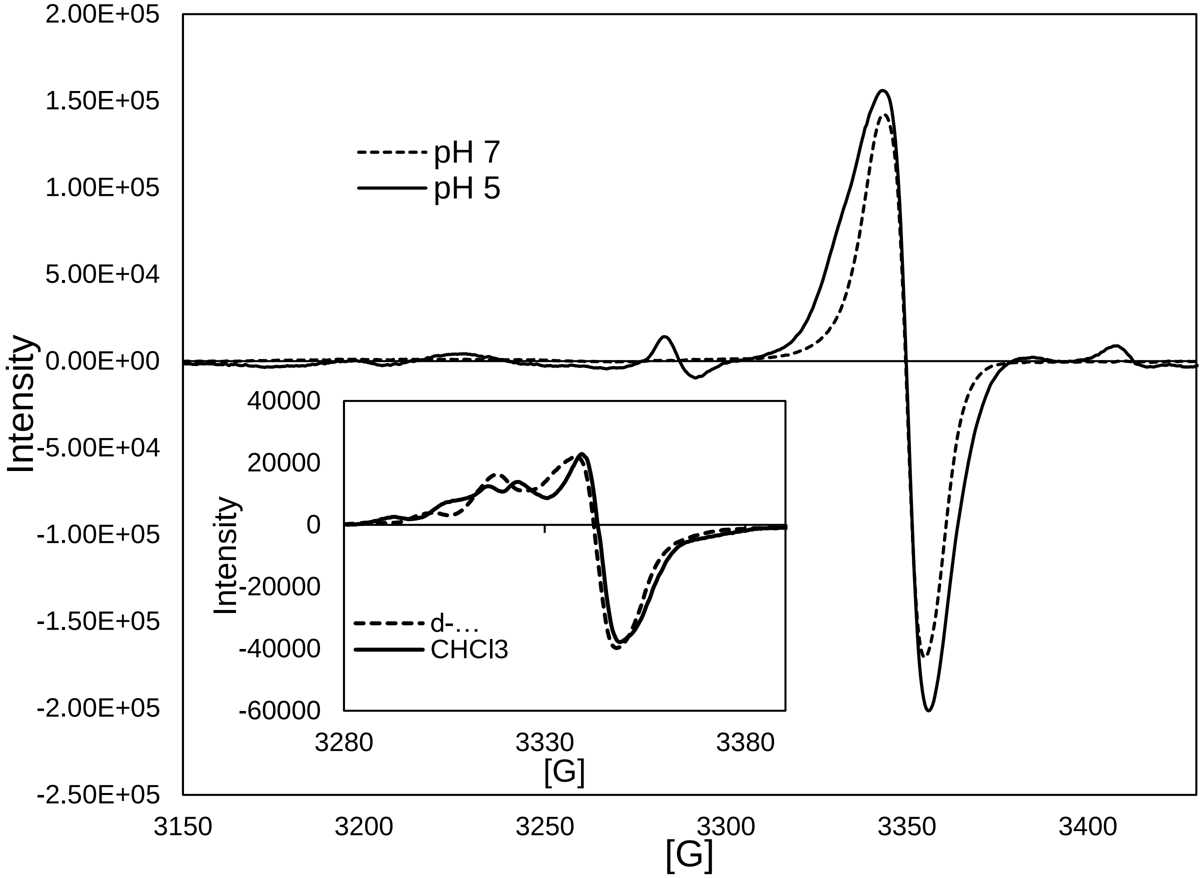

Figure 2.6. EPR spectra collected at 77 K from air-free aqueous solutions of 0.018 M SPEEK, 0.36 M HCO_2^- photolyzed with $I_0 = 3.8 \times 10^{-6}$ M (hν)/s. Sample at pH = 7 prepared via room temperature photolysis for 5 min followed by fast freezing under illumination with liquid N_2; samples at pH = 5 made from 2 h illuminations at 77 K of aqueous or D_2O solution. Inset: spectra from solutions at pH = 7 also containing $CHCl_3$ or $CDCl_3$ photolyzed at 77 K.

Included in the inset of Figure 2.6 is a spectrum acquired after illumination at 77 K of degassed SPEEK/formate solutions at pH = 7 in the presence of $CHCl_3$. Multiple paramagnetic species were present as the spectrum consisted of several broad signals, including some partially overlapping with the SPEEK• peaks. Such interpretation was supported by results from simulations based on subtraction of the SPEEK• peaks. An additional spectrum included in the inset shows that substitution of $CHCl_3$ by $CDCl_3$ collapsed some of the broad signals. Alterations of this kind are typical isotopic effects resulting from H-D substitution such as when $\bullet CDCl_2$ is generated instead of $\bullet CHCl_2$.[43] These changes supported the notion that radicals derived from the chloroform reduction were photogenerated. However, the data displayed in the inset of Figure 2.6 diverged somewhat from the $\bullet CHCl_2$ spectrum consisting of multiple evenly spaced signals.[44] Obviously, additional paramagnetic species were formed together with $\bullet CHCl_2$; further experiments have been planned to elucidate the nature of these species photogenerated in the presence and absence of $CHCl_3$.

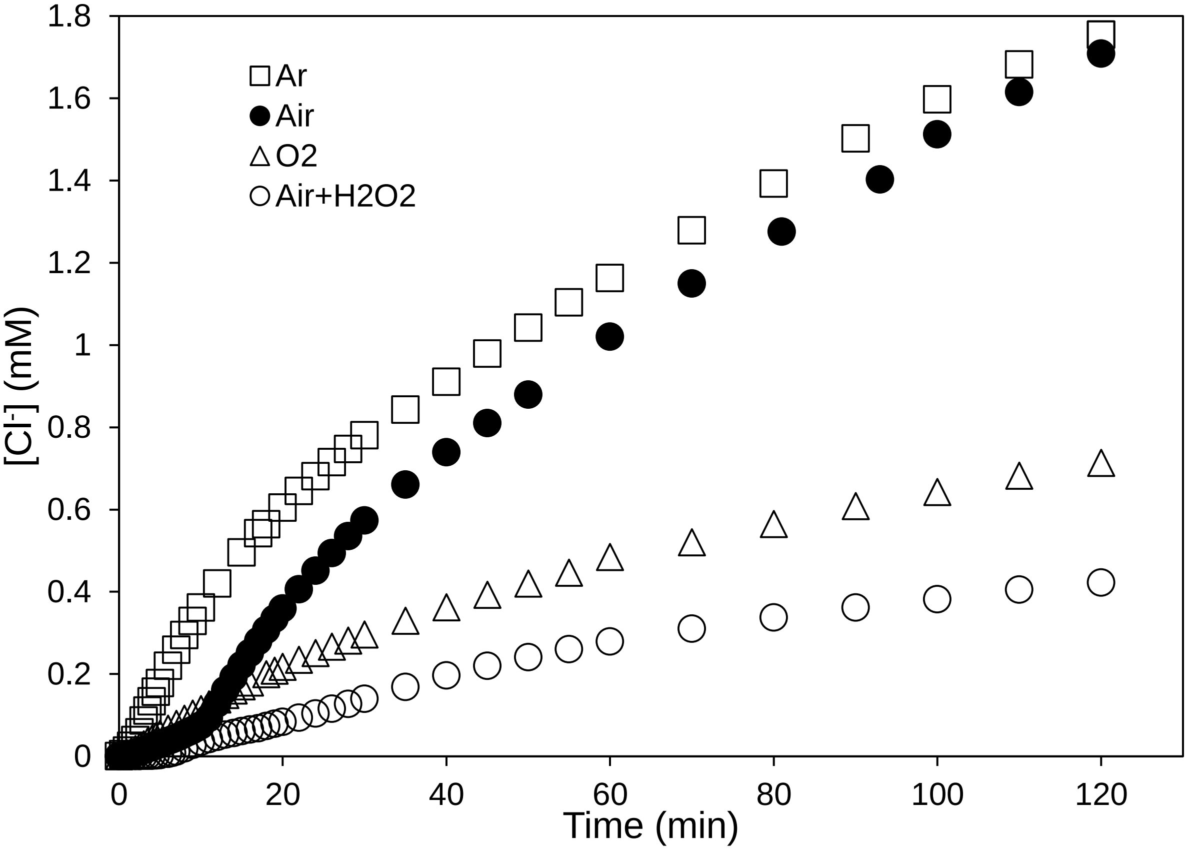

Figure 2.7. Generation of Cl^- ion during photolysis of solutions containing 0.018 M SPEEK, 0.36 M of formate buffer and 2 mL $CHCl_3$ at pH = 7.3 with $I_0 = 3.8 \times 10^{-6}$ M (hν)/s. The solutions were saturated with: (□) Ar, (●) air, (△) O_2; (○) air-saturated solution also containing 1×10^{-4} M H_2O_2.

GC-MS analysis of degassed solutions that were extensively irradiated identified CO_2 and CH_2Cl_2 as main products. Dimerization of $\bullet CHCl_2$ also took place since $CHCl_2$-$CHCl_2$ was detected in small amounts. Experiments with degassed SPEEK/HCO_2^- solutions at pH = 7.3 containing excess CH_2Cl_2 (2 mL) resulted in $\phi(Cl^-) = 0.02$, despite the much higher solubility (0.2

M) of this compound in water.[32] Clearly, the slow reduction of dichloromethane was unable to compete with the dechlorination of $CHCl_3$. Degassed solutions of SPEEK and formate buffer in the presence of either $CHCl_3$ or CCl_4 turned yellow after several hours of illumination. Optical determinations revealed that the coloration originated from a uniform increase in optical density at wavelengths above 360 nm. Somewhat similar changes noticed during extensive irradiation of SPEEK/PVA films were attributed to formation of LAT, or light absorbing transients.[23] LAT were first identified as byproducts during photolysis of BP in 2-propanol formed via insertion of $(CH_3)_2C{\bullet}OH$ into different positions of the aromatic rings from $(Ph)_2C{\bullet}OH$.[45] In analogy, LAT formation in the SPEEK/HCO_2^- system probably resulted from a combination of $\bullet CO_2$ with SPEEK•. Other radical-radical reactions were also possible, including SPEEK• dimerization/disproportionation processes noticed during photolysis of SPEEK/PVA films.[23]

Numerous findings of the present study were consistent with a chain photoreduction of $CHCl_3$ to CH_2Cl_2. The main aspects of the photoreaction can be rationalized in terms of the following mechanism analogous to the one proposed earlier for the chain phototransformation of CCl_4 in air-free SPEEK/formate solutions:[20]

$$\{RRC{=}O\}_z + h\nu \rightarrow {}^3\{RRC{=}O\}_z^* \quad (1)$$

$$^3\{RRC{=}O\}_z^* + HCO_2^- \rightarrow \bullet CO_2^- + \{RRC{\bullet}OH\}_z \quad (2)$$

$$\{RRC{=}O\}_z + \bullet CO_2^- \rightarrow CO_2 + \{RRC{\bullet}O^-\}_z \quad (3)$$

$$\{RRC{\bullet}O^-\}_z + H^+ \leftrightarrows \{RRC{\bullet}OH\}_z \quad (4)$$

$$\{RRC{\bullet}OH\}_z + CHCl_3 \rightarrow \bullet CHCl_2 + Cl^- + H^+ + \{RRC{=}O\}_z \quad (5)$$

$$\bullet CHCl_2 + HCO_2^- \rightarrow \bullet CO_2^- + CH_2Cl_2 \quad (6)$$

$$R\bullet + R'\bullet \rightarrow \text{products} \quad (7)$$

For simplicity reasons, the mechanism was formulated in terms of elementary steps taking place in homogeneous solution. As will be shown later, this simplistic approach is unable to rationalize all the observations in part due to the rather heterogeneous nature of the polyelectrolyte solutions. In the simplified notation $\{R'RC{=}O\}_z$ corresponded to SPEEK whereas the triplet excited state of the polyketone was symbolized by $^3\{R'RC{=}O\}_z^*$. The polyelectrolyte radical and the corresponding deprotonated form were represented by $\{R'RC{\bullet}OH\}_z$ and $\{R'RC{\bullet}O^-\}_z$, respectively; both formulas implied that on average a single unpaired electron was present per polymer chain. Furthermore, step 7 represents a summary of three possible termination processes: dimerization of the dichloromethane radical (R• = R'• = $\bullet CHCl_2$), formation of LAT (R• = SPEEK•, R'• = $\bullet CO_2^-$), and dimerization/disproportionation of the polymer radical (R• = R'• = SPEEK•).

A thorough discussion of steps 1-4 was presented before,[20] only a few comments relevant to the $CHCl_3$ system are pertinent. Step 3 probably occurs in a way similar to the reduction of the negatively charged 4-carboxybenzophenone (4-CB) by $\bullet CO_2^-$, that takes place with $k = 3 \times 10^7$ M^{-1} s^{-1}.[46] While the anionic benzophenone molecule is a reasonable model for the BP functions present in SPEEK, the rate constant of step 3 was anticipated to be lower than that for the reaction of 4-CB with $\bullet CO_2^-$. The reason for such expectation is the strong electrostatic repulsions between $\bullet CO_2^-$ and SPEEK as the polyelectrolyte contains between 150-200 SO_3^- groups per chain. Similarly, the rate constant for the reduction of $CHCl_3$ by $\bullet CO_2^-$ remains unknown but this process was not expected to be faster than the reaction between $CFCl_3$ and the carboxylate radical anion with $k = 7 \times 10^4$ M^{-1} s^{-1}.[26] Considering these rate constants and the fact that [SPEEK] >> [$CHCl_3$] leads to the conclusion that the carboxylate radical anion reacted mainly via step 3, which was the reason for excluding the reduction of $CHCl_3$ by $\bullet CO_2^-$ from the mechanism. While the rate constant for step 5 is not known, k_5 is probably similar to the value for the CH_2Cl_2 reduction by $(CH_3)_2C•OH$, $k \sim 1 \times 10^6\ M^{-1}\ s^{-1}$.[47] Also, step 6 occurs most likely with a rate constant somewhat lower than the value for H-atom abstraction from HCO_2^- by $•CCl_2F$, $k = 2 \times 10^3\ M^{-1}\ s^{-1}$.[26] In this mechanism, reactions 3 through 6 encompass the propagation steps, whereas SPEEK•, $•CO_2^-$, and $•CHCl_2$ are the chain carriers.

The cross-reaction between SPEEK• and $•CO_2^-$ was identified as a possible termination channel but only when solutions were illuminated extensively, given that generation of LAT was slow in solutions containing either $CHCl_3$ or CCl_4. For this reason, LAT formation was not considered a significant termination pathway in the present study. Detection of $CHCl_2$-$CHCl_2$ provided solid evidence that $•CHCl_2$ dimerization also contributed to termination, which is not surprising given that this reaction is fast in CH_2Cl_2, $k \sim 1 \times 10^9\ M^{-1}\ s^{-1}$.[48] Dimerization/disproportionation (or just dimerization) of SPEEK• is an alternative termination channel recognized as important in studies on SPEEK photoreactions.[20,22,24] This reaction resulted in polymer crosslinking and also in reduction of SPEEK ketone functions.[23] Typical α-hydroxy radicals, such as $(Ph)_2C•OH$, a reasonable molecular model for SPEEK•, decay via diffusion-controlled dimerizations, $k = 9 \times 10^8\ M^{-1}\ s^{-1}$.[49] Something different was noticed during photolysis of SPEEK in air-free solutions containing PVA or HCO_2^- since a small amount of polyelectrolyte radicals, ϕ(SPEEK•) = 0.02-0.03, survived for several min.[20,22] They decayed via a slow radical-radical process with $k = 3\text{-}6 \times 10^2\ M^{-1}\ s^{-1}$, but the reaction accelerated significantly upon stirring the solutions due to the low mobility of the surviving radicals. Hence, the polyelectrolyte radicals seemed to decay first via a fast step, followed by a slower process thereafter.

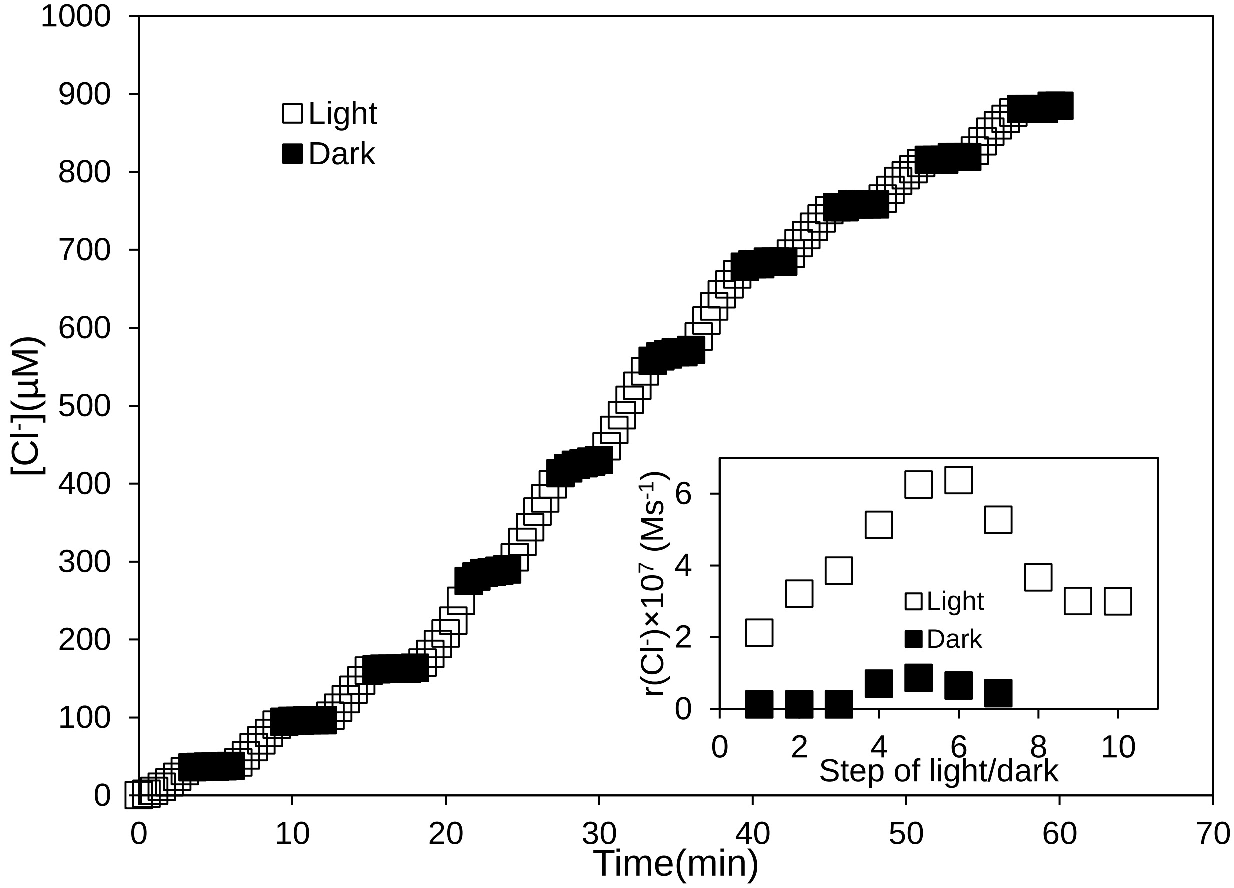

Figure 2.8. Change of Cl^- ion concentration during alternating (●) illumination and (■) dark periods for an air-saturated aqueous solution containing 0.018 M SPEEK, 0.36 M formate buffer, 2 mL $CHCl_3$ at pH = 7.3 with $I_0 = 3.8 \times 10^{-6}$ M (hν)/s. Inset illustrates the evolution of the instantaneous rate of Cl^- formation with increasing number of (●) illumination and (■) dark periods.

Attempts to derive a simple rate law using the steady-state approximations failed when two or more termination channels were considered simultaneously. A rate law predicting a linear dependence of $\phi(Cl^-)$ on both $I_0^{-1/2}$ and [$CHCl_3$] according to the data of Figures 2 and 3 resulted under some conditions. As in the case of CCl_4,[20] the first condition required the protonated form of SPEEK• to be the only reductant of $CHCl_3$. Furthermore, termination needed to proceed exclusively through a second-order SPEEK• decay; dimerizations of $\bullet CHCl_2$ or $\bullet CO_2^-$ as well as the cross-reaction between SPEEK• and $\bullet CHCl_2$ yielded rate laws inconsistent with the experimental data. Values of the kinetic chain length (kcl) were evaluated as outlined in the case of CCl_4 and amounted to 5 and 15 for SPEEK samples made from the Evonik and Solvay precursors, respectively. Derivation of the rate law was feasible without the classical assumption of long chains, implying that steady-state conditions prevailed despite the low resulting kcl values. The proposed mechanism accounted well for numerous important findings, including the reaction products as well as the majority of the kinetic and EPR results.

On the other hand, significant shortcomings of the mechanism were evident, including the prediction by the derived rate law of a first-order dependence of $r(Cl^-)$ on [SPEEK]. Such relationship seemed unlikely as the reaction conditions employed in the present study were those that ensured an optimum photoreduction of CCl_4, but which also yielded a complex relationship between $r(Cl^-)$ and [SPEEK].[20] The mechanism was also unable to account for the very drastic $\phi(Cl^-)$ increases when $[H_3O^+] < 10^{-5}$ M including the maximum at pH = 7.3, and the subsequent efficiency drop depicted in Figure 2.4. Participation of the SPEEK• deprotonated form provided a rationalization for the sharp $\phi(Cl^-)$ increase in neutral solutions but failed to explain the ensuing efficiency evolution at higher pH values. Lastly, the redox processes taking place within the interfacial region between $CHCl_3$ droplets and aqueous phase were not specifically incorporated in the mechanism.

Successful derivation of the rate law also required SPEEK• to decay according to the familiar second-order rate law typical of small molecular species. However, as mentioned before, dimerization of the polyelectrolyte radicals proceeded via a complex process. This is unsurprising as dimerization of PVA• takes place with second-order rate constants that decrease as the reaction unfolds.[50] This behavior indicates a rather restricted motion of PVA• because solution regions with high concentrations exhibit a diffusion-controlled decay, whereas the reaction rate progressively decreased for macromolecular radicals located farther away from each other. On the other hand, polyelectrolyte radicals from ionized poly(acrylic acid), PAA, survived for hours because their slow diffusion in H_2O was further affected by inter-chain electrostatic repulsions.[51] Hence, the SPEEK• decay can be envisioned as initially dominated by fast dimerizations much alike the PVA• case. Although the majority of the polyelectrolyte radicals were consumed in this process, a fraction of SPEEK• persisted for tens of minutes in a way reminiscent to the behavior of PAA radicals.

The unusual decay of SPEEK• impacted severely the efficiency of reductions induced by this radical. Values of ϕ(SPEEK•) > 0.02-0.03 were determined for solutions containing oxidizers (O_2, Ag^+, etc.) but the efficiency increased by a factor of only 2-4.[22,24] Thus, the oxidizers were unable to compete efficiently with the SPEEK• dimerization, in contrast to the outcome foreseen for homogeneous reactions. The diffusion-controlled O_2 reductions by $(CH_3)_2C{\bullet}OH$ and $\bullet CO_2^-$, $k = 2\text{-}4 \times 10^9\ M^{-1}\ s^{-1}$,[47] are relevant examples of such homogeneous processes. SPEEK• was anticipated to reduce O_2 with a similar rate constant and also experience a fast dimerization ($k = 9 \times 10^8\ M^{-1}$) as the model radical $(Ph)_2C{\bullet}OH$. From such rate constants, the inevitable conclusion was that oxygen reduction in air-saturated solutions always predominated over radical dimerization, because under steady state conditions $[O_2] >> [SPEEK•]$. Yet, the opposite occurred when O_2 was photoreduced by SPEEK;[24] additional observations also exist that conflicted with attempts to rationalize SPEEK• reactions solely in terms of solution processes.[20,24,31] This means that the proposed mechanism based only on homogeneous reactions provides a rather limited understanding of the photoprocesses occurring in SPEEK solutions.

Several of the unusual observations in this case were consistent with the presence of polyelectrolyte structures in SPEEK solutions originating from overlap and entanglement, or agglomeration, of the macroions. [20,24,31] This is not an unexpected possibility, given that the SPEEK concentration employed was above the onset for entanglement.[20] For instance, formation of the polymer radicals within SPEEK structures can be envisioned as facilitating SPEEK• dimerization. Reaction of radical scavengers with SPEEK• failed to compete with radical dimerization simply because transport of the oxidizers into the polyelectrolyte structures was not very efficient. An example is the limited fraction of photogenerated SPEEK• that ultimately was able to reduce $CHCl_3$ and also CCl_4.[20] Support for this explanation was provided by the 10 times higher $\phi(H_2O_2)$ found using crosslinked SPEEK/PVA films swollen in H_2O as compared with those determined for polymer solutions.[24,31] SPEEK• dimerization was hindered in the films because the crosslinks impeded radical diffusion but no such restriction existed for O_2 migration into the solid matrices where reduction occurred.

The photoreduction of CCl_4 initiated by SPEEK was previously shown to occur as well in solutions saturated with air.[20] However, 10 times longer induction periods were noticed in such systems as compared with the one in the presence of Ar, and $\phi(Cl^-)$ reached the value of O_2-free solutions only after extended photolysis. Presented in Figure 2.7 is a comparison of data gathered during illuminations of SPEEK/HCO_2^- solutions containing $CHCl_3$ that were saturated with Ar, air and O_2. Most kinetic plots resembled closely those of Figure 1, exhibiting induction periods of slow chloride ion formation in which the kinetic data was irreproducible. This step was followed by a faster and linear increase in $[Cl^-]$ and a subsequent non-linear concentration change. The brief induction period of Ar-saturated solutions extended to 7-10 min for air-saturated solutions irrespective of the $CHCl_3$ concentration. Reproducible formation of Cl^- occurred during the second step lasting about 10 min with $\phi(Cl^-) = 0.14$, that is 30 % lower than the value measured with Ar. Thereafter $[Cl^-]$ increased non-linearly following closely the changes noticed in the absence of air. Photoreduction of $CHCl_3$ initiated by SPEEK made from the Solvay precursor was efficient even in the presence of air, $\phi(Cl^-) = 0.59$, after an induction period of only 3 min. Such unexpected efficiency was essentially the value determined under Ar, implying that for this sensitizer the inhibiting effect of O_2 was entirely restricted to the induction period.

A reasonable rationalization for the data gathered in air-containing solutions involved photoreduction of the O_2 to H_2O_2, as found in the absence of $CHCl_3$.[24] H_2O_2 formation can be envisioned to take place through the same route as proposed earlier:

$$O_2 + \bullet CO_2^-/\{RRC\bullet OH\}_z \rightarrow \bullet O_2^- + CO_2/\{RRCO\}_z + H^+ \quad (8)$$

$$2\bullet O_2^- + 2H^+ \rightarrow O_2 + H_2O_2 \quad (9)$$

Generation of H_2O_2 at pH = 7.3 proceeded mainly by the slow step 9 involving O_2^- given that $pK_a = 4.8$ was reported for the acidic form $\bullet HO_2$.[52] In this scenario O_2 reduction took place mainly during the induction period, which was longer for air saturated SPEEK solutions because such systems contain more oxygen, $[O_2] = 0.26$ mM identical to the value found in plain water.[24] As mentioned previously, reasonable values for k_5 and k_8 seemed to be 1×10^6 M^{-1} s^{-1} and $2\text{-}4 \times 10^9$ M^{-1} s^{-1}, respectively. These rate constants together with the corresponding $[CHCl_3]$ and $[O_2]$ enabled estimation of pseudofirst-order rate constants for steps 5 and 8 of 7×10^4 s^{-1} and $0.5\text{-}1 \times 10^6$ s^{-1}, respectively. According to this analysis, the reductions of $CHCl_3$ and O_2 occurred concurrently, but until the significant fraction of the dissolved oxygen was consumed, the latter reaction predominated initially.

Following this reasoning, an additional [O_2] increase was projected to further lengthen the induction period and decrease modestly the efficiency of the $CHCl_3$ reduction. However, the results obtained in O_2-saturated solutions deviated from this predicted behavior. O_2-saturated water exhibits a solubility of this gas equal to 1.3 mM;[53] however, an analogous oxygen saturation concentration was likely for SPEEK solutions. As shown in Figure 7, a 5-fold increase in [O_2] drastically affected the photoreaction, lowering $\phi(Cl^-)$ to 0.05 and repressing the Cl^- generation throughout the entire exposure to light. The experiments with both air and O_2 clearly indicated that oxygen affected the $CHCl_3$ dechlorination in a complex way not just merely via competing with chloroform for the reducing radicals. While O_2 is an efficient quencher of $^3BP^*$ with $k_q = 4 \times 10^8$ M^{-1} s^{-1} in water,[49] no evidence of an analogous deactivation of $^3\{RRC{=}O\}_z^*$ was obtained during the oxygen reduction by SPEEK• in the presence of air.[24] Preliminary determinations also showed no changes in the SPEEK phosphorescence in solutions with and without air. Thus, quenching of $^3\{RRC{=}O\}_z^*$ by O_2 constituted, at best, only a minor deactivation pathway unlikely to compete with step 2.

The oxygen photoreduction in stirred SPEEK/PVA solutions saturated with air or with O_2 generated H_2O_2 with a quantum yield of 0.02 for both systems.[24] Considering that the H_2O_2 formation prevailed initially in the presence of air, an inhibiting effect of the photogenerated peroxide on the subsequent reduction of chloroform seemed plausible. Such possibility was tested via photolysis of air-saturated solutions also containing 0.1 mM H_2O_2, the results are also presented in Figure 2.7. Inclusion of the peroxide decreased $\phi(Cl^-)$ to 0.025, which is only 50 % of the efficiency achieved in oxygen-saturated solutions. Furthermore, the peroxide-induced inhibition was more pronounced throughout the irradiation period than the effect induced by saturation with O_2. In contrast, illumination of the same solution but Ar-saturated resulted an evolution of [Cl^-] versus time nearly identical to the data of Figure 2.1 obtained in the absence of H_2O_2. The only difference was a slightly longer induction period of the peroxide-containing systems, which yielded $\phi(Cl^-) = 0.2$ as in the absence of H_2O_2.

Earlier findings help to understand the unusual results gathered in the presence of H_2O_2 with and without O_2. The reaction between $\bullet CO_2^-$ and H_2O_2 proceeds differently in HCO_2^- solutions when O_2 is present or absent.[54,55] In air-containing solutions, peroxide is the net product given that $\bullet CO_2^-$ reduces O_2 much faster ($k = 2 \times 10^9\ M^{-1}\ s^{-1}$) than H_2O_2, $k = 7 \times 10^5\ M^{-1}\ s^{-1}$.[47] Peroxide formation was also the main process during the O_2 reduction by SPEEK• in stirred solutions saturated with air or oxygen, where [H_2O_2] increased continuously until leveling off at 0.17 or 0.3 mM, respectively.[24] The O_2 reduction also predominated when air-saturated solutions containing $CHCl_3$ were photolyzed in the presence of peroxide as indicated by the very low [Cl^-] formed under such conditions. Given that no peroxide was consumed, the high [H_2O_2] present ensured efficient inhibition of the chloroform reduction.

According to the data of Figure 2.7, the strongest inhibiting effect occurred when both air and peroxide were present, suggesting that [H_2O_2] was higher in such system than during peroxide photogeneration in O_2-saturated solutions. Something very different occurred in the earlier study using degassed HCO_2^- solutions, where H_2O_2 was reduced via an efficient chain process (kcl $\approx$ 19) involving $\bullet CO_2^-$.[54] Attack of the carboxylate radical on the peroxide yields •OH,[47] which reacts fast with HCO_2^- reforming $\bullet CO_2^-$. The very slight retardation noticed during Cl^- generation in Ar-saturated SPEEK/HCO_2^- solutions containing $CHCl_3$ and H_2O_2 can be understood if the peroxide was consumed fast through a similar chain transformation. Reduction of $CHCl_3$ and H_2O_2 took place via simultaneous chain reactions; the minor retardation in Cl^- formation probably originated because some SPEEK radicals were diverted into attacking the peroxide.

Comparison of the data obtained in the absence and presence of air revealed some intriguing patterns. For instance, a few photolytic experiments were performed using air-saturated SPEEK solutions containing $[CHCl_3] = 0.37$ and 0.54 mM. After the induction period, Cl^- formed with quantum yields values of 0.1 and 0.12, respectively. Such efficiencies were, within experimental error, the same as the results depicted in Figure 3 for air-free solutions. As mentioned before, the induction period of air-free solutions containing traces of O_2 amounted to ~ 2 min. Unexpected short induction periods of only 7-10 min occurred in air-saturated solutions although they contained a much higher $[O_2]$. Reduction of O_2 via step 8 predominated during the induction period, but Cl^- formed simultaneous although with erratic kinetics. Analogous observations were made during the photoreductions of CCl_4, CCl_3F and CCl_2FCClF_2 involving SPEEK• or $•CO_2^-$.[20,26,27,36] Furthermore, the same rates of $CHCl_3$ reduction were obtained with air saturated solutions using vessels open or closed to air. Given that all experiments were conducted under stirring, part of the oxygen consumed during photolysis was replenished with O_2 present in the headspace of the solutions. While a steady state $[O_2]$ lower than the solubility limit was established under such conditions, reduction of $CHCl_3$ still occurred. These findings mean that partial dechlorination of halocarbons was feasible even when some oxygen was present.

Evidence gained during the radical reduction of CCl_4 in solutions containing 50% or more of 2-propanol indicated that dehalogenation in the presence of O_2 was viable.[8,40] This transformation took place through a chain process that was actually faster with air than without. When air was absent $•CCl_3$ acted as chain carrier but this species transformed into $•OOCCl_3$ upon reaction with O_2. A quicker dehalogenation occurred because $•OOCCl_3$ was a more effective chain carrier than

•CCl_3.[40,56] The chain process involving •$OOCCl_3$ was only possible at low [O_2]; under such conditions part of the reducing radicals still reacted with CCl_4 and the resulting •CCl_3 was transformed into the peroxyl radical by the remaining oxygen. Formation of the analogous peroxyl radical •$OOCHCl_2$ occurs fast in $CHCl_3$ ($k = 5 \times 10^9$ M^{-1} s^{-1}) via reaction between •$CHCl_2$ and O_2.[57] A chain photoreduction of $CHCl_3$ in oxygenated solutions seemed feasible if •$OOCHCl_2$ was able to abstract an H-atom as in propagation step 6. Thus, post-irradiation experiments were conducted as a means to detect a possible chain reduction under such conditions.

Figure 2.8 illustrates the evolution of [Cl^-] determined when an air-saturated SPEEK/HCO_2^- containing $CHCl_3$ was subjected to cyclic irradiation and dark periods lasting 3 min each. In general, the observed trends were reminiscent of those shown in Figure 2.5 for air-free solutions. The similarities included linear [Cl^-] increases during both periods of photolysis and darkness, sub-linear changes at longer times and slower dark generations of Cl^-. Most important, generation of Cl^- in the absence of light constituted unequivocal evidence that $CHCl_3$ was reduced through a chain process even in the presence of oxygen. Included in the inset of Figure 8 are rates derived from the linear [Cl^-] increases for both photochemical and dark reactions. The photolytic r(Cl^-) experienced a smooth rise from 2×10^{-7} M/s to 6.4×10^{-7} M/s during the first 6 cycles, followed by a decline to 3×10^{-7} M/s in the tenth cycle. A somewhat similar progression was noted for the dark reaction that exhibited a constant rate of 1×10^{-8} M/s during the first 3 cycles. Thereafter r(Cl^-) increased reaching 9×10^{-8} M/s at the 5th cycle and decreased thereafter to half of the maximum value.

In spite of some similarities discussed previously, comparison of Figures 5 and 8 revealed significant differences between the processes that took place with and without air. While the speeds of both photolytic and dark reactions in systems free of O_2 declined with increasing number of cycles, r(Cl$^-$) increased within the first 6 cycles for solutions containing air. This is consistent with the notion that $CHCl_3$ and O_2 competed for the reducing radicals, with the oxygen reduction prevailing initially. For this reason, the initial photolytic r(Cl$^-$) was more than a factor of 2 lower in the presence of O_2 than without this gas. However, the subsequent increases in r(Cl$^-$) depicted in Figure 2.8 agreed well with the assumption that the steady-state [O_2] decreased with increased number of cycles, enabling step 5 to compete with step 8. Optimum conditions were achieved between 5 and 6 cycles where the r(Cl$^-$) values of both photolytic and dark reaction were higher than the rates determined in the absence of air. At longer times, the rates of both reactions declined reaching values similar to those obtained without air.

As in the case of experiments performed in the absence of O_2, post-irradiation formation of Cl$^-$ was not detected upon illumination of air-saturated solutions contained a [$CHCl_3$] equal to the solubility limit in water. This observation further supports the notion that the chain reduction of chloroform was facilitated by the presence of an interfacial film between the $CHCl_3$ droplets and the aqueous solution. GC/MS analysis of photolyzed air-saturated solutions revealed that CO was formed (data not shown) in addition to CO_2 and CH_2Cl_2, but no $CHCl_2$-$CHCl_2$ was detected. Generation of CO was a significant finding because this compound is a known product of the formyl chloride decay in water.[58] Thus, detection of carbon monoxide strongly suggested the participation of HC(O)Cl as an intermediate of the photoreaction. As indicated previously, a plausible mechanism for such transformation involves $\bullet OOCHCl_2$ since this oxidizer forms during the $CHCl_3$ reduction in O_2-containing aqueous solutions.[59] Reduction of isoflurane ($CHF_2OCHClCF_3$) under similar conditions was explained by the participation of an alkylperoxyl radical analogous to $\bullet OOCHCl_2$.[60] The chain photoreduction of $CHCl_3$ in the presence of air can be rationalized using a modified version of the mechanism proposed for the reductive dehalogenation of $CHF_2OCHClCF_3$:

$$\bullet CHCl_2 + O_2 \rightarrow \bullet OOCHCl_2 \quad (10)$$

$$\bullet OOCHCl_2 + HCO_2^- \rightarrow HOOCHCl_2 + \bullet CO_2^- \quad (11)$$

$$HOOCHCl_2 + H_2O \rightarrow H_2O_2 + HOCHCl_2 \quad (12)$$

$$HOCHCl_2 \rightarrow H^+ + Cl^- + HC(O)Cl \quad (13)$$

$$HC(O)Cl \rightarrow H^+ + Cl^- + CO \quad (14)$$

$$\bullet OOCHCl_2 + \bullet O_2^- + H^+ \rightarrow HOOCHCl_2 \quad (15)$$

Step 10 was envisioned to occur fast given that this reaction proceeded in a diffusion-controlled fashion when $CHCl_3$ served as the solvent.[57] Propagation step 11 is a H-atom abstraction that probably took place with a rate constant somewhat lower than that of step 6. The rate constant for step 12 is not available but $HOCHCl_2$ is a short-lived intermediate decaying in water within the same time scale as $HOCCl_3$ (a few tens of μs).[58] Thus, k_{13} was expected to be close to the decay rate constant of $HOCCl_3$ ($k > 7 \times 10^5$ s^{-1}), whereas k_{14} was previously estimated at $\approx 1 \times 10^4$ s^{-1}.[58] The chain transformations in the presence and absence of air shared some similarities except that for the former process reactions 10 and 11 substituted step 6, given that $\bullet OOCHCl_2$ acted as a chain carrier instead of $\bullet CHCl_2$. Termination step 15 involved two peroxyl radicals presumed to react with a rate constant analogous to that for step 9, which at pH = 7.3 amounts to 3×10^5 M^{-1} s^{-1}.[52]

Generation of CH_2Cl_2 in air-containing solutions provided evidence that steps 5 and 6 were able to partially compete with steps 8 and 10. However, the absence of $CHCl_2$-$CHCl_2$ under such conditions indicated that step 10 predominated over step 6, meaning that termination via step 15 prevailed over step 7 given the role of •$OOCHCl_2$ as the chain carrier. Comparison of the data shown in Figure 2.7 made evident that the photochemical Cl^- generation in solutions containing Ar or air proceeded with comparable rates under extended photolysis. An analogous conclusion was reached from the r(Cl^-) values of Figures 2.5 and 2.8 determined at long reaction times. Interestingly, the mechanism proposed for the $CHCl_3$ photoreduction with air predicted generation of 3 Cl^- ions via steps 5, 10 through 15 whereas only one halide ion was projected to form from the propagation process when O_2 was absent. Complete $CHCl_3$ dehalogenation also resulted from step 15 although such process terminated the chain transformation.

The similar rates obtained during extensive exposure indicated that the $CHCl_3$ photoreduction in the absence of O_2 was about 3 times more efficient than in solutions with air. A lower efficiency was actually consistent with the mechanism operating under air given that a fraction of SPEEK• and •CO_2^- was diverted through step 8, and the resulting •O_2^- terminated the chain process via step 15. In addition, step 12 generated H_2O_2 that, as shown in Figure 2.7, interfered with the chain process through scavenging of SPEEK• and •CO_2^-.[24,54] H_2O_2 reduction by these radicals generated •OH,[47] which reformed •CO_2^- by reacting with HCO_2^-. Hence, the detrimental effect of hydrogen peroxide in solutions with air involved a retardation process in which the reducing radicals were consumed and then reformed by the combined action of O_2 and H_2O_2.

2.4 Conclusions

Illumination of air-free aqueous solution containing the polymeric sensitizer SPEEK and HCO_2H/HCO_2^-, or PVA, has been found to reduce chloroform to dichloromethane and Cl^-. This transformation was most effective under conditions optimized for the CCl_4 photoreduction initiated by SPEEK, including excess of halomethane.[20] Although the photoreduction of $CHCl_3$ was more complex than that of CCl_4, both processes shared several kinetic features. Among them was an initial linear $[Cl^-]$ increase during irradiation implying that the primary process of SPEEK• photogeneration acted as a controlling factor. Other common features included higher efficiencies when formate served as H-atom donor instead of PVA, largest $\phi(Cl^-)$ values in neutral solutions where formation of SPEEK• was optimal,[24] the dependence of $r(Cl^-)$ on $I_0^{1/2}$ and the post-irradiation formation of Cl^-. The last two findings provided evidence that a chain process operated as well in the case of chloroform. However, the $CHCl_3$ photoreduction was ≈ 10 times less efficient than the dehalogention of CCl_4. Such finding was not surprising given that the thermodynamic driving force for the $CHCl_3$ reduction by α-hydroxy radicals amounted to about half of the value estimated for CCl_4. A simple mechanism that ignored the complexities inherent to polyelectrolyte systems was able to explain most of the kinetic features.

SPEEK derived from PEEK manufactured by Solvay yielded photoreduction efficiencies 3 times higher than those obtained with the sensitizer made via sulfonation of the Evonik precursor. Also, photolysis of SPEEK derived from the Solvay precursor generated SPEEK• stable only at 77 K, whereas polymer radicals that survived for several min at room temperature resulted using other precursors.[20,22,23] However, no difference was observed in the EPR spectra of the paramagnetic species irrespective of the nature of the precursor. Hence, SPEEK derived from the Solvay precursor exhibited the highest efficiency to photogenerate polymer radicals and the resulting

SPEEK• experienced fast radical-radical decay reactions. A logical explanation assumes that Solvay PEEK exhibited less chain branching than the other precursors. The reason is that chain branching can decrease the efficiency of radical generation by enhancing self-quenching involving neighboring carbonyl groups,[20] and also diminish the mobility of macromolecular radicals thereby hindering their decay reactions.[50]

Evidence was obtained that the photoreduction of $CHCl_3$ was feasible as well in air-saturated solutions but at a slower pace. A more complex process operated under such conditions that included a chain dehalogenation pathway together with a retardation effect induced by H_2O_2. The ability to dehalogenate $CHCl_3$ in the presence of air is particularly interesting as such process provides support to the notion that protective barriers able to photodegrade toxic chemicals can be achieved by means of SPEEK-based films.[31] Such photoactive materials may also find uses in current strategies aiming to remove air-borne halocarbons that contribute to the greenhouse effect.[61]

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Chapter III

Free Radical Chain Photoreduction of $CHCl_3$ Using Swollen SPEEK/PVA Films in Air Saturated Solutions

3.1 Introduction

The results presented in Chapter II showed that the photoreduction of $CHCl_3$ occurred upon illumination with 350 nm photons of aqueous solutions containing sulfonated poly(ether-etherketone), SPEEK, together with poly(vinyl alcohol), PVA. This polymer combination (or blend) was designed to function in a way analogous to the well-known photochemical system consisting of benzophenone (BP) and 2-propanol.[1] In the polymeric system SPEEK functions as a sensitizer alike BP, whereas PVA acts as the H-atom donor in a fashion analogous to 2-propanol. A photogenerated triplet excited state of SPEEK (^{3}SPEEK*) abstracts an H-atom from PVA to produce an α-hydroxy radical of SPEEK, known as SPEEK•, together with a radical of PVA (PVA•).[2-4] Evidence of SPEEK• formation was gathered from optical as well as ESR determinations made possible because this radical survives for several minutes at room temperature in aqueous solutions free of O_2, and also in crosslinked films of SPEEK/PVA blends. SPEEK• exhibits an optical signal with a wavelength of maximum absorbance (λ_{max}) at 565 nm, enabling optical detection of this species. Detection of the concomitantly formed PVA• was not possible since this species reacts fast with another BP group of SPEEK forming an additional SPEEK•. Hence, absorption of a photon by SPEEK generates two SPEEK• species according to:

$$2\{R'RC{=}O\}_z + h\nu + \{CH_2CHOH\}_y \rightarrow 2\{R'RC{\bullet}OH\}_z + \{CH_2C{=}O\}_y \qquad (3.1)$$

where $\{R'RC{=}O\}_z$ and $\{CH_2CHOH\}_y$ represent SPEEK and PVA, respectively whereas $\{R'RC{\bullet}OH\}_z$ and $\{CH_2C{=}O\}_y$ correspond to SPEEK• and an oxidized PVA molecule, respectively.

Subsequent investigations on the photoreductions of CCl_4 and $CHCl_3$ initiated by photolysis of SPEEK solutions have shown that formate ions can also function as efficient H-atom donors generating SPEEK• through an analogous overall process:[5,6]

$$\{R'RC{=}O\}_z + hv + HCO_2^- \rightarrow \{R'RC{\bullet}OH\}_z + {\bullet}CO_2^- \qquad (3.2)$$

In fact, reduction of both chloromethanes was more effective when formate buffers (consisting of HCO_2^- and HCO_2H) were utilized as H-atom donors instead of PVA. Such observations implied ${\bullet}CO_2^-$, the intermediate generated through H-atom abstraction from HCO_2^-, reacted with SPEEK more efficiently than PVA•. Another important finding was that photoreduction of the chloromethanes was feasible even in the presence of air although O_2 is a known scavenger of reducing radicals.

Investigations of the photochemical properties of SPEEK/PVA blends were motivated by their potential to function as protective barriers against toxins and microorganisms. The blends were designed to be light-sensitive, that is, to employ photons as the energy source for formation of reactive species able to attack and deactivate toxic chemicals and pathogens. However, ascertaining the ability of the films to function as reactive barriers is not a simple task. A significant advantage of SPEEK/PVA blends is that both of their polymeric components are soluble in aqueous solutions enabling preparation of water-insoluble films using simple solution casting procedures followed by crosslinking of PVA. This, in turn, made possible to test the photochemical properties of polymer blends either by illuminating crosslinked films in contact with water, or via photolyzing aqueous solutions containing both SPEEK and PVA.

Illuminations on solutions containing both SPEEK and PVA provided important information about the reactivity of the photogenerated SPEEK•.[3-7] For instance, they firmly established that the polymer radical behaves as a reductant able of transforming several metal ions to metallic crystallites, dehalogenating CCl_4 and $CHCl_3$, as well as reducing oxygen to H_2O_2. Also, kinetic and mechanistic information on the reactions induced by SPEEK• were gained from such investigations. Experiments with dry films showed that SPEEK• was able to reduce Ag^+ within the solid matrices, confirming the ability of this radical to act as a reductant even in the absence of water.[2,4] Additional information on the reactivity of dry SPEEK/PVA films is required in order to assess the potential properties of such solid polymer blends to deactivate toxins and microorganisms in their role as protective barriers. However, no simple procedures exist that would allow performing the needed experiments in a straightforward way. For instance, efficient diffusion of the relevant reactant into dry polymer films, and products out of them, is not easy to accomplish. Such diffusional problems make quantification of products from reactions taking place inside films a problematic task.

Interestingly, kinetic data on the transformations of PVC films was shown to be accessible upon utilization of a medium (fluid or gas) able to facilitate extraction of products from the solid matrix.[8] A recent adaptation of this method allowed quantification of H_2O_2 formed during the O_2 photoreduction by SPEEK/PVA films.[9] In this method, continuous extraction of the produced peroxide was possible via illumination of swollen SPEEK/PVA films immersed in aqueous solutions. Quantitative determination of $[H_2O_2]$ then occurred upon subjecting the photolyzed solution to conventional analytical procedures. An analogous strategy seamed feasible to test the ability of SPEEK/PVA films to chemically attack undesirable chemicals. Chloroform was selected as a test material given that this is a toxic chemical frequently found as a contaminant in groundwater.[10,11] Furthermore, results from the first two chapters indicated that the reduction of $CHCl_3$ by SPEEK• in air-free solutions was more difficult than that of CCl_4. On the other hand, the $CHCl_3$ photodehalogenation was only slightly affected by the presence of air. Such findings suggested that testing of the properties of SPEEK/PVA films was feasible under air, which represented conditions more realistic for probing their usefulness as photoactivated protective barriers.

In addition, such experiments seemed useful for assessing the feasibility of using crosslinked SPEEK/PVA films for detoxification of water contaminated with $CHCl_3$. Previous photochemical strategies for decontamination of water have used suspensions of semiconducting or clay particles as sensitizers (also called "photocatalysts").[12,13] These efforts yielded mainly slow oxidations of $CHCl_3$ in air-containing aqueous systems. Presented in this chapter are results from an investigation on the $CHCl_3$ dehalogenation initiated by illumination of crosslinked SPEEK/PVA films immersed in aqueous solutions saturated with air. This study utilized a modified version of the method previously used for following the kinetics of the O_2 photoreduction.[9] Cl^- ions photogenerated inside films were continuously extracted into the solution, making possible to gather kinetic data by means of *in situ* potentiometric determinations of the product in the aqueous phase. Highest quantum yields of Cl^- were obtained when the aqueous solutions contained formate buffers consisting of HCO_2^- and HCO_2H, suggesting that the $CHCl_3$ dehalogenation took place via a chain process.

3.2 Experimental

Poly(ether etherketone), PEEK, Ketaspire KT-880 FP powder, $M_n = 4 \times 10^4$ g mol^{-1}, provided as a gift by Solvay, USA, was sulfonated via reaction with sulfuric acid according to established procedures.[9] The resulting acidic product was subsequently converted into the Na^+ salt of the sulfonated polymer (called SPEEK) and characterized as indicated before;[3] the generated polyelectrolyte was then utilized for the preparation of aqueous solutions that served as precursors of the polymer films. $CHCl_3$ was acquired from Macron, all other chemicals including PVA (99 % hydrolyzed, average $M_n = 8.9\text{-}9.8 \times 10^4$ g mol^{-1}) were purchased from Sigma-Aldrich or VWR. All aqueous solutions were made using water from a Millipore Milli-Q Biocel system; formate buffers consisted of $[HCO_2H] + [HCO_2^-] = 0.36$ or 0.1 M and the presence of high amounts of $NaCO_2H$ in solution maintained a constant ionic strength required for the potentiometric measurements. Unless otherwise stated, most experiments were carried out at room temperature, 23 ^{0}C.

Solutions of SPEEK and PVA were prepared separately as mentioned previously,[3] except that they contained 0.085 M polyketone and 1.47 M polyol (the molarities refer to the monomers units). Mixtures of these solutions were employed for the preparation of the cross-linked films following a procedure outlined before.[9] Slight variations were introduced, included filtering the polyketone solution using a Whatman # 4 filter prior to mixing, as well as utilizing a 0.5 M HCl solution to accelerate the PVA cross-linking. Most photolyzed films contained 30/70 SPEEK/PVA wt %, other compositions were achieved varying the polyketone/polyol molarity ratio. On average the resulting dry films were 60 (± 10) µm thick and alterations of the casting method enabled variations of thicknesses (20 – 80 µm). While typical samples for photolysis were 2.5 cm wide and 5 cm long, each dimension increased by a factor of 1.3 after film swelling in H_2O. The films were cleaned by soaking in a 50:50 CH_3OH/H_2O mixture for 1 h and then rinsing briefly with water. Storage of the films at 4 ^{0}C ensured that reproducible data were obtained independent of their age.

Illuminations were conducted using photoreactors from borosilicate glass (internal volume = 84 mL) designed with features used in prior potentiometric and film experiments.[5,9] Displayed in Figure 3.1 a)

(a) (b)

Figure 3.1. a), image of the photochemical reactor including the lower section of the ISE. b), combination of vertically positioned glass tube, FETFE o-ring and nylon bushing cap

is an image of a typical photoreactor consisting of two vertical cylinders connected by two short and narrow (3.5 cm length, 1.1 cm diameter) glass tubes positioned horizontally; a tube placed on the top connection enabled introduction of $CHCl_3$. SPEEK/PVA films were located in the wider compartment and positioned around a glass tube placed vertically along the main axis of this vessel. Securing of the vertical tube (2.3 cm external diameter, 10.4 cm length) was achieved using a combination of FETFE o-ring and nylon bushing cap shown in Figure 3.1b. The cap was screwed to a glass adaptor fitted on top of the wider compartment; films occupied a small region defined by the inner surface of the photoreactor and the outside surface of the vertical tube. Placement of the chloride selective electrode in the wider cylindrical chamber (3 cm diameter, 11 cm height) occurred through the vertically positioned glass tube. The light-sensitive reference electrode was located in the darkened, narrower cylindrical compartment (2 cm diameter, 11 cm height) to prevent any exposure to the incoming photon flux. Perforated septa, through which tightly fitted electrodes were immersed into the solution, served to close the photoreactor. A glass joint placed on top of the narrower compartment enabled tight fitting of the septa with the reference electrode. Fitting of the septa with the ISE was ensured via widening the top 2 cm of the vertical tube by about 5 mm.

The photoreactor was filled with 54 mL of an electrolyte solution and 2 mL of $CHCl_3$ (washed several times with water to extract the stabilizer) were introduced into the closed vessel with a gas-tight syringe. Fast stirring induced circulation of the solution through the connecting tubes, ensuring that efficient equilibration was established between the two vertical compartments. $CHCl_3$ exhibits a water solubility of only 6.6×10^{-2} M (or 0.3 mL of chloroform in 54 mL of H_2O at 20 ^{0}C).[14] Hence, a large fraction of the injected chloroform remained phase-separated from the solution. Equilibration of the mixtures with the SPEEL/PVA films took place under stirring for 5 min prior to illumination; as a result the excess $CHCl_3$ was mostly present as dispersed small droplets. For equilibration times $\geq$ 5 min the rates of Cl^- photogeneration were independent on the length of this period. A few experiments with solutions of SPEEK and PVA were performed as described in Chapter II with larger vessels containing 80 mL. An ion selective electrode (ISE) from Thermo Scientific, Orion 9417BN, together with a Radiometer K601 mercurous sulfate reference electrode were used to monitor [Cl^-] *in situ* during photolysis in conjunction with a Radiometer PHM 95 instrument. Calibrations of the ISE were performed daily and yielded identical results, within experimental error, when performed in the dark or under illumination.

All irradiations were carried out, at least, twice and took place inside a Rayonet RPR-100 source equipped with 16 RPR-3500A generating of 350 (± 15 nm) photons; the temperature in the cavity of the circular illuminator was 29 °C. Variations of light intensity (I_0) were achieved via changing the number of lamps in the illuminator and I_0 was quantified by means of the Amberchrome 540 actinometer.[15] Spectrophotometric measurements employed a Shimadzu UV-Vis 2050PC instrument whereas fluorescence spectra were collected on a Shimadzu RF-5301 PC fluorimeter with an excitation wavelength of 350 nm using 1 cm quartz cuvettes. FTIR spectra were acquired by means of a Shimadzu IR Prestige-21 instrument. GC/MS determinations were conducted on samples from solutions photolyzed for 2 h by means of a Hewlett Packard 5890 Series II gas chromatograph in conjunction with a Trio 2000-1133 quadrupole mass spectrometer. A Mettler Toledo SevenMulti S80 meter in conjunction with an Accumet electrode served for [H^+] measurements.

3.3 Results and Discussion

Photolysis of SPEEK/PVA films in contact with aqueous solutions containing $CHCl_3$ and electrolytes, such as $NaClO_4$ or $NaHCO_2$, yielded significant amounts of Cl^-. No halide ions were detected during blank experiments carried out in the dark, and also when irradiation occurred without either films or electrolytes in the solution. On the other hand, the data of Figure 3.2 shows that Cl^- ions were generated upon exposure to light of an air-saturated solution containing $CHCl_3$ and $NaClO_4$ in contact with a swollen SPEEK/PVA film. An erratic formation of Cl^- took place after about 4 min, similar intervals of time (called induction periods) were noticed in all photochemical experiments and lasted between 3-14 min. These periods exhibited irreproducible changes in $[Cl^-]$ and increased in length under conditions leading to slower photoreactions including high solution pH and low I_0 values. An even longer induction period of 14 min resulted from illumination of a film in an open photoreactor, which also decreased the rate of $CHCl_3$ reduction by a factor of 2. Induction periods were also occurred during the photoassisted electrocatalytic reduction of $CHCl_3$ and CCl_4 using plasma polymerized vinylferrocence film electrodes.[16] Occurrence of such periods was interpreted as an indication that the haloamethanes needed to access specific sites on the film for the reduction to take place.

However, reduction of CCl_3F, (CFC 11) and CCl_2FCClF_2 (CFC 113) by $\bullet CO_2^-$ photogenerated in air-free TiO_2 suspensions also yielded induction periods,[17-19] and their length increased non-linearly with the O_2 amount in the suspension. Similar observations were made during the photoreduction of CCl_4 upon photolysis of degassed SPEEK/HCO_2^- solutions.[5] Increases in the length of this period were noticed under conditions leading to slow reactions, such as low light intensities and the presence of air. In addition, the findings of Chapter II included observation of short induction periods when $CHCl_3$ was photoreduced in SPEEK/HCO_2^- solutions free of O_2, but their length increased about 5 times in air saturated solutions. All these observations related the occurrence of induction periods with scavenging of the photogenerated reducing agents by O_2. Shorter induction periods were noticed in degassed solutions because they contained only traces of oxygen.

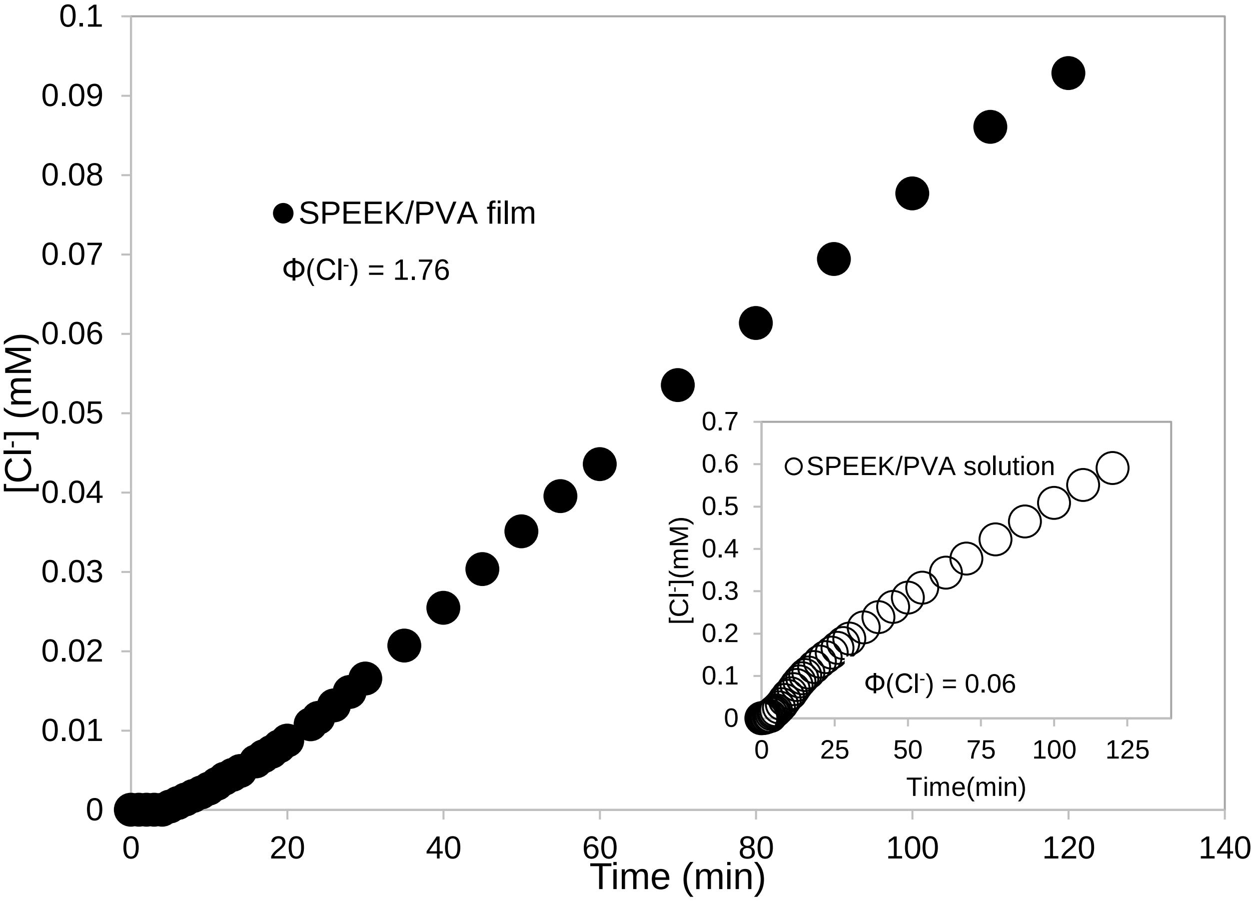


Figure 3.2 Evolution of Cl^- formation during illumination of a 80 µm SPEEK/PVA film in a 0.1 M ClO_4^- solution of pH = 6.4 containing 2 mL $CHCl_3$ under air, $I_0 = 2.2 \times 10^{-6}$ M(h*ν*)/s. Inset: photolysis of an air-saturated solution (80 mL) at pH = 7.3 containing 0.018 M SPEEK, 0.36 M PVA, 0.1 M ClO_4^- and 2 mL of $CHCl_3$, $I_0 = 3.8 \times 10^{-6}$ M(h*ν*)/s.

Such interpretation is consistent with the fact that SPEEK• photogenerated in solutions and films of SPEEK/PVA blends reduce O_2 to H_2O_2.[7,9] While the rate constant for the reaction between SPEEK• and $CHCl_3$ is not known, the α-hydroxy radical of 2-propanol, $(CH_3)_2C{\bullet}OH$, is probably a good model for the SPEEK radical. Reduction of CH_2Cl_2 and O_2 by $(CH_3)_2C{\bullet}OH$ occur rate constants of ~ 1×10^6 M^{-1} s^{-1} and 4×10^9 M^{-1} s^{-1}, respectively.[20] For air-saturated SPEEK/PVA solutions $[O_2]$ = 0.26 mM in,[7] and the solubility of $CHCl_3$ in water amounts to 66 mM,[14] If

SPEEK• reduced oxygen and chloroform with rate constants similar to those of $(CH_3)_2C•OH$ then pseudofirst-order rate constants of 1×10^6 and 6.6×10^4 s^{-1} result for the two reactions, clearly showing that the O_2 reduction predominated. Hence, in the closed photoreactors most SPEEK• reacted initially with O_2 to form H_2O_2, resulting in an induction period where very little Cl^- was generated. In addition, the data of Chapter II showed that H_2O_2 inhibited the $CHCl_3$ reduction by SPEEK• in air-containing solutions. Gradual consumption of oxygen (and H_2O_2) enabled $CHCl_3$ to increasingly compete for SPEEK•, resulting in fast Cl^- formation at the end of the induction period.

Figure 3.2 depicts a linear increase in $[Cl^-]$ with time after the induction period and the resulting slope was employed to evaluate the rates of chloride ion formation, $r(Cl^-) = d[Cl^-]/dt$. The fact that Cl^- formed according to a linear function of time indicates that the photon flux absorbed by the film controlled the $CHCl_3$ reduction. In other words, the reaction rate depended directly on the photoprocess taking place in the film that generated the reducing radicals. An analogous conclusion was reached in the case of the O_2 photoreduction induced by SPEEK/PVA films.[9] Although the Cl^- ions were photogenerated inside the swollen films, due to the continuous extraction process they migrated into solution allowing detection with the potentiometric method. Therefore, the plotted results represent concentrations resulting from dilution of the photogenerated halide ions by the solution. In order to obtain the amount of product generated inside the film a correction is required; this can be accomplished using the ratio of volumes D_f = V(solution)/V(film), where V(solution) corresponds to the solution volume and V(film) represents the volume of the swollen film.[9] Only the length and width of swollen films were accessible by direct determinations, but observations of the present study indicated each of these dimensions increases by a factor of 1.3 in during swelling. Assuming that a similar increase in thickness took place, then V(film) corresponds to $(1.3)^3$ of the volume of the dry film. A very similar relationship was found in a previous study on the photoreduction of O_2 by SPEEK/PVA films.[9] Thus, the rate of Cl^- formation corrected for dilution, $r_c(Cl^-)$, was evaluated using: $r_c(Cl^-) = D_f\, r(Cl^-)$.

Another correction pertained the light intensity reaching the polymer films, which covered only a fraction of the internal surface area of the vessel. A simple way to estimate the flux of photons absorbed by the films used the ratio of surface areas between irradiation vessel and swollen polymer blend to correct the intensity of light entering the photoreactor determined via actinometry.[9] In this approximation the intensity of photons absorbed by the films (I_c) resulted from the correction: $I_c = I_o \times SA_f$, where SA_f corresponds to the ratio of surface area of swollen film and vessel. The efficiency of chloride ion formation, $\phi(Cl^-)$, was evaluated from the corrected reaction rate and the photon flux absorbed by the film, $\phi(Cl^-) = r_c(Cl^-)/I_c$. Quantifications of $[Cl^-]$ potentiometrically exhibited a typical error of < 5% but deviations of about 20% were observed during photolysis of the SPEEK/PVA films. Similar deviations were noticed when CCl_4, $CHCl_3$ and O_2 were photoreduced in SPEEK/PVA solutions.[5-7] The deviations noticed in the present study were lower (by about 10%) than those encountered during the O_2 photoreduction induced by SPEEK/PVA films,[9] presumably because the SPEEK material derived from Solvay PEEK was significantly more photoactive than the sulfonated polyketones prepared from other precursors.[5,6] A contributing source of error, not accounted for by the actinometric determinations, involved scattering of light originating from numerous interfaces present in the photoreactor. At any rate, the large deviations in quantum yields probably reflected the rather heterogeneous nature of the polymeric photochemical systems. For these reasons the $\phi(Cl^-)$ probably represent lower limits of the reaction efficiencies.

The quantum yield of Cl^- formation derived from the data of Figure 3.2 amounted to 1.76, significantly higher than the efficiency (0.59) determined for air-saturated solutions containing HCO_2^- and SPEEK prepared from the Solvay precursor, see Chapter II. Considering that formate performed significantly better than PVA as H-atom donor in prior halomethane photoreduction experiments,[5,6] the solution experiment was repeated in the presence of the polyol instead of HCO_2^-. Displayed in the inset of Figure 3.1 are the results of such experiments, indicating that a slow Cl^- formation, $\phi(Cl^-) = 0.06$, occurred after an induction period of about 3 min. The shorter induction period of the solution experiment as compared with that obtained with the film is not surprising given that a higher light intensity was employed in the former case. Also, the headspace of the photoreactor employed in the film experiment was about 1/3 larger than that of 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.

Interestingly, the $CHCl_3$ photoreduction initiated by the film was 29 times faster than reaction induced in the SPEEK solution. A comparison of efficiencies for photoreductions initiated by SPEEK/PVA films revealed that the $CHCl_3$ transformation was 9 times higher than that of O_2.[9] These comparisons hinted the possibility of a chain process being involved in the photodehalogenation of $CHCl_3$. To test if such a possibility was reasonable, several electrolytes that could potentially act as H-atom donors were used as substitutes for $NaClO_4$. Presented in Figure 3.3 are data gathered in experiments that employed $NaHCO_2$, $NaCH_3CO_2$, K_2HPO_4 and $NaClO_4$ as electrolytes. Replacement of $NaClO_4$ by the other salts increased significantly $\phi(Cl^-)$ to values of 4.2, 11 and 19 for KH_2PO_4, $NaCH_3CO_2$ and $NaHCO_2$, respectively. Such large quantum yields are definitive evidence that chain processes took place in the presence of HPO_4^{2-}, $CH_3CO_2^-$ and HCO_2^- ions.

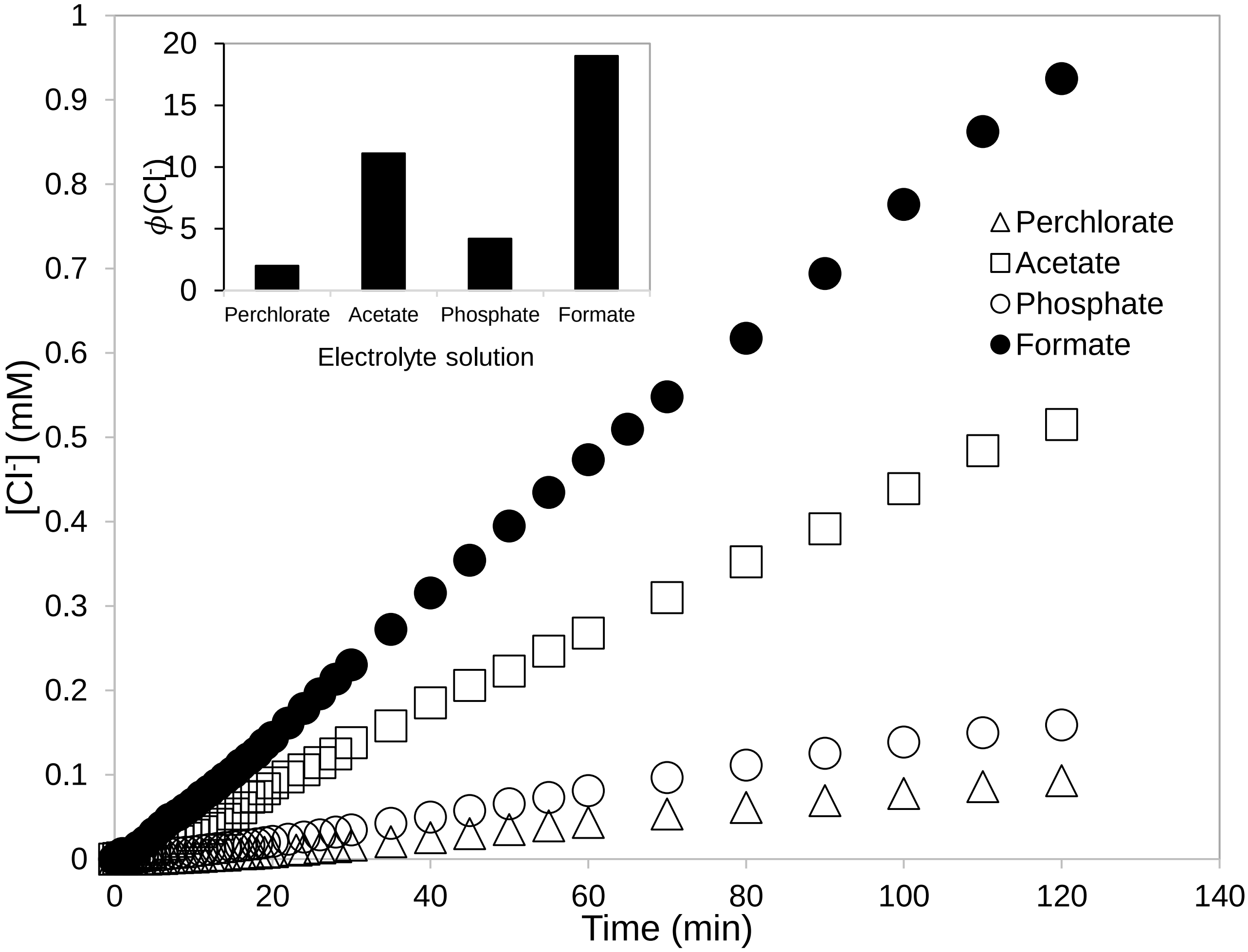


Figure 3.3. Evolution of the chloride ion concentration with time during illumination of SPEEK/PVA films (79 µm average thickness) immersed in solutions with 2 mL $CHCl_3$ and 0.1 M of: (●) HCO_2^-, pH = 7.3; (□) $CH_3CO_2^-$, pH = 7.6; (○) $H_2PO_4^-$, pH = 7.4 and (△) ClO_4^-, pH = 6.3; $I_0 = 2.2 \times 10^{-6}$ M(hν)/s. Inset: quantum yields of Cl^- ion formation using different electrolyte solutions.

Hence, the salts not only acted as inert electrolytes (needed for the proper function of the ISE) but also served as H-atom donors able to reduce the photogenerated ^{3}SPEEK* yielding SPEEK•. Thus, in systems containing electrolytes other than $NaClO_4$ the triplet excited state of SPEEK reacted not only with PVA according to reaction 3.1, but also with HCO_2^- to generate SPEEK• via reaction 3.2, as well as with the other anions through analogous H-atom abstraction steps. Since

H-atom abstraction by ^{3}SPEEK* from ClO_4^- is not possible, the $CHCl_3$ reduction observed in the presence of $NaClO_4$ was due to formation of SPEEK• via reaction of by ^{3}SPEEK* with PVA present in the film. The higher $\phi(Cl^-)$ values obtained with electrolytes different from $NaClO_4$ indicate not only that HPO_4^{2-}, $CH_3CO_2^-$ and HCO_2^- were able to diffuse into the swollen SPEEK/PVA films, but that they also reacted with ^{3}SPEEK* via H-atom abstraction reactions in a way more efficient than PVA. Although acetate and formate contain C-H functions (known to act as H-atom

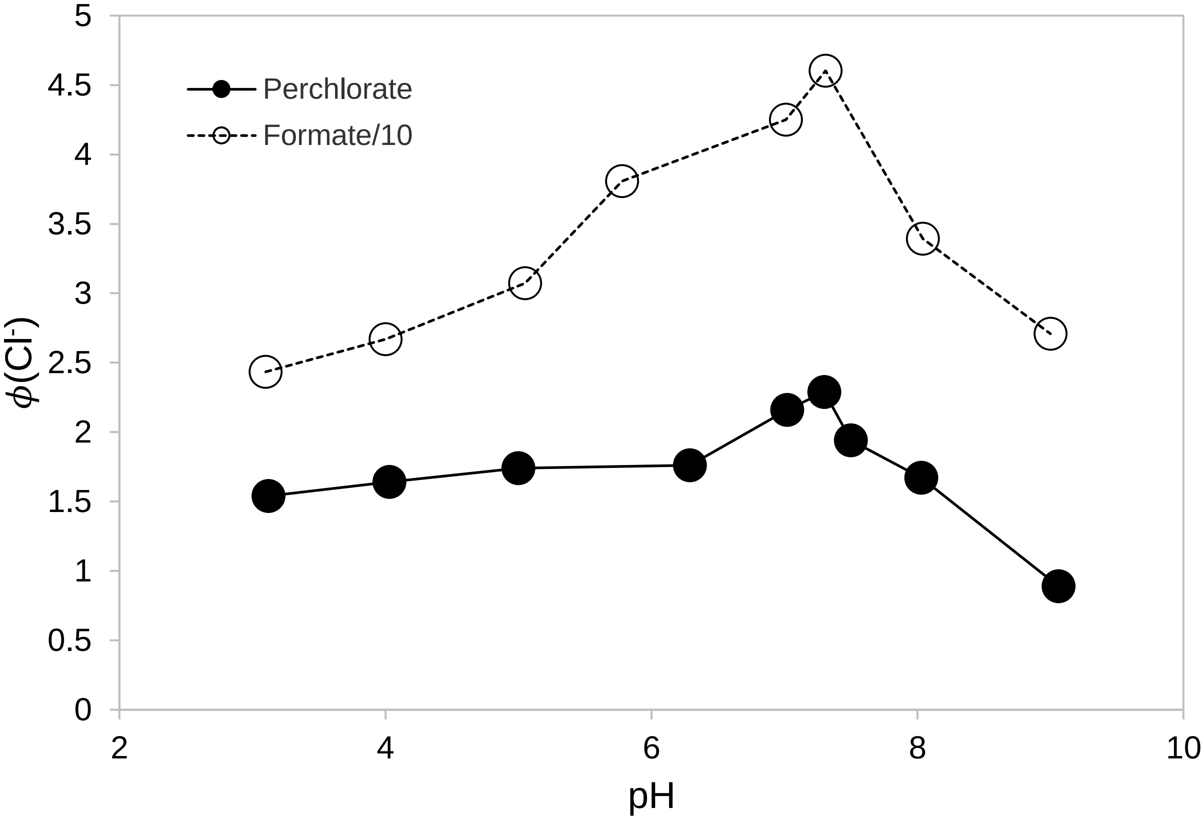


Figure 3.4. Efficiency of Cl^- ion formation as a function of pH during photolysis of SPEEK/PVA films (80 μm average thickness) in solutions containing 2 mL $CHCl_3$ and: (●) 0.1 M ClO_4^-, or (○) 0.36 M HCO_2^-, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s. The reaction efficiencies of formate solutions were divided by 10.

donors), no such groups are found in the case of the phosphate ions. The fact that $\phi(Cl^-)$ was larger in the presence of HPO_4^{2-} than with $NaClO_4$ suggested that the phosphate ions were more efficient donors of H-atoms that PVA, which constituted a somewhat surprising finding.

According to the data from the solution photoreduction of $CHCl_3$ presented in Chapter II, the highest efficiency occurred at a pH of 7.3 and $[HCO_2^-] = 0.36$ M. Therefore, the pH dependence of the $CHCl_3$ photoreduction induced by polymer films was explored using 0.36 M HCO_2^- in attempts to optimize the efficiency of this process. Illustrated in Figure 3.4 are the results, the data collected in experiments with formate ions was divided by 10 in order to simplify the presentation. For all pH values the efficiency obtained using HCO_2^- ions was about 20 times higher than the $\phi(Cl^-)$ values from $NaClO_4$ solutions. These results agree completely with observations from earlier studies with SPEEK solutions indicating that HCO_2^- acted as a more efficient H-atom donor than PVA.[5,6] Another significant observation was that, except for the $\phi(Cl^-)$ decline above pH 7.3, the efficiencies obtained in the presence of $NaClO_4$ were not very sensitive to the solution pH. Although the O_2 photoreduction induced by SPEEK/PVA films exhibited a fairly constant efficiency in the neutral range, $\phi(Cl^-)$ decreased substantially in the acidic and basic regions.[9] These results reflected the rather constant photogeneration efficiency for SPEEK• in neutral solutions, together with the decreases (by a factor of about 3) in radical formation efficiencies outside this pH range.[7]

Quantum yields in excess of 20 were obtained in solutions containing HCO_2^- and the efficiencies increased by about 2 with decreasing $[H_3O^+]$. This resulted in a $\phi(Cl^-)$ maximum of 46 at pH = 7.3, followed by a decline when [OH-] increased. Changes in $\phi(Cl^-)$ even more drastic than those depicted in Figure 3.4 were observed during the photoreductions of both CCl_4 and $CHCl_3$ induced by SPEEK in air-free solutions containing the presence of formate ions.[5,6] Since the triplet excited state of BP is quenched efficiently by H_3O^+ ($k_q = 7 \times 10^8$ M^{-1} s^{-1});[21] an analogous quenching of ^{3}SPEEK* by hydronium ions was proposed to explain the lower efficiencies of the SPEEK photochemistry in acid solutions.[5-7,9]

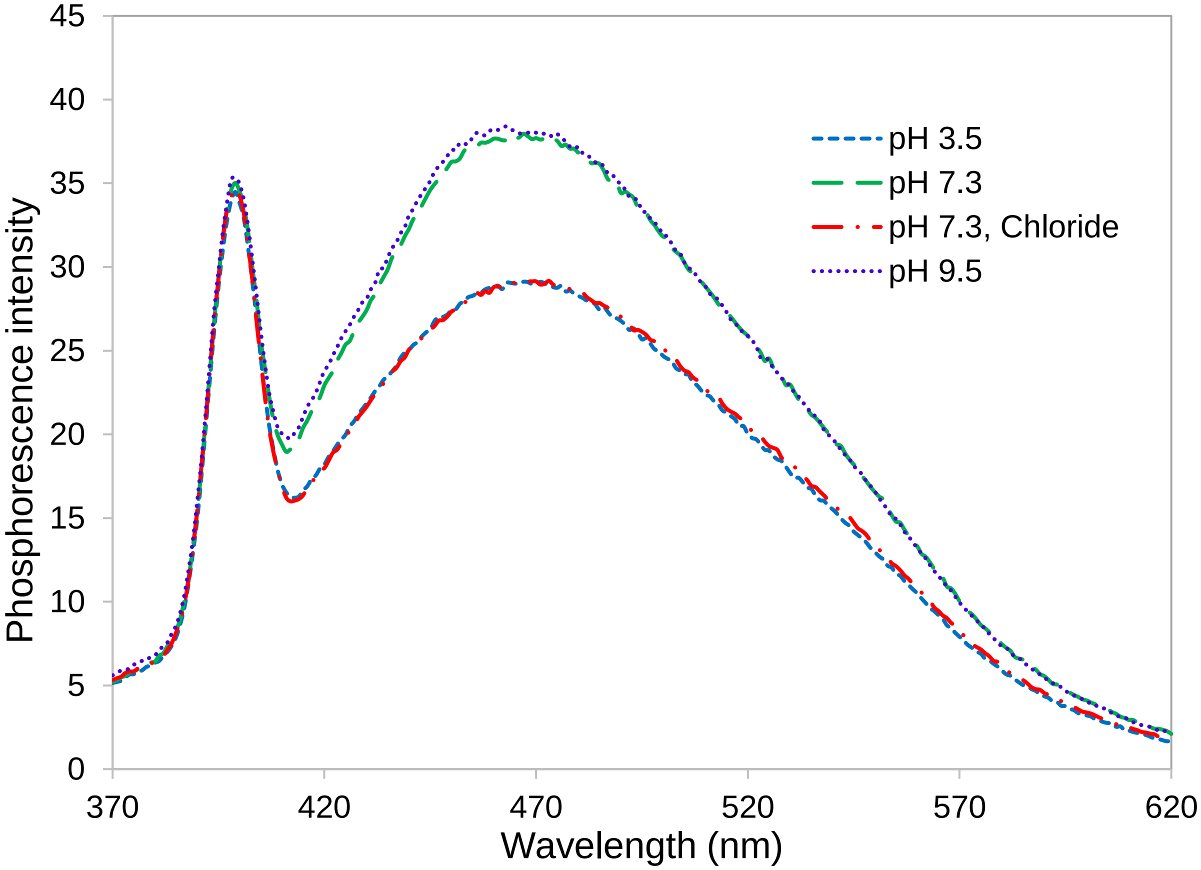


Figure 3.5. Emission spectra of 0.018 M aqueous SPEEK solutions at different pH values and in the presence of 1 x 10^{-4} M Cl^- at pH = 7.3; excitation wavelength = 370 nm.

Such possibility was tested via monitoring the emission of SPEEK in solution, depicted in Figure 3.5 are the results of the experiments. The emission spectrum in water at pH = 7.3 exhibited a spectrum with a broad signal centered at λ_{max} = 465 nm resembling somewhat the one determined for poly(p-vinylbenzophenone), pVBP, a compound frequently used as a model of polymeric benzophenones.[22] No changes in the emission spectrum of SPEEK were noticed in solutions with and without air, supporting an earlier conclusion that quenching of ^{3}SPEEK* by O_2 is not important in H_2O.[7] On the other hand, increasing $[H_3O^+]$ to 1 mM with $HClO_4$ lowered the SPEEK emission by about 30%. Obviously, quenching of ^{3}SPEEK* by hydronium ions via energy transfer caused the drop of $\phi(Cl^-)$ shown in Figure 3.4 at low pH values.

The BP triplet excited state is quenched by OH^- with $k = 5 \times 10^6\ M^{-1}$,[23] implying that an analogous quenching process involving ^{3}SPEEK* may have contributed to the lowering of $\phi(Cl^-)$ at high pH values. However, raising the pH from 7.3 to 9.5 had no impact in the SPEEK emission spectrum presented in Figure 3.5, indicating that quenching of ^{3}SPEEK* by OH^- was not a relevant factor. As was shown in Chapter II, significant curvature of plots depicting $[Cl^-]$ vs irradiation time was noticed during the $CHCl_3$ reduction in SPEEK solution, but only when the halide ion concentrations resulting from the photoreaction exceeded about 0.2 mM. Cl^- is a weak quencher of the BP triplet excited state, $k_q = 2.2 \times 10^5\ M^{-1}\ s^{-1}$,[23] and the behavior noticed during the solution photoreduction of $CHCl_3$ may have resulted from quenching of ^{3}SPEEK* by the halide ion. If that was the case, relatively high Cl^- concentrations would be required for the quenching effect to be noticeable. As illustrated in Figure 3.5 the presence of 0.1 mM Cl^- in the solution decreased the emission intensity at 465 nm by about 30%, supporting the rationalization of the previous investigation.

Interestingly, very little curvature was noticed during the evolution of $[Cl^-]$ presented in Figure 3.3 for concentrations lower than 0.5 mM. Thus, the Cl^- quenching effect seemed to be even weaker when SPEEK was confined to films instead of being dissolved in solution. Such scenario appeared reasonable as the continuous extraction method involved conditions (large D_f values) favoring migration of Cl^- into the solution and away from the film. Unequivocal confirmation that the growth in $[Cl^-]$ deviated from a linear pattern resulted from an experiment lasting 5 h of continuous exposure to light. The data shown in Figure 3.6 clearly demonstrated that significant curvature in the formation of Cl^- with time occurred when halide ion concentrations higher than 2.5 mM were reached. A significant yellow coloration of the film took place during the long exposure due to LAT formation, which was discussed extensively in Chapter II. No significant pH changes occurred in that experiment since the HCO_2^-/HCO_2H mixture present in the aqueous phase buffered any H_3O^+ ions produced during the $CHCl_3$ photoreduction.

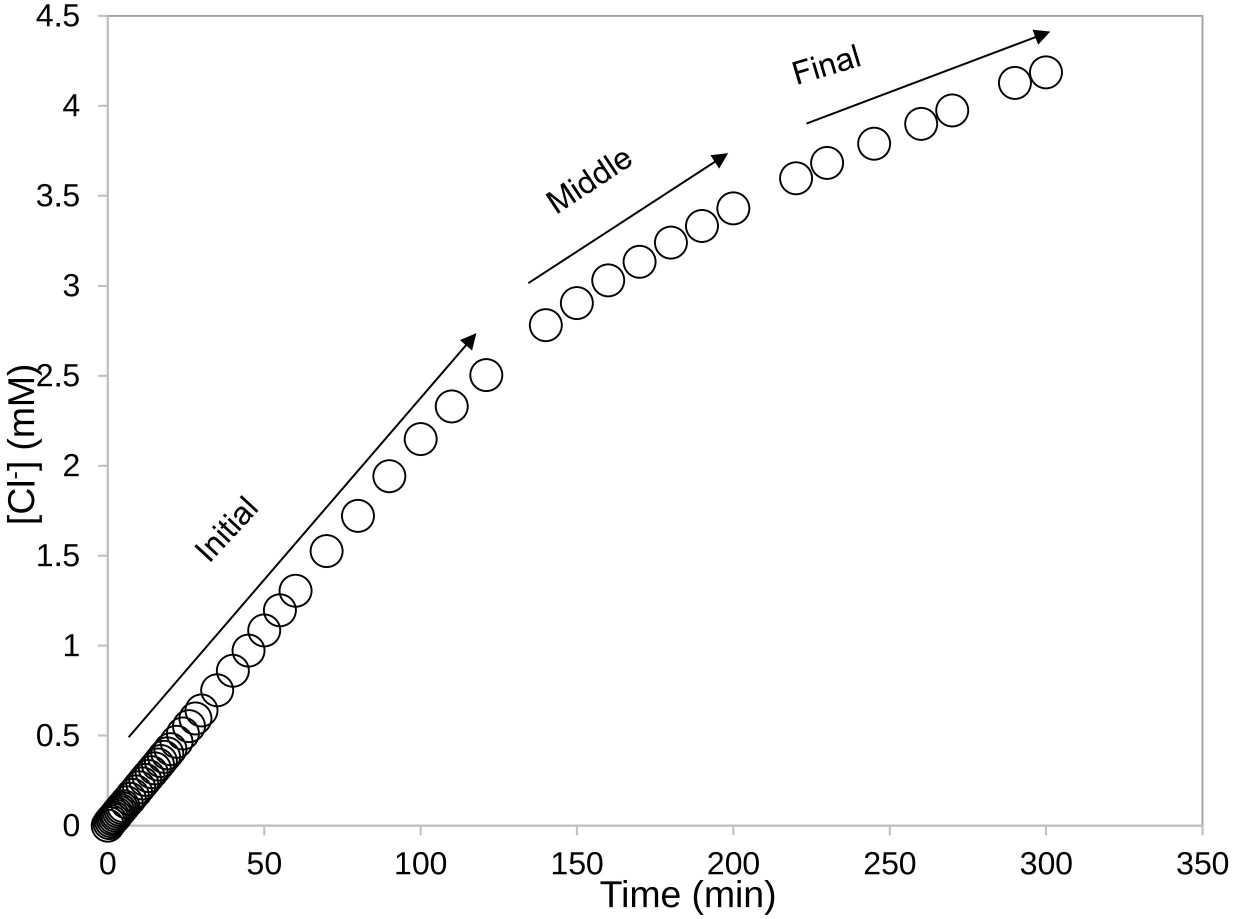


Figure 3.6. Evolution of the chloride ion concentration with time for long time illumination of a 77 µm SPEEK/PVA film in 0.36 M HCO_2^- solution of pH 7.3 containing 2 mL $CHCl_3$, $I_0 = 2.2 \times 10^{-6}$ M (hν)/s.

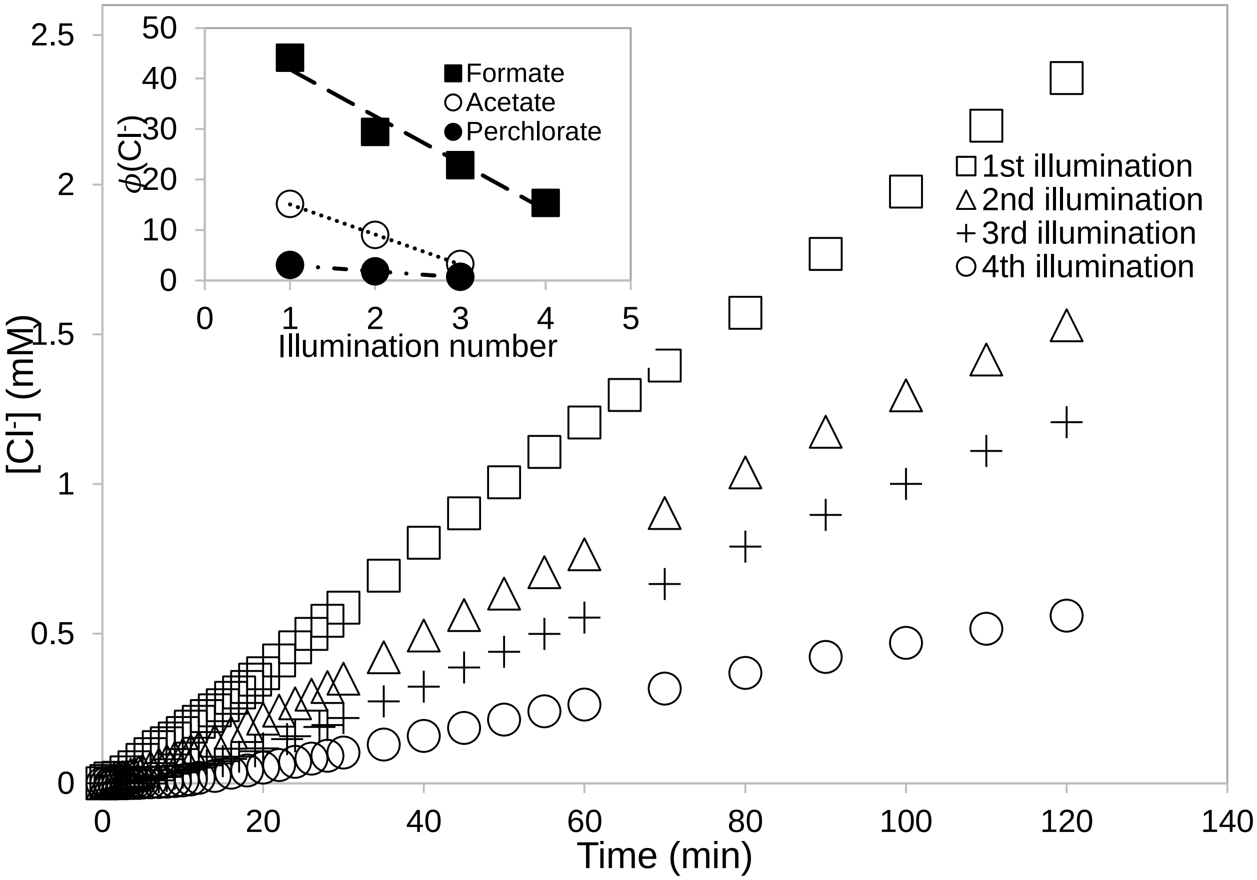


Figure 3.7. Evolution of Cl^- ion concentration with time during repeating illumination of a SPEEK/PVA film in 0.36 M HCO_2^- solution of pH 7.3 containing 2 mL $CHCl_3$ with $I_0 = 2.2 \times 10^{-6}$ M (hν)/s. The inset shows the dependence of ϕ(Cl^-) on illumination cycle for films photolyzed in the presence of: (■) 0.36 M HCO_2^-, film thickness = 80 μm); (○) 0.1 M $CH_3CO_2^-$, film thickness = 64 μm); and (●) 0.1 M ClO_4^-, film thickness = 80 μm. Other conditions as described in the main figure.

Another plausible explanation for a non-linear increase in [Cl^-] with illumination time involved a change in the photochemical reactivity of the SPEEK/PVA films. In order to test this possibility a photoreduction of $CHCl_3$ was carried out for 2 h and then the employed film was cleaned according to the procedure outlined in the Experimental Section to extract any remaining reaction products. The treated film then experienced further cycles of illumination and cleaning. Illustrated in Figure 3.7 are kinetic results regarding Cl^- formation from a SPEEK/PVA film in solutions containing 0.36 M HCO_2^- subjected to 4 cycles of exposure to light followed by cleaning. Although linear increases in $[Cl^-]$ resulted for all experiments, the efficiency of the photoreduction decreased steadily as the number of cycles increased. As shown in the inset of Figure 3.7, $\phi(Cl^-)$ declined nearly linearly with increasing illuminations. Included in the inset of Figure 3.7 are data from analogous experiments carried out in solutions containing either acetate or perchlorate ions, indicating that similar decreases in $\phi(Cl^-)$ also occurred in such systems. Despite the losses of photochemical efficiency the SPEEK/PVA films still exhibited impressive quantum efficiencies in the presence of HCO_2^- after long illumination periods.

The decreases in photoreaction efficiency of the films even after thorough and repeated cleansing are not well explained in terms of $^3SPEEK^*$ quenching by Cl^- ions trapped in the film. In fact, HCl serves as a catalyst during cross-linking of PVA present in the solid polymer blends and the acid was successfully eliminated from the films with the same cleaning procedure employed after each photolytic exposure. An obvious possibility involved chemical changes of the films originating from the irradiations. Analysis of IR spectra seemed a straightforward way to determine if such changes took place given that the infrared signals displayed by the films have been assigned.[4] Presented in Figure 3.8 are typical IR bands of SPEEK/PVA films located in the frequency range of 1550 -1800 cm^{-1}. The signals centered at 1599 and 1648 cm^{-1} were previously assigned to the CO group from SPEEK, whereas the broad absorption above 1700 cm^{-1} originates from CO groups of PVA.[4]

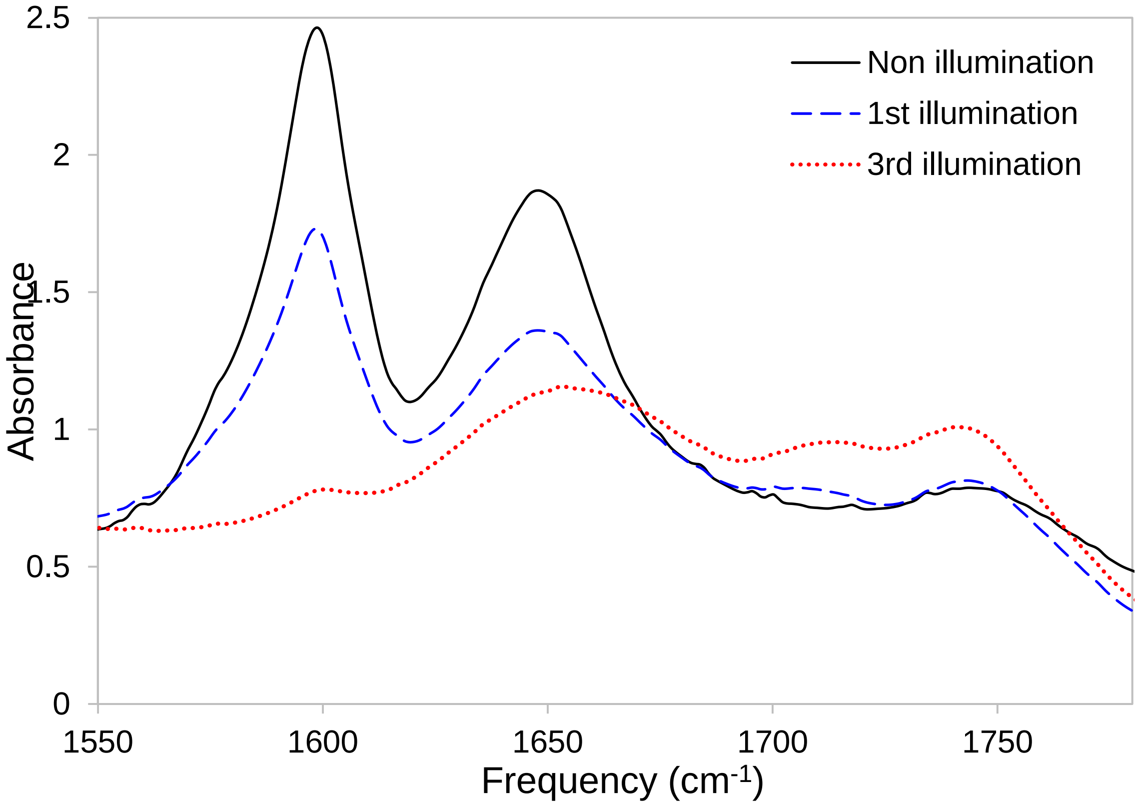


Figure 3.8. FTIR spectra from the non-illuminated 80 µm SPEEK/PVA film, and also after the 1st and 3rd illumination cycles in a 0.1 M ClO_4^- solution at pH = 7.3 with 2 mL $CHCl_3$, $I_0 = 2.2 \times 10^{-6}$ M (hν)/s.

The data of Figure 3.8 clearly shows that the intensity of the SPEEK carbonyl group decreased while that from the CO functions of PVA increased as a result of illumination, and that these changes grow with increasing cycles of light exposure. Given that oxidation of OH functionalities from PVA produced carbonyl groups, the FTIR data clearly showed that illumination induced consumption of the functional groups involved, via reaction 3.1, in the photogeneration of SPEEK•. Similar changes were previously detected during photochemical reactions of dry SPEEK/PVA films.[4] Oxidation of some OH groups from PVA was not expected to affect significantly the film photochemistry due to the large excess of polyol present in the solid blends.

However, consumption of the CO groups from SPEEK was definitely a key contributor to the decline in the film photoactivity since they are critical for the absorption of photons by SPEEK. As mentioned in Chapter II, dimerization of SPEEK• and reaction of this species with $\bullet CO_2^-$ (or PVA•) are possible pathways leading to cross-linking of the polymers or LAT formation. Both of these processes lead to consumption of SPEEK carbonyl groups and loss of photochemical activity.

Previous investigations with SPEEK/PVA films have employed a polyketone/polyol composition of 30/70 wt % which resulted from optimizations of the Ag^+ photoreduction.[2,4,9] Efforts were made to find out if such composition was well suited to achieve efficient photoreactions. The results presented in Figure 3.9 indicate that a maximum in efficiency occurred with films exhibiting a composition of 17/83 wt % SPEEK/PVA. A drastic drop of efficiency was noted for films with a SPEEK concentration lower than 17%. Since PVA remains in excess for all films the findings were analyzed only in terms of effects induced by the SPEEK changes. As the chomophoric BP groups are located on SPEEK chains, lowering the amount of polyketone beyond such concentration diminished the ability of the solid blends to absorb photons effectively. Increasing the SPEEK content above 17% seemed to decrease the efficiency of the photoreaction as well. However, the differences in $\phi(Cl^-)$ for films containing between 17 and 45% SPEEK were not far from those originating from experimental error. A maximum $\phi(Cl^-)$ also occurred during the CCl_4 photoreduction in SPEEK solutions and decreases in efficiency were noticed at polyketone concentrations above the maximum.[5] Quenching of the BP triplet excited state by benzophenone molecules is fast in H_2O, $k_q = 1.8 \times 10^8 M^{-1} s^{-1}$.[24]

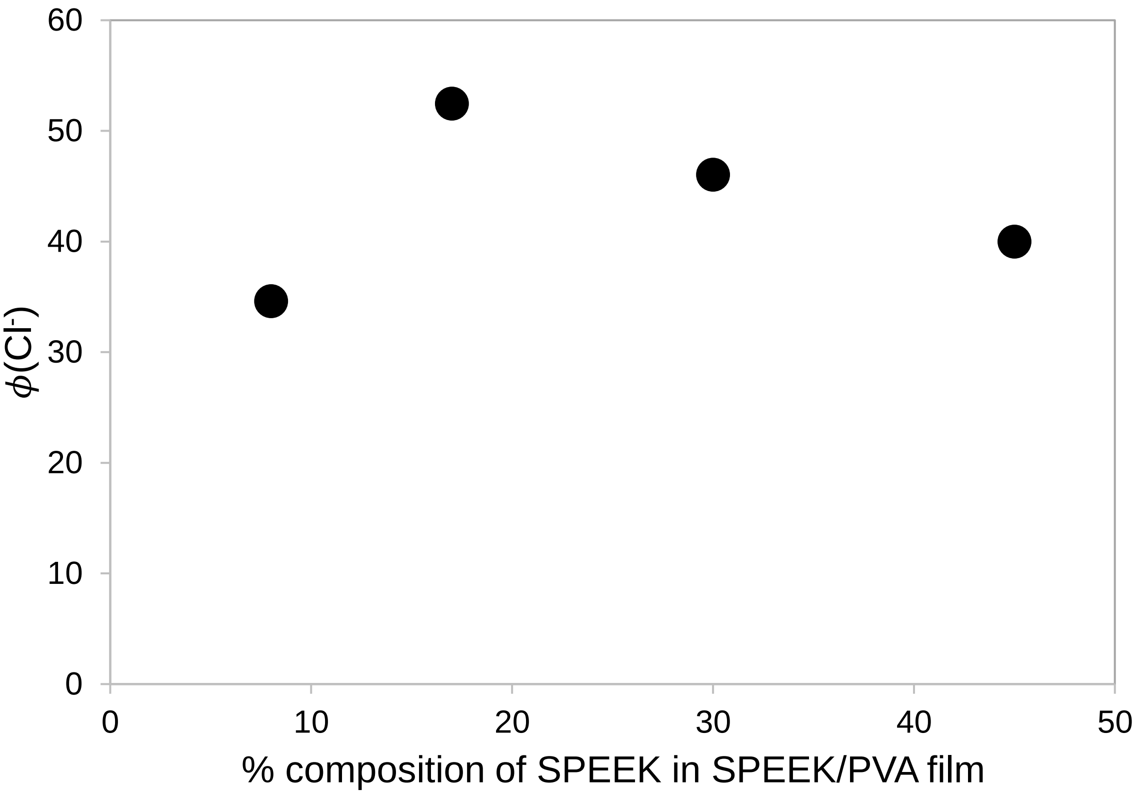
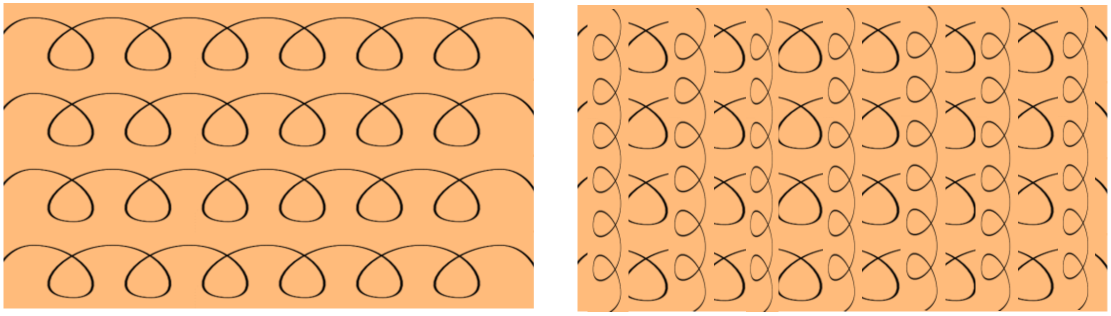


Figure 3.9. Change of $\phi(Cl^-)$ as a function of % composition of SPEEK in SPEEK/PVA film during illumination of films (60 μm average thickness) immersed in 0.36 M HCO_2^- aqueous solutions at pH = 7.3 containing 2 mL $CHCl_3$, $I_0 = 2.2 \times 10^{-6}$ M (hν)/s.



(a)

(b)

Figure 3.10. Assumed schematic structure of: (a) film with a low % of SPEEK and: (b) film containing a high content of SPEEK.

In the case of pVBP simultaneous intramolecular self-quenching of CO groups and triplet-triplet annihilation occurred.[25] The latter process requires formation of two or more ^{3}SPEEK* per chain, an unlikely event at the low I_0 employed. The data of Figure 3.9 can be understood if intermolecular quenching of SPEEK triplet states by benzophenone groups from other SPEEK molecules took place, as in the BP case.[24] Figure 3.10 shows idealized representations of the changes envisioned when the SPEEK concentrations increased. These changes lowered the PVA concentration, inducing closer packing of the polyketone chains that forced a closer proximity of BP groups from different chains. This, in turn, facilitated intermolecular quenching of excited BP groups functions and decreased the efficiency of SPEEK• generation.

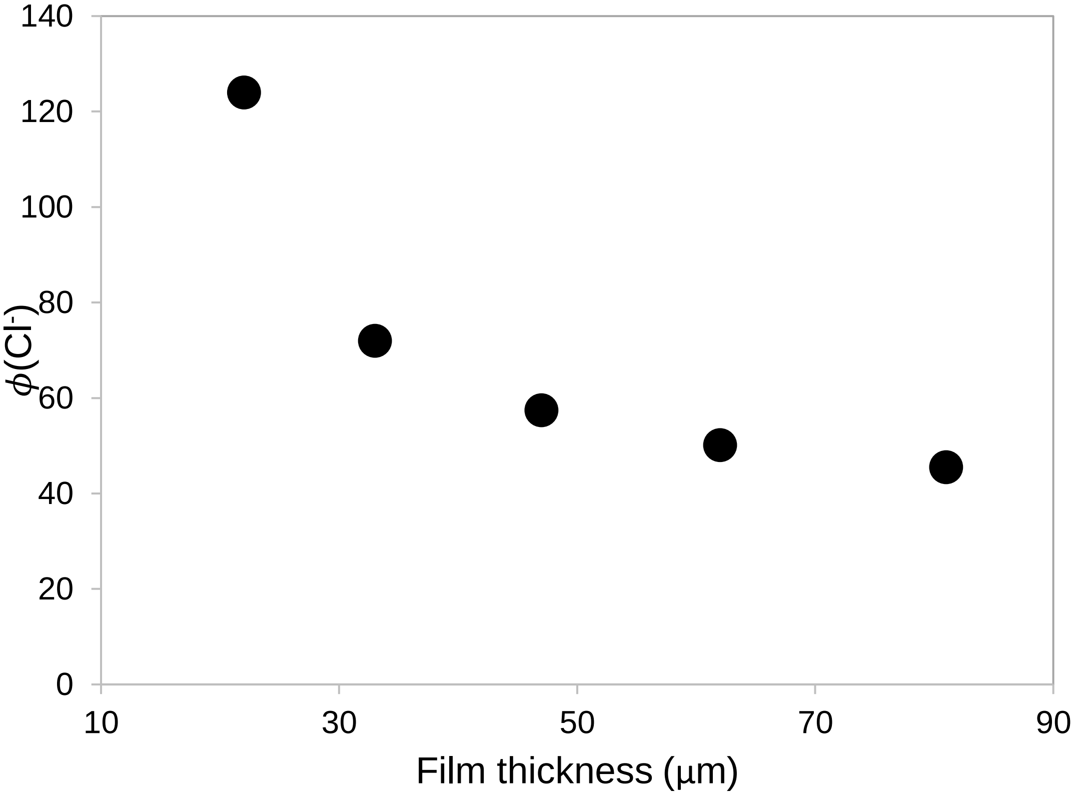


Figure 3.11. Dependence of $\phi(Cl^-)$ on the thickness of the SPEEK/PVA films containing 30% of SPEEK, immersed in solutions at pH = 7.3 with 0.36 M HCO_2^- and 2 mL $CHCl_3$; $I_0 = 2.2 \times 10^{-6}$ M (hν)/s.

Further tests were conducted to ascertain if film thickness influenced the rate of the $CHCl_3$ photoreduction maintaining all other experimental parameters constant. Interestingly, the data presented in Figure 3.11 indicate that $\phi(Cl^-)$ followed an inverse dependence on thickness. Changes in efficiency within experimental error were determined in the thickness range of 47 - 80 µm, but much larger enhancements occurred for thinner films. A simple rationalization of these observations assumes that for thicker films the chain photoreduction of $CHCl_3$ occurred mainly inside the swollen polymer matrix. However, migration of mobile chain carriers into the solution bulk became feasible for films with a thickness lower than about 40 µm. EPR results shown in Chapter II identified $\bullet CH_2Cl$ and SPEEK• as carriers of the chain $CHCl_3$ photoreduction in SPEEK solution. However, only $\bullet CH_2Cl$ can migrate outside the films as the macromolecular radicals are trapped within the cross-linked solids. H-atom abstraction from HCO_2^- by $\bullet CH_2Cl$ was anticipated to generate $\bullet CO_2^-$, a species that is a stronger reductant than SPEEK•.[5] Hence, propagation of the chain process in solution probably involved reduction of $CHCl_3$ by $\bullet CO_2^-$. As will be shown below, such process seemed not feasible inside the swollen films as this radical experienced dimerizarion, or reaction with SPEEK•, when confined within the solid polymer matrices. Chain processes involving $\bullet CO_2^-$ were anticipated to occur with higher efficiencies in solution given that no SPEEK macromolecules (able to scavenge the carboxyl radical anion) were present outside the films. In this scenario chain reductions involving only SPEEK• were confined within swollen SPEEK/PVA films. More efficient chain reductions involving $\bullet CO_2^-$ as a chain carrier spilled outside the swollen polymer matrices, which was possible only for thinner films.

The solution data presented in Chapter II indicated that increases in $\phi(Cl^-)$ occurred when $CHCl_3$ amounts higher than the solubility limit in water were employed during photochemical experiments. Similar findings were noticed in the reduction of CFC11 that involved participation of photogenerated $\bullet CO_2^-$.[26] Presented in Figure 3.12 are results obtained from a series of experiments that tested the influence of the $CHCl_3$ amount present during illumination. The data indicated that a roughly constant efficiency resulted when the amount of halomethane present was within the solubility limit in water.

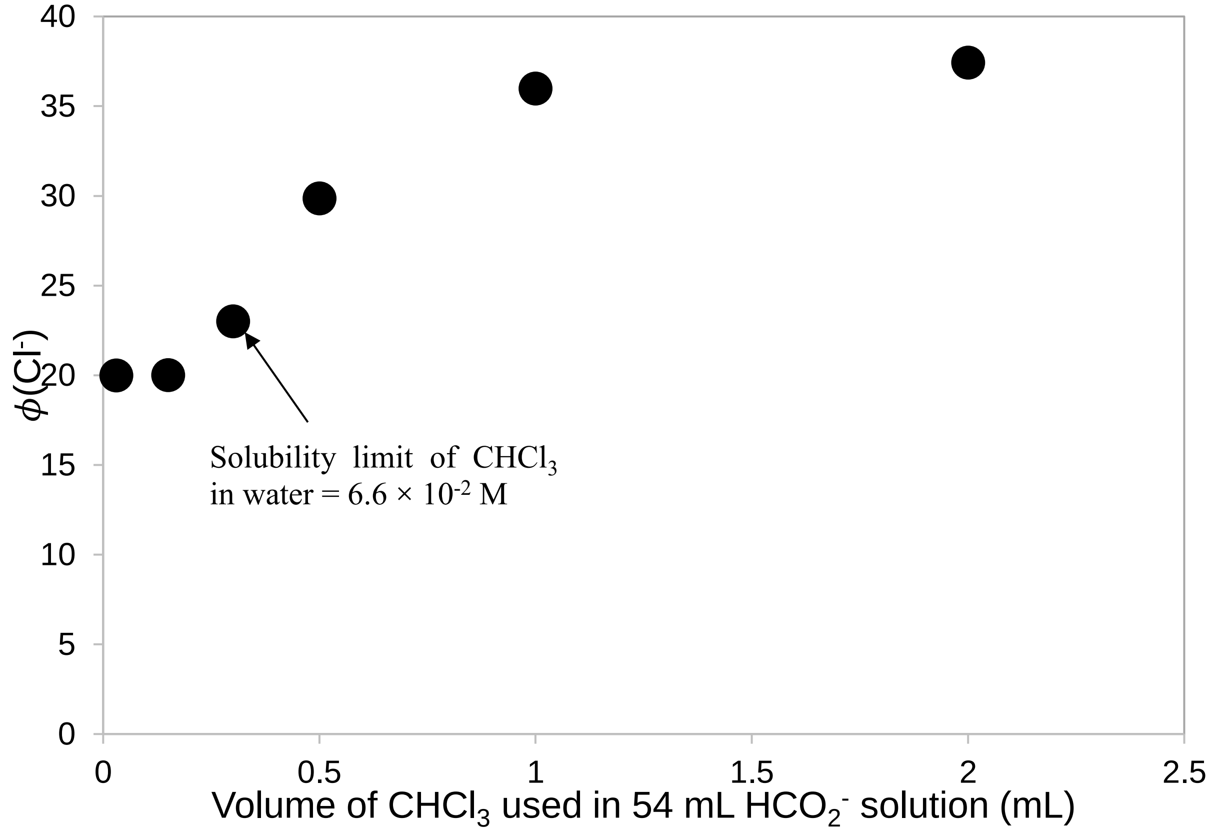


Figure 3.12. Efficiency of Cl^- photogeneration as a function of the $CHCl_3$ volume present in solutions containing 0.36 M HCO_2^- at pH 7.3 equilibrated with immersed SPEEK/PVA films (60 µm average thickness), $I_0 = 2.2 \times 10^{-6}$ M(hν)/s.

In contrast, a significant increase in $\phi(Cl^-)$ was noticed when $CHCl_3$ volumes larger than the solubility limit were added, reaching about a 100% increase in efficiency in systems containing 2 mL of halomethane. As discussed in Chapter II, these observations implied that the phase-separated $CHCl_3$ was able to participate in the photoreaction. Transformations of reactants located in different phases can be rationalized qualitatively assuming that partially miscible liquids are separated by a thin interfacial region.[27] In this explanation, a gradient of $[CHCl_3]$ exists across the interfacial region with the highest concentration at the organic phase and the lowest (the solubility limit in H_2O) at the border with water.[27] The photoreduction was assisted by the interfacial region via facilitating the transport of $CHCl_3$ between organic and aqueous phases. This explanation required the presence of $CHCl_3$ droplets within the swollen films in order for the bonded SPEEK• to be able to reach the water-containing interfacial region where reduction of $CHCl_3$ took place. The higher $[CHCl_3]$ present in the interfacial enabled an additional reduction channel operating in conjunction with the reduction process occurring away from the droplets.

GC-MS determinations were conducted on solutions photolyzed in the presence of films for extended times. Only CH_2Cl_2 was detected as a product from the photoreaction while CO_2 and $CHCl_2$-$CHCl_2$ were not found. These two compounds were identified in Chapter II as by-products photogenerated in air-free solutions. Since dimerization of $\bullet CH_2Cl$ generates $CHCl_2$-$CHCl_2$ the absence of this compound excluded such possible radical termination process. CO was identified in Chapter II as a product during the $CHCl_3$ photoreduction in the presence of air. Although the present experiments were conducted in air-saturated systems, the absence of CO as a product supports the assumption that the photoreduction of $CHCl_3$ started only after most of the O_2 was reduced by SPEEK•. Hence, the photoreaction seemed to have occurred in an environment closed to air-free .

The absence of CO_2 as a reaction product implies that most of the photogenerated $\bullet CO_2^-$ reacted either with SPEEK• to form LAT, or dimerized forming oxalate ions. Unfortunately, detection of such ions in solutions containing high [HCO_2^-] is not feasible experimentally. SPEEK/PVA films turned intense yellow under extended illumination, which is known to result from LAT formation.[4] The main features of the photoreaction are well rationalized in terms of a mechanism analogous to the one proposed in Chapter II for the chain phototransformation of $CHCl_3$ in air-free SPEEK/formate solutions:

$$\{RRC{=}O\}_z + h\nu \rightarrow {}^3\{RRC{=}O\}_z^* \tag{3.3}$$

$$^3\{RRC{=}O\}_z^* + HCO_2^- \rightarrow {\bullet}CO_2^- + \{RRC{\bullet}OH\}_z \tag{3.4}$$

$$^3\{RRC{=}O\}_z^* + \{CH_2CHOH\}_y \rightarrow \{CH_2C{\bullet}OH\}_y + \{RRC{\bullet}OH\}_z \tag{3.5}$$

$$\{RRC{=}O\}_z + \{CH_2C{\bullet}OH\}_y \rightarrow \{CH_2CO\}_y + \{RRC{\bullet}OH\}_z \tag{3.6}$$

$$\{RRC{\bullet}OH\}_z + CHCl_3 \rightarrow {\bullet}CHCl_2 + Cl^- + H^+ + \{RRC{=}O\}_z \tag{3.7}$$

$${\bullet}CHCl_2 + \{CH_2CHOH\}_y \rightarrow \{CH_2C{\bullet}OH\}_y + CH_2Cl_2 \tag{3.8}$$

$$R{\bullet} + R'{\bullet} \rightarrow \text{products} \tag{3.9}$$

Step 3.9 represents a summary of three possible termination processes: dimerization of the carboxyl radical anion ($R{\bullet} = R'{\bullet} = {\bullet}CO_2^-$), formation of LAT ($R{\bullet}$ = SPEEK• = $\{RRC{\bullet}OH\}_z$, $R'{\bullet} = {\bullet}CO_2^-$), and dimerization/disproportionation of the polymer radical ($R{\bullet} = R'{\bullet}$ = SPEEK•, or $R{\bullet} = R'{\bullet}$ = PVA• = $\{CH_2C{\bullet}OH\}_y$). In this mechanism the chain carriers are SPEEK•, PVA• and ${\bullet}CHCl_2$; higher reaction efficiencies were achieved than in solution because dimerization of the polymer radicals was restricted by their bonding to the film.[9] This mechanism captures the main features of the photoreaction but fails to explain the sharp $\phi(Cl^-)$ increase shown Figure 3.4 that takes place in neutral solutions. The results confirmed that such unusual feature is characteristic of solutions containg HCO_2^-. A possible origin for such behavior may be related to specific interactions between formate ions and the polyelectrolyte domains present in SPEEK systems.

3.4 Conclusion

These results demonstrated that an efficient reduction of $CHCl_3$ was achieved via illumination of swollen SPEEK/PVA films. A chain process more efficient than the one taking place in aqueous solutions containing both the polyketone and the polyol was induced using the crosslinked-films as sensitizers. Very large quantum yields of reaction were determined in neutral solutions that contained additional H-atom donors such as HCO_2^-, but the efficiency dropped in the acidic range due to quenching of the excited state from SPEEK by hydronium ions. Although the films continued to function efficiently after long illumination periods, a decrease in the photoactivity resulted under repeated use because of consumption of the benzophenone groups acting as chromophres. Further optimization work is needed to circumvent this problem and need to address radical recombination and LAT formation processes, which are the origins for the reduction of the BP groups.

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Chapter IV

Radical Chain Reduction of CCl_4 Initiated by Illumination of SPEEK Solutions

4.1 Introduction

Chemical reductions provide a direct and efficient pathway for the elimination of halide ions from halogenated organic compounds. Dehalogenations are particularly attractive in the case of compounds that are resistant to oxidative attack, such as CCl_4. Earlier studies have identified α-hydroxy radicals of simple alcohols as suitable reactive intermediates able to reduce CCl_4.[1-5] Efforts to transform this chlorocarbon effectively are motivated by the toxicity coupled with the frequent presence of CCl_4 as a contaminant in water.[6,7] Light-induced reductions of halocarbons are particularly appealing since photons serve as the energy source for radical formation. Oxide semiconducting or mineral particles have served as sensitizers dispersed in aqueous solutions for the reduction of halocarbons via free radicals.[8-11] Efficient reductions of CCl_4 also occurred in homogeneous solutions when molecular sensitizers photogenerated the reducing radicals.[12-19] Dehalogenations initiated by photoreactive macromolecules have been limited to the use of a copolymer of sodium poly(styrenesulfonate) and 2-vinylnaphthaline.[20] While this polymer enabled some dissolution of hexachlorobiphenyl in water, only slow transformations resulted under irradiation presumably because the reaction involved singlet oxygen instead of reducing radicals.

An alternative approach for the photogeneration of reducing radicals employs mixtures of the Na^+ salt of sulfonated poly(ether-etherketone), SPEEK, and poly(vinyl alcohol), PVA.[21-24] Formation of α-hydroxy radicals of the polymeric ketone proceeds in a way analogous to that for the system comprising of benzophenone (BP or $(Ph)_2C=O$) and 2-propanol.[25] Exposure to light forms a triplet (n, π*) excited state of BP groups present in the polyketone, which then abstracts an H-atom from PVA forming a radical denoted as SPEEK•. The concurrently formed α-hydroxy radical of PVA (PVA•) may reduce a second polymeric BP functionality, resulting in up to two SPEEK• per absorbed photon. SPEEK• is able to reduce O_2 forming H_2O_2 either in aqueous solutions or in swollen SPEEK/PVA polymer films.[21,22] Several metal ions (Ag^+, Au^{3+} and Cu^{2+}) are reduced by this radical to metallic crystallites in the absence of air.[24] Furthermore, the sensitizing ability of SPEEK persists over long times in the presence of radical scavengers that regenerate the polyketone via oxidation of SPEEK•.[23]

Prior observations indicated that the sensitizing properties of solutions containing SPEEK/PVA mixtures (or blends) resemble those of heterogeneous and also of homogeneous systems. For instance, attempts to analyze the photochemical data of such solutions using kinetic parameters of homogeneous systems result in contradictions.[21,22] This is not surprising since polyelectrolytes partially aggregate in water,[26] implying that solutions of a charged macromolecule such as SPEEK were anticipated to contain some aggregates. Also, polymeric benzophenones exhibit a "local reactant concentration" effect, as demonstrated for poly(vinylbezophenone), pVBP.[27] This means that the amount of reactant present next to the BP groups of SPEEK is different from the bulk concentration. Further evidence of the non-ideal behavior of SPEEK/PVA solutions included a very slow second-order decay of SPEEK radicals via dimerization/disproportionation with a rate constant of $k = 290\ M^{-1}\ s^{-1}$.[24] Such a value is more than 6 orders of magnitude smaller than rate constants for the diffusion controlled radical-radical decay of PVA•, and of $(Ph)_2C{\bullet}OH$ (the α-hydroxy radical of BP).[28,29] In fact, SPEEK• persists for several min in the absence of air but the decay is accelerated upon stirring the solutions.

The dehalogenation of CCl_4 via reaction with SPEEK• seemed feasible, particularly in view of the long lifetime of this radical in air-free solutions. Relevant thermodynamic data includes the oxidation potential for the polyketone radical estimated to be about 1.2-1.4 V,[24] whereas E°[CCl_4/•CCl_3, Cl^-)] amounts to -0.23 V.[30] Also, reduction of CCl_4 was shown to occur upon reaction with $(CH_3)_2C$•OH, •CO_2^- and the α-hydroxy radical of 4-(dimethylamino)benzophenone (4DMBP).[1-5,10,11,14-18] Redox data for the first two radicals exist, E°[$(CH_3)_2C$•OH/$(CH_3)_2C$=O, H^+] = 1.4 V and E°[•CO_2^-/CO_2] = 1.8 V.[31] For the radical of 4DMBP the reduction potential in CH_3CN is about 20% higher than that of $(Ph)_2C$•OH.[32] Hence, a similar relationship between the oxidation potentials of these benzophenone radicals was anticipated in H_2O, where E°[$(Ph)_2C$•OH/$(Ph)_2C$=O, H^+] = 1.31 V.[33] These results are indicative that a substantial driving force exists for the CCl_4 reduction by the α-hydroxy radicals originated from photolysis of SPEEK systems.

Pathways for the dehalogenation of CCl_4 involving α-hydroxy radicals proceed sometimes via selective and efficient chain reactions.[1-5] Such processes seemed attractive as potential means for the selective transformation of CCl_4 into $CHCl_3$ since chloroform is an industrially valuable chemical.[34] Experiments were, therefore, conducted to test the ability of SPEEK/PVA blends as photoinitiators of the CCl_4 reductive dehalogenation. Previous investigations have shown that efficient and selective dehalogenations of CCl_3F and CCl_2FCClF_2 were possible in systems that photogenerated •CO_2^- as the reducing agent.[35,36] Interestingly, quenching of the BP excited state by HCO_2^- ions efficiently forms $(Ph)_2C$•OH in a process involving •CO_2^-.[29,37] For this reason the carboxyl radical anion was expected to form via reaction of the triplet (n, π*) excited state of BP groups from SPEEK with formate ions. Experiments were, therefore, conducted to test the ability of SPEEK as a photoinitiator for the CCl_4 reduction using either PVA or HCO_2^- ions as donors of

H-atoms. Evidence will be presented that CCl_4 undergoes a chain dehalogenation, which is particularly efficiently in the presence of HCO_2^- ions.

4.2 Experimental

Poly(vinyl alcohol), 99 % hydrolyzed with an average molar mass of 8.9-9.8 x 10^4 g/mol as well as CCl_4 and $CHCl_3$ were obtained from Sigma Aldrich. KCl, NaOH, $NaClO_4$, $NaCO_2H$, HCO_2H, H_2SO_4 and $HClO_4$ were purchased from Fisher Scientific. Samples of poly(ether etherketone), PEEK, were provided as gifts by Victrex (APTIV 1000-075, average molar mass of $M_n = 4.5 \times 10^4$ g/mol) and Evonik (VESTAKEEP L4000G, $M_n = 5 \times 10^4$ g/mol or L5000G, $M_n = 5.7 \times 10^4$ g/mol). PEEK served as a precursor of the sodium salt of SPEEK, which was obtained via sulfonation in H_2SO_4 as described before.[21,24] SPEEK samples derived from Evonik PEEK will be denoted as E-SPEEK whereas those prepared from the Victrex precursor will be called V-SPEEK. All aqueous solutions were prepared with water purified with a resin deionizer (U.S. Filter Service), or by means of a Milli-Q Biocel system.

Unless otherwise stated, the photolyzed solutions contained 1.6 wt.% PVA and 0.7 wt.% SPEEK, which in terms of monomer units correspond to 0.36 M of polyol and 0.018 M of polyketone. They were prepared from concentrated stock solutions that, as usual, were filtered (Whatman cat # 1450) prior to mixing and dilution. SPEEK/PVA solutions also contained 0.1 M $NaClO_4$ as an inert electrolyte needed for potentiometric determinations; pH values were adjusted with NaOH and $HClO_4$. Alternatively, solutions containing 0.018 M SPEEK and $HCO_2H/NaCO_2H$ buffers were utilized, where sodium formate served as the inert electrolyte. Throughout this study the buffer concentration is given in terms of $[HCO_2H] + [HCO_2^-]$.

Air-free systems were obtained by bubbling 75 mL of aqueous solutions with Ar for 30 min under stirring in sealed photochemical reactors. CCl_4 was washed several times with H_2O to eliminate the stabilizer and then degassed via three freeze-pump-thaw cycles. Gas-tight syringes were subsequently used to inject 1-2 mL of degassed CCl_4 into sealed photoreactors containing Ar-saturated solutions. Two liquid phases formed due to the low solubility of carbon tetrachloride in H_2O (5.1×10^{-3} M or 37.5 μL CCl_4 in 75 mL of aqueous solution).[38] The mixtures were stirred for an equilibration period of 5 min prior to illumination, which created numerous small droplets of CCl_4 liquid distributed throughout the aqueous phase. Rates of the photochemical reaction were independent on the length of this period for equilibration times ≥ 5 min. Concentrations of Cl^- were monitored *in situ* using an ion selective electrode (ISE) from Thermo Scientific in conjunction with a Radiometer K601 mercurous sulfate reference electrode and Radiometer instrumentation as described previously.[35]

Given that the reference electrode is sensitive to light, special photochemical reactors of borosilicate glass with an internal volume of 96 mL were utilized. The vessels consisted of two vertical cylinders connected by two short and narrow (2 cm length, 1.2 cm diameter) glass tubes positioned horizontally; a narrow tube vertically positioned on top enabled Ar bubbling (an image of a photoreactor is included in the TOC graphic). Glass joints located on top of the vertical cylinders served to seal the vessel by means of perforated septa, through which tightly fitted electrodes were immersed into the solution. The ISE was placed in the wider cylindrical chamber (3.5 cm diameter, 8 cm height) whereas the narrow compartment (1.8 cm diameter, 8 cm height) contained the reference electrode. This compartment was darkened to shield the reference electrode from light. Fast equilibration of the liquid present in the vertical compartments occurred under stirring, which induced circulation of the solution through the connecting tubes. Calibration and actinometry experiments were also conducted with the narrow compartment shielded from light.

Photolysis experiments were conducted at room temperature (23 °C) using a PTI 1010S system equipped with a 150 W Xe arc lamp producing photons with $320 \leq \lambda \leq 385$ nm. To extend the range of light intensities, a Rayonet circular illuminator equipped with sixteen RPR-3500Å lamps was also employed. Photons with $\lambda = 350 \pm 15$ nm were generated in this fashion and the temperature inside the illuminator was 29 °C. Irradiations at lower temperatures were possible using a photoreactor featuring a water jacket connected to a Fisher Isotemp 9500 bath circulator. Both photochemical systems have been described before, including the actinometric method for light intensity (I_0) determinations.[22,35] Illuminations were performed, at least, in duplicate under constant stirring; deviations of 25% were noted periodically. Optical spectra were recorded on a Shimadzu UV-Vis 2501PC spectrophotometer; GC/MS determinations utilized a Hewlett Packard 5890 Series II gas chromatograph coupled to a Trio 2000-1133 quadrupole mass spectrometer whereas detection of oxalate ions employed a Dionex QX-120 chromatograph. Differential scanning calorimetry (DSC) data were acquired using a Mettler Toledo FP90 instrument equipped with a FP84HT hot stage. Measurements of $[H^+]$ employed a Mettler Toledo SevenMulti S80 meter in conjunction with an Accumet electrode. In this chapter, all of the data for V-SPEEK has been imported from the previous work done by J. R. Black.

4.3 Results and Discussion

Illumination of aqueous SPEEK solutions with or without air that contained only CCl_4 failed to generate any Cl^- ions. In contrast, an earlier study has shown that photolysis of ketones dissolved in CCl_4 yields HCl and C_2Cl_6, the product from the dimerization of $\bullet CCl_3$ radicals.[39] This transformation was rationalized in terms of formation of an exciplex involving the excited ketone and CCl_4, which subsequently decayed to the observed products. The lack of Cl^- photogeneration in SPEEK solutions without H-atom donors seemed reasonable since formation of an analogous exciplex was impeded by the inability of the charged polyketone to migrate into the CCl_4 phase. Further control experiments performed in the dark, as well as irradiations of solutions containing PVA or HCO_2^- but without either SPEEK or CCl_4, also failed to produce Cl^- ions. Photolysis of SPEEK solutions free of air and CCl_4 that contained PVA yielded a signal due to SPEEK• with a wavelength of maximum absorbance (λ_{max}) at 565 nm.[24] This optical signal was also detected in systems containing HCO_2^- as the H-atom donor, but not in the presence of CCl_4 indicating that SPEEK• was able to reduce the chlorocarbon.

Presented in Figure 4.1 are kinetic results illustrating the evolution of [Cl^-] as a function of irradiation time for air-free solutions at pH = 6 containing 0.018 M SPEEK and 0.36 M formate buffer for SPEEK polymer prepared from either Evonik or Victrex precursors. Included in this Figure are values of [Cl^-], multiplied by 10, obtained from photolysis of a solution at pH = 6 containing 0.018 M V-SPEEK, 0.36 M PVA as the H-atom donor and 0.1 M $NaClO_4$. All photoreactions proceeded via two steps: an initial induction period lasting up 0.5-3 min, followed by a step where [Cl^-] increased linearly as a function of time. Rates of Cl^- photogeneration, r(Cl^-) = d[Cl^-]/dt, were determined from the slope of the linear increase in [Cl^-]. The reaction rates remained unchanged in SPEEK solutions containing 1 or 2 mL of excess CCl_4, or when 0.1 M $NaClO_4$ was added to SPEEK solutions containing the formate buffer. Systematic deviations of 20% were noticed during evaluations of the quantum yield of chloride ion formation, $\Phi(Cl^-) = r(Cl^-)/I_0$. Similar variations occurred during the photogenertion of H_2O_2 in SPEEK solutions, and seemed to originate from the rather heterogeneous nature of the polymer systems.[22] Light scattering from the CCl_4 droplets formed upon stirring the solutions with excess chlorocarbon also contributed to the error. Hence, the calculated Φ(Cl^-) values represent lower limits of the quantum efficiencies of Cl^- formation.

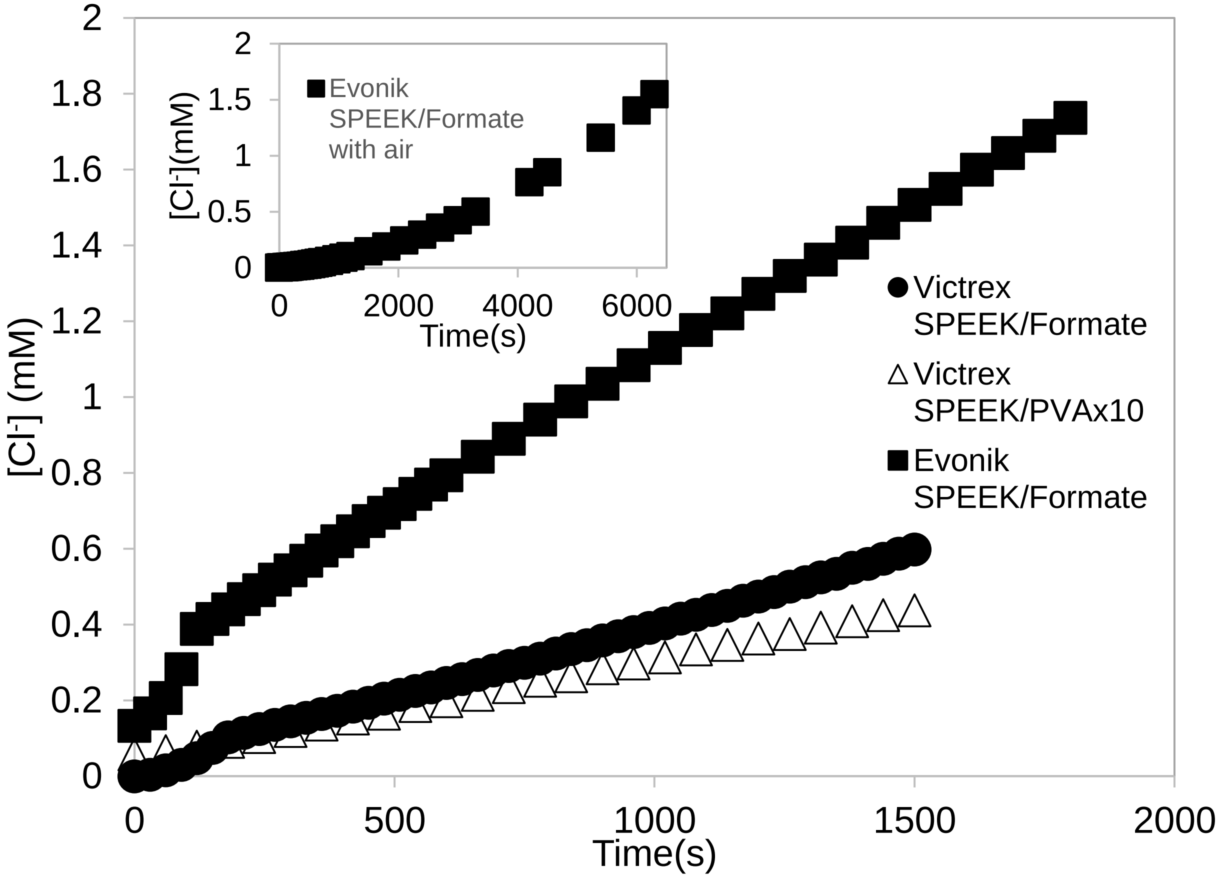


Figure 4.1. Evolution of the chloride ion concentration during photolysis of degassed solutions at pH = 6 containing 1 mL CCl_4, 0.018 M SPEEK and 0.36 M formate buffer (●), or [PVA] = 0.36 M and 0.1 M $NaClO_4$ (△) with $I_0 = 9 \times 10^{-7}$ M (hν)/s, T = 23 °C. SPEEK from Victrex precursor; [Cl^-] values multiplied by a factor of 10 for system with PVA and $NaClO_4$. Experiments with SPEEK from the Evonik precursor used similar solutions with 0.36 M formate buffer, T = 29 °C, $I_0 = 7.8 \times 10^{-7}$ M(hν)/s in the absence of air (■); inset: data obtained with air (□) and $I_0 = 4.3 \times 10^{-7}$ M(hν)/s.

In general, the length of the induction period was irreproducible and independent of reaction conditions but increased markedly with decreasing I_0. During the induction period the amount of Cl^- formed constituted a small fraction of the linear change noticed thereafter. Most of the $[Cl^-]$ increases during this period were slow and obeyed no simple rate law but short bursts of Cl^- formation took place occasionally. Similar observations made during the reduction of CCl_3F and CCl_2FCClF_2 in TiO_2 suspensions were consistent with scavenging of the photogenerated reducing radicals by trace amounts of O_2 left after degassing.[35,36] Different findings were obtained for solutions containing 50% or more of 2-propanol, where the chain transformations of CCl_4 was faster with air than without.[2,5] This behavior appeared odd since radical reactions are usually inefficient when air is present but O_2 transforms $\bullet CCl_3$ into $CCl_3O_2\bullet$,[40] which can oxidize 2-propanol 100 times faster than the precursor radical.[4,41] In fact, $CCl_3O_2\bullet$ acted as an efficient chain carrier during the CCl_4 reduction in water/alcohol mixtures containing air.[42] These findings prompted speculations that CCl_4 reductions were always accelerated by O_2 even in the presence of only traces of this gas.[2]

Possible effects of O_2 on the reduction of CCl_4 were tested using an air-saturated solution containing formate buffer and E-SPEEK; the results are shown in the inset of Figure 4.1. Obviously, the presence of air increased the induction period by a factor of about 10; similar observations were made previously during the photoreductions of CCl_4 and CCl_3F.[16,43] The induction period originates from the competition between O_2 and CCl_4 for the photogenerated reducing radicals but oxygen reduction by SPEEK• yields H_2O_2, another radical scavenger.[22] Thus, longer induction periods were expected for systems containing significant amounts of O_2, in agreement with the findings shown in Figure 4.1. Unlike the results of H_2O/2-propanol systems,[2,5] the data of Figure 4.1 clearly demonstrated that $r(Cl^-)$ was higher for the degassed solution. In fact, the quantum efficiency of solutions initially containing O_2 approached the value determined for the air-free system only after ≈ 90 min of photolysis.

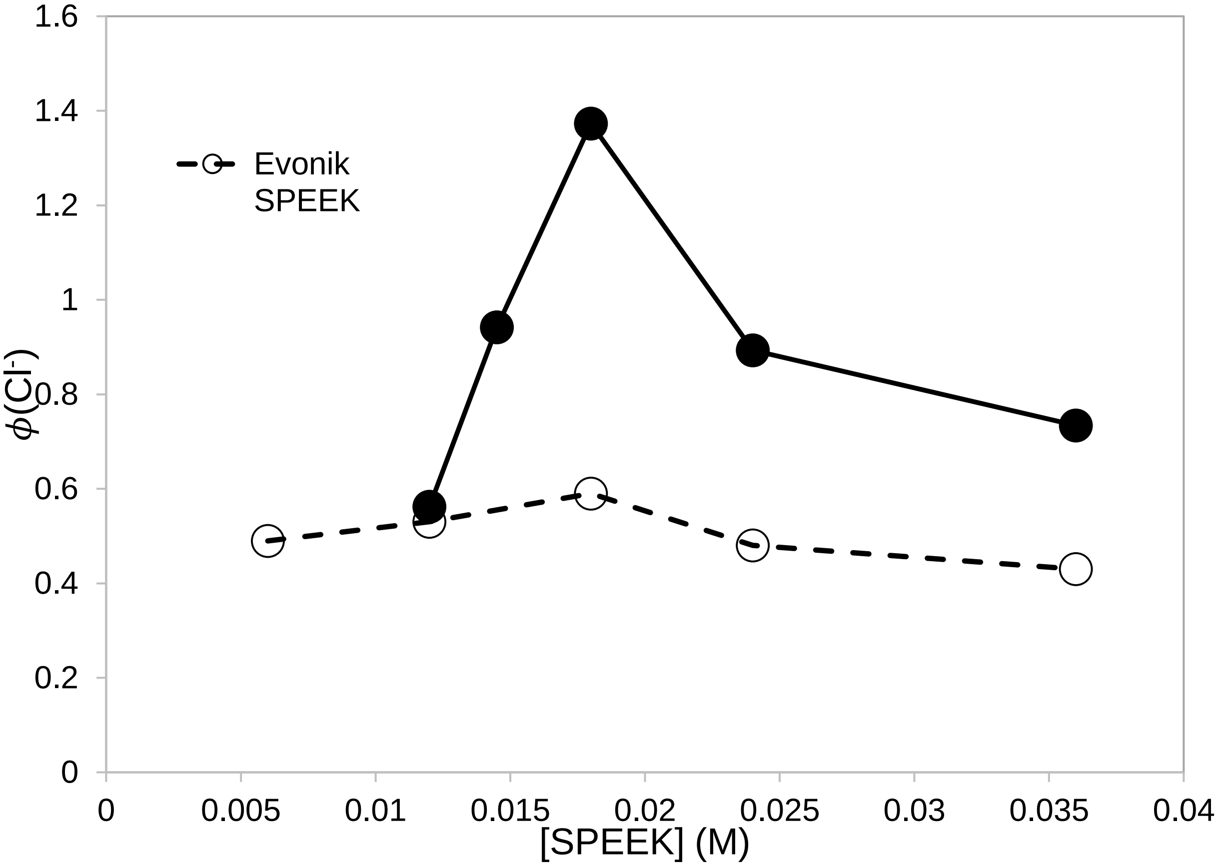


Figure 4.2. Dependence of quantum yield of Cl^- formation on [SPEEK] for polyketone prepared from Victrex PEEK (●). Degassed solutions at pH = 7.3 containing of 1 ml of CCl_4, 0.36 M formate buffer exposed to 9×10^{-7} M(hν)/s, T = 23 °C. Data obtained from Evonik precursor (○) was done at I_0= 2.15×10^{-6} M(hν)/s, T = 29 °C.

According to Figure 4.1 the rate determined for the PVA solution was about 10 times smaller than the $r(Cl^-)$ value obtained in the presence of formate ions although the concentration of polymeric alcohol groups was equal to $[HCO_2^-]$. Such findings seemed to indicate that HCO_2^- acted more efficiently as a H-atom donor than PVA. However, further results to be presented later made evident a more complex origin for the different rates obtained with PVA and HCO_2^-.

Another significant finding was that the photoreaction occurred with $\Phi(Cl^-) = 0.97$ in degassed HCO_2^- solutions containing E-SPEEK whereas the quantum yield amounted to 0.38 using the polyketone derived from the Victrex precursor. As will be shown later, the CCl_4 photoreduction took place via chain processes irrespective of the precursor used to prepare the sensitizer. Utilization of Arrhenius parameters typical for such processes indicated that the difference in temperature between the experiments with E-SPEEK and V-SPEEK only partially accounted for the variation in reaction efficiencies.

Figure 4.2 shows the evolution of $\Phi(Cl^-)$ as a function of [polyketone] for V-SPEEK or E-SPEEK solutions at pH = 7.3 containing 0.36 M HCO_2^- ions. The efficiency of the photoreduction increased rapidly with rising [SPEEK] until a maximum was reached at 0.018 M, followed by gradual decreases in $\Phi(Cl^-)$ upon further augmenting the polymer concentration. Complete absorption of the photons entering the solution by the macromolecular sensitizer seemed certain in view of the extinction coefficient (900 M^{-1} cm^{-1} for V-SPEEK and 600 M^{-1} cm^{-1} for E-SPEEK) per monomer unit at 350 nm.[24] Furthermore, the triplet excited state of SPEEK was anticipated to form with a quantum yield close to 1 given that pVBP exhibited such a formation efficiency.[44] In this scenario, a maximum quantum yield of reducing radicals of 2 was predicted but lower $\phi(Cl^-)$ values were found. Thus, a significant fraction of the photogenerated radicals were lost before reacting with CCl_4 most probably via radical-radical combination. Self-exchange processes entail electron and proton transfer to ketone groups located nearby and are known to occur for α-hydroxy radicals of BP.[45] Occurrence of self-exchange reactions provided a pathway for SPEEK• to escape combination and obviously became faster with increasing [polyketone]. Consequently, the initial rise of $\Phi(Cl^-)$ in Figure 4.2 can be understood if higher amounts of radicals escaped combination because of self-exchange processes facilitated by increases in [SPEEK].

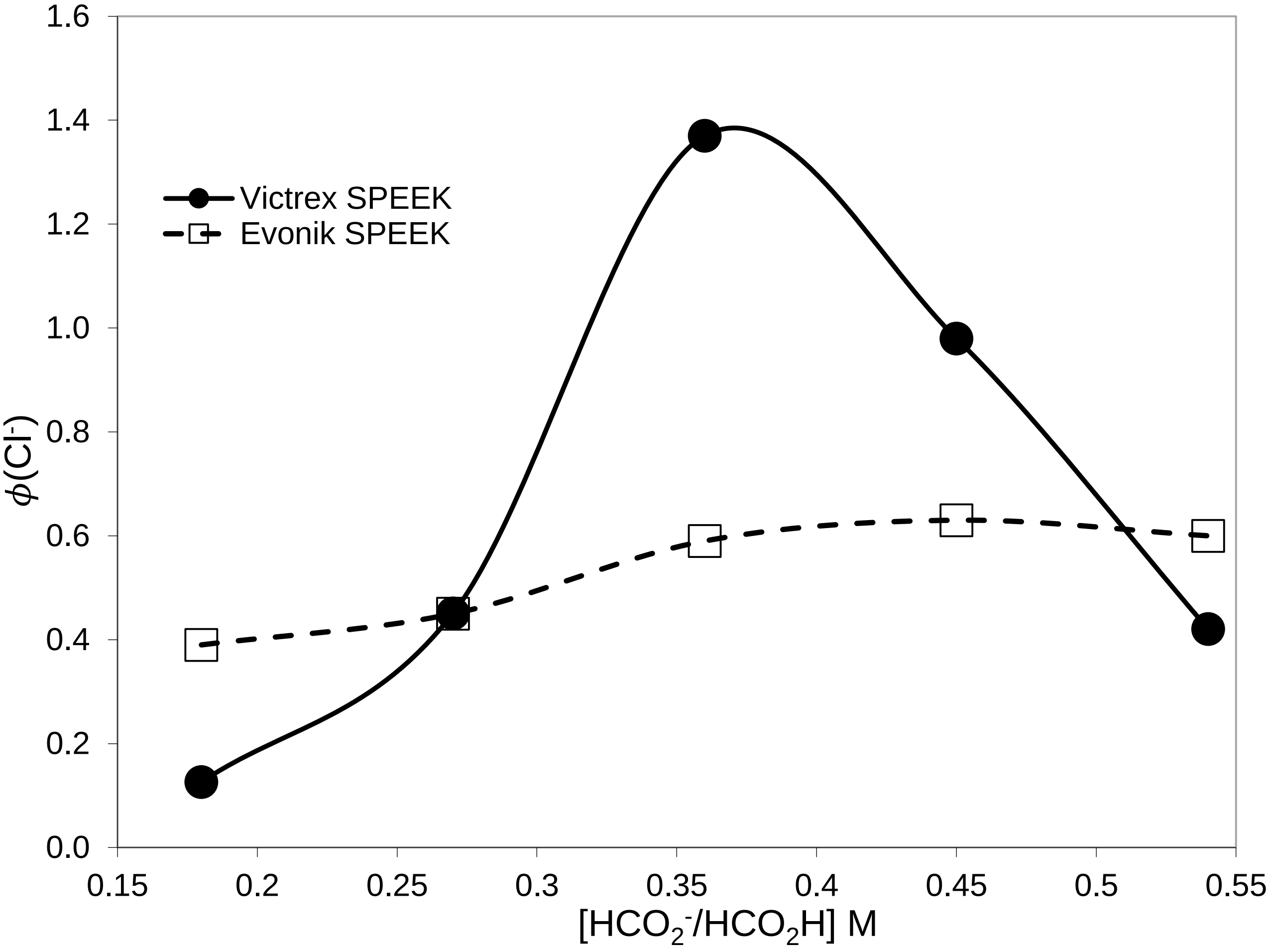


Figure 4.3. Quantum yield of Cl^- formation as a function of $[HCO_2/HCO_2^-]$ for degassed solutions at pH = 7.3 containing 1 ml of CCl_4, 0.018 M V-SPEEK (●) exposed to light with I_0 = 9×10^{-7} M(hν)/s, T = 23 °C and E-SPEEK (☐) exposed to light with $I_0 = 2.13 \times 10^{-6}$ M(hν)/s, T = 29 °C.

On the other hand, quenching of the BP triplet excited state (^{3}BP*) by benzophenone molecules is known to occur fast in H_2O, $k_q = 1.8 \times 10^8$ M^{-1} s^{-1}.[29] Intramolecular self-quenching of the pVBP carbonyl groups occurred simultaneously with triplet-triplet annihilation.[46] Formation of two or more triplet excited states per SPEEK chain is needed for triplet-triplet annihilation to be operative, a process not likely in SPEEK solutions because of the high [chains] (≈ 0.1 mM) present and the low I_0 employed. Since intramolecular self-quenching is independent of [polyketone], evaluation of the impact of this process on the evolution of $\Phi(Cl^-)$ was not possible. The data of Figure 4.2 can be rationalized assuming that intermolecular quenching of the triplet state by benzophenone groups from other SPEEK molecules also took place as in the case of BP.[29] Such process turned increasingly significant at high [SPEEK] and lowered the efficiency of SPEEK• generation. When [SPEEK] = 0.018M the positive influence of the self-exchange processes was counterbalanced by the effect of intermolecular quenching resulting in a $\Phi(Cl^-)$ maximum. Lower $\phi(Cl^-)$ obtained for E-SPEEK solution was because this set of experiments were performed at high light intensity which also affect the reduction efficiency as discussed in the later section of this chapter.

In view of the previous results, measurements of $\phi(Cl^-)$ with varying the HCO_2^- concentration were conducted in solutions containing 0.018 M SPEEK. As illustrated in Figure 4.3, $\Phi(Cl^-)$ increased with mounting formate concentration reaching a maximum at $[HCO_2^-]$ = 0.36 M but decreased thereafter. Incrementing the concentration of the hydrogen atom donor induced faster quenching of the triplet SPEEK excited state, leading to a more efficient formation of SPEEK• which accelerated the reduction of CCl_4. However, solutions of polyelectrolytes experience increases in light scattering by several orders of magnitude upon rising the concentration of salts above 10^{-2} M.[47] Since SPEEK is a polyelectrolyte, increasing $[NaHCO_2]$ also augmented the intensity of light scattering and thereby decreased the amount of photons reaching the polymeric sensitizer. Both opposing effects compensated each other at $[HCO_2^-]$ = 0.36 M resulting in a maximum reaction rate. Losses in photon flux predominated at higher formate concentrations, originating the subsequent decreases in $\Phi(Cl^-)$.

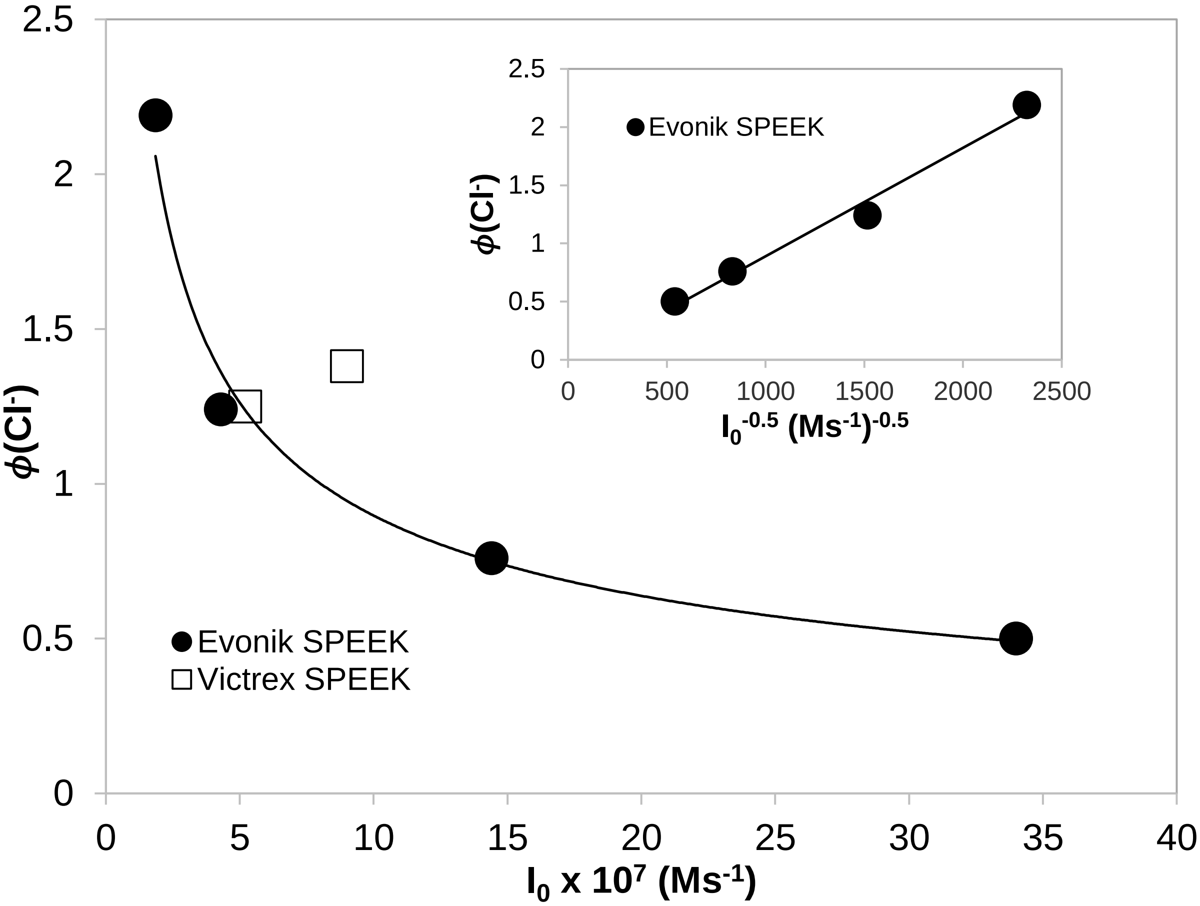


Figure 4.4. Dependence of the quantum yield of Cl$^-$ formation on light intensity for degassed solutions at pH = 7.3 containing 1 mL CCl_4, 0.018 M SPEEK and 0.36 M formate buffer. Sulfonated polyketone derived from Evonik (●) or Victrex (□) precursor. Presented in the inset is a plot of ø(Cl$^-$) as a function of $(I_0)^{-0.5}$.

Earlier attempts to optimize the efficiency of the Ag$^+$ photoreduction in air-free aqueous solutions faced some restrictions due to the use of PVA as the H-atom donor.[24] Large PVA concentrations were desirable to efficiently quench the SPEEK triplet state and generate polymer radicals in high yield, but detrimental high solution viscosities resulted at [PVA] > 0.36 M. Nevertheless, the optimum polyketone concentration was determined to be 0.018 M using [polyol] = 0.36 M, which coincided well with the results of Figure 4.2. Thus, the same optimum [SPEEK] was identified irrespective of the nature of the H-atom donor and SPEEK precursor, suggesting that the sensitizing efficiency of the polymer system was directly related to the photophysical properties of the chromophore. The data of Figure 4.3 also appeared to imply that both PVA and HCO_2^- exhibited maximum efficiencies as H-atom donors at the same concentration. Lower $\phi(Cl^-)$ was acquired for E-SPEEK solution since this set of experiments were performed at high light intensity instead of low light intensity as in case of V-SPEEK. This outcome seems coincidental as the experiments on Ag^+ photoreduction were conducted at [PVA] ≤ 0.36 M due to solution viscosity issues. In contrast, only slight changes in viscosity have been determined in the wider range of formate ion concentrations shown in Figure 4.3.[48]

Figure 4.4 shows the dependence of $\Phi(Cl^-)$ on I_0 for solutions containing V-SPEEK and E-SPEEK utilizing HCO_2^- as the H-atom donor. Light intensities in the range of $1.2 - 9.1 \times 10^{-7}$ M(hν)/s were accessible with the PTI system. However, induction periods lasting longer than 0.5 h together with irreproducible results were noticed at $I_0 < 5 \times 10^{-7}$ M(hν)/s with the less efficient V-SPEEK sensitizer. Only the highest photon fluxes yielded reproducible data with $\Phi(Cl^-)$ values of 1.3 and 1.4 at 5.2×10^{-7} M(hν)/s ≤ I_0 ≤ 9.1×10^{-7} M(hν)/s. In this narrow range $\Phi(Cl^-)$ was independent of the photon flux, implying a direct proportionality of $r(Cl^-)$ with I_0. The data of Figure 4.4 hinted participation of an unusual termination step, possibly via addition of $\bullet CCl_3$ radicals to the benzene rings of SPEEK chains. Such rationalization appears plausible since reduction of CCl_4 in C_6H_6 leads to addition of $\bullet CCl_3$ to the aromatic ring forming (thrichoromethyl) benzene.[49] In the case of E-SPEEK higher photons fluxes accelerated the photoreduction but, as shown in Figure 4.4, $\phi(Cl^-)$ decreased with increasing light intensity; the plot included in the inset demonstrates that $\phi(Cl^-)$ varied linearly with $I_0^{-1/2}$. This is a typical feature of chain reactions involving second-order radical terminations,[50] such as the reductions of CCl_4, CCl_3F and CCl_2FCClF_2.[4,5,18,35,36]

The large quantum yields of Cl^- formation shown in Figures 4.2 through 4.4 supported the notion that photoreduction of CCl_4 involved a chain process. Post-irradiation effects are typical of chain processes and experiments that tested such possibility involved periodic exposures to photons of solutions at pH = 7.3 containing E-SPEEK, HCO_2^- ions and CCl_4. Figure 4.5 depicts data gathered from illuminations extending for 3 min followed by a dark period of equal length. After an initial induction period of about 2 min, $[Cl^-]$ increased linearly during each illumination step with an average rate of 9.4×10^{-7} M s^{-1}. The results displayed in Figure 4.5 confirmed the occurrence of a post-irradiation reaction as $[Cl^-]$ continued to increase in the dark but this process yielded sub-linear changes. Initial $r(Cl^-)$ values were derived from data acquired within 0.5 min after photolysis was stopped, producing an average rate 4 times lower than the one determined with light. An analogous but little bit slower post-irradiation process was noticed in the case of solutions containing V- SPEEK as a sensitizer.

The inset of Figure 4.5 depicts the obtained data of average $r(Cl^-)$ of Cl^- ion formation during illumination and post-illumination period. Termination of photolysis yielded a slow dark reaction with a rate 4 times smaller than the value obtained with light. The post-irradiation processes shown in Figure 4.5 resembled those induced via reduction of CCl_4 and CCl_3F,[2,51] providing further evidence that the CCl_4 reduction involved a chain process. Data obtaining for V-SPEEK, After 27 min of dark reaction, air was admitted into the solution resulting in a linear increase of $[Cl^-]$ with a rate of 4×10^{-9} M s^{-1}. This step lasted only 2 min generating about 77% of the Cl^- formed during the air-free dark reaction. No further changes were detected thereafter, demonstrating that the slow dark increase in $[Cl^-]$ shown in the inset of Figure 5 was not an artifact due to thermal drift of the ISE. The shorter chains obtained in the presence of air are consistent with the results illustrated in the inset of Figure 4.1. Despite such shorter chains, the four-fold faster dark dechlorination induced by O_2 was not unexpected since participation of CCl_3O_2• yielded 4 Cl^- ions per CCl_4 reduced instead of the single anion produced when •CCl_3 was the chain carrier.[2,42] The average r(Cl^-) increases in the dark period only because of CCl_4 reduction goes through chain process as the data presented inset figure 4.5.

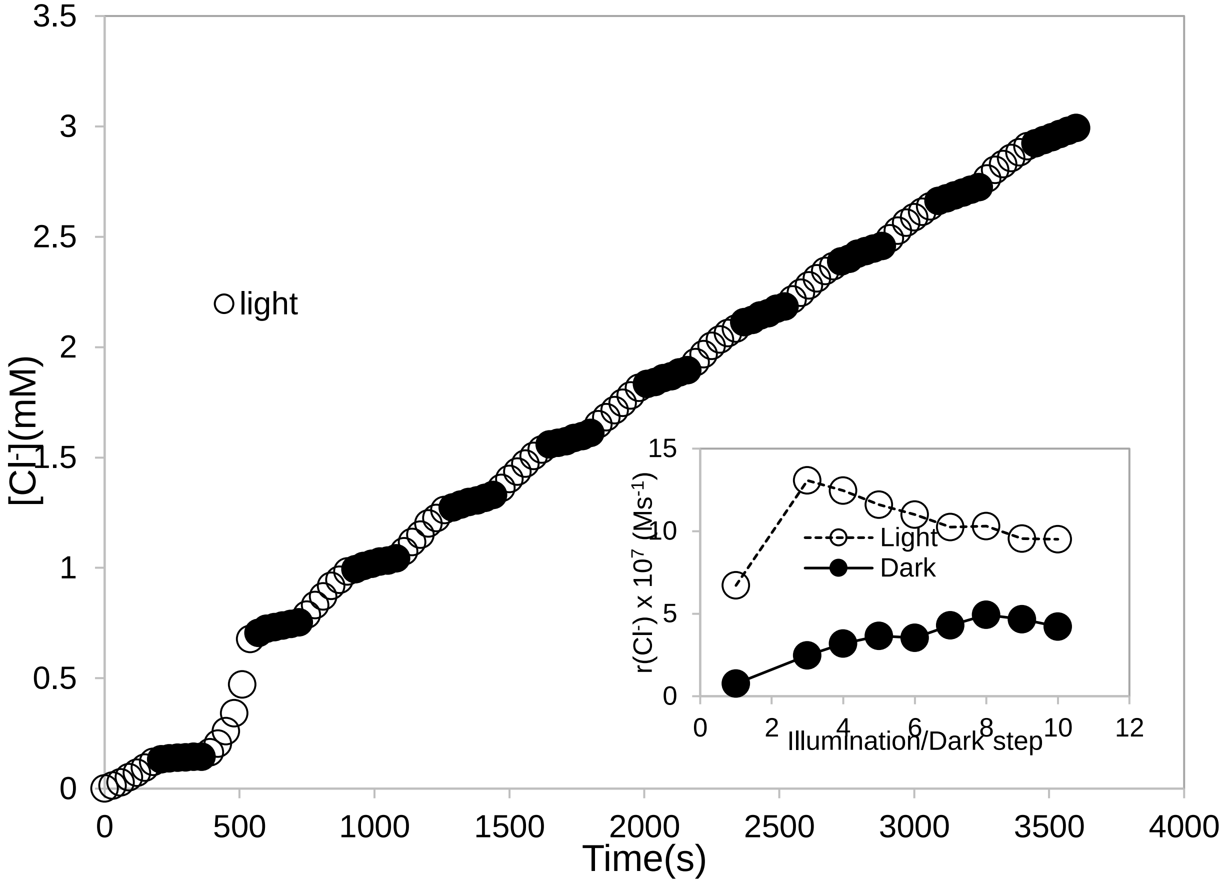


Figure 4.5. Changes in [Cl^-] during alternating illumination (○) and dark periods (●) of a degassed solution at pH = 7.3 containing 1 mL CCl_4, 0.018 M E-SPEEK, 0.36 M formate buffer and $I_0 = 2.12 \times 10^{-6}$ M(hν)/s. The inset depicts the rate of Cl^- ion formation during photolysis (○) and in the dark (●) under the same conditions.

Presented in Figure 4.6a is a comparison of quantum yields of Cl^- formation as a function of pH for systems containing either formate ions or PVA as H-atom donors and V-SPEEK. Determinations of $[Cl^-]$ in solutions with pH > 8.2 were not possible because OH^- ions interfered with the potentiometric measurements. Values of $\Phi(Cl^-)$ from experiments using PVA as the H-atom donor were multiplied by 10 to simplify the presentation of data. In the PVA system $\Phi(Cl^-)$ changed only slightly between 0.032 and 0.027 within $6 \leq pH \leq 8$. Similar efficiencies resulted when SPEEK• reduced O_2 in photolyzed solutions containing V-SPEEK and PVA at $6 \leq pH \leq 9$, with an average quantum yield of hydrogen peroxide formation of $\phi(H_2O_2) \approx 0.02$.[22] The evolution of $\phi(Cl^-)$ also matched that of $\phi(H_2O_2)$ at pH < 6 where both quantum yields decreased rapidly. Efficient quenching of $^3BP^*$ by H_3O^+ occurs with a rate constant of $k_q = 3.8\text{-}6.4 \times 10^8\ M^{-1}\ s^{-1}$.[29,52] An analogous quenching of the triplet excited state of SPEEK explained the decrease in quantum yields of SPEEK• formation, ϕ(SPEEK•), with increasing $[H_3O^+]$.[22] The fact that $\phi(Cl^-)$ and $\phi(H_2O_2)$ declined in parallel with ϕ(SPEEK•) in the acidic range indicated that the α-hydroxy polyketone radical participated in the reductions of CCl_4 and O_2.

Values of ϕ(SPEEK•) between 0.014 and 0.02 have been determined for solutions with V-SPEEK and PVA in the neutral pH range.[22,24] These formation efficiencies resulted from steady-state measurements made possible due to the unusual stability of SPEEK•. In contrast, α-hydroxy macromolecular radicals such as PVA• exhibit second-order decay constants of $k(decay) \geq 1 \times 10^9\ M^{-1}\ s^{-1}$.[29] Thus, ϕ(SPEEK•) measured the polyketone radicals that survived radical-radical combination processes. In the presence of air O_2 was able to scavenge some of the SPEEK• species that otherwise would have reacted via the radical decay process. This explains the similarities between (SPEEK•) and (H_2O_2), which, at a first sight, appeared odd given that peroxide formation required two polyketone radicals. Most probably the long lifetime of SPEEK• was a key factor enabling chain reductions of CCl_4 to occur in such systems.

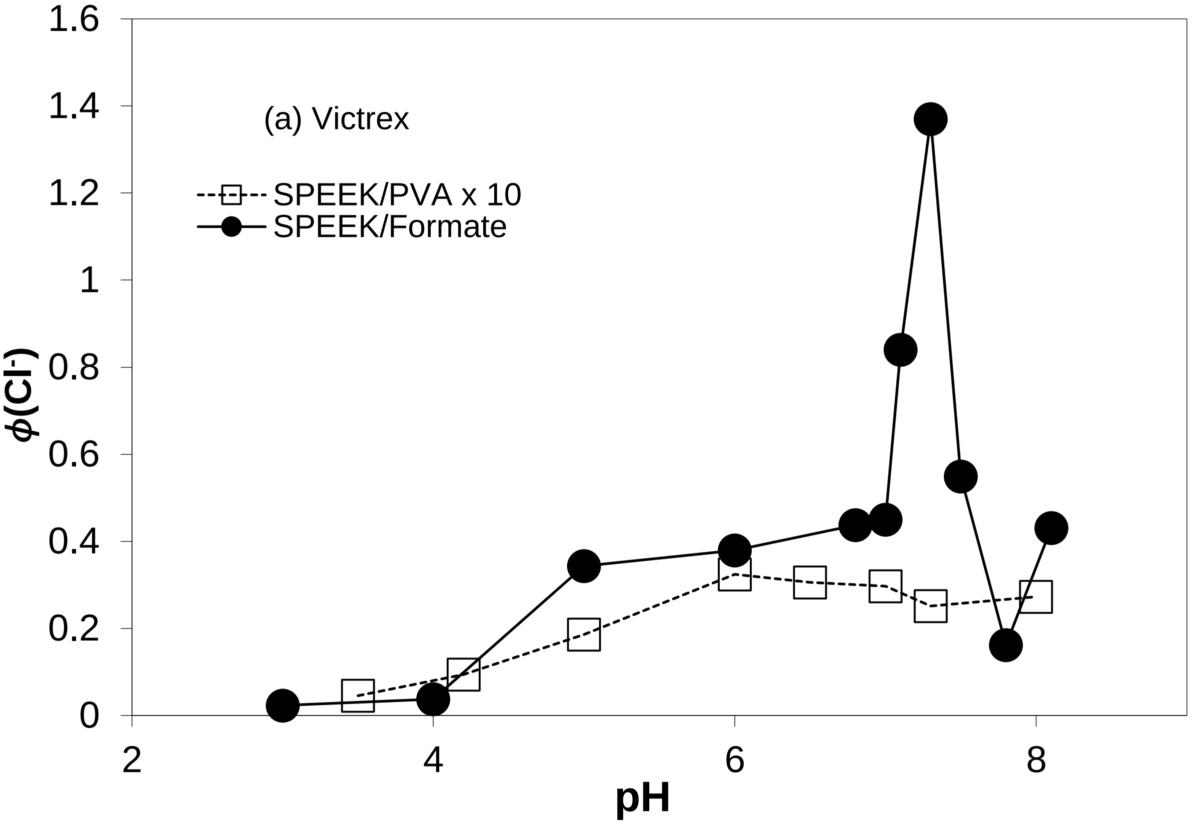
Included in Figure 4.6a is the evolution of $\Phi(Cl^-)$ versus pH for solutions of V-SPEEK and formate buffer. Similar to the PVA systems, $\phi(Cl^-)$ declined with increasing acidity at pH < 5 but the quantum yields determined in HCO_2^- solutions were higher by at least a factor of 4. This trend continued at pH > 5, with quantum efficiencies more than 10 times higher than the values determined for PVA solutions. After increasing smoothly in the range of 5 ≤ pH ≤ 7, $\Phi(Cl^-)$ raised sharply to a maximum of 1.4 at pH = 7.3 that was followed by a steep decrease thereafter. Because of the sudden evolution of the photoreduction efficiency at pH > 7, analogous experiments were carried out with HCO_2^- solutions where E-SPEEK served as the sensitizer. The results are depicted in Figure 6b and resemble the data obtained with the formate system shown in Figure 4.6a. Utilization of HCO_2^- ions as H-atom donors clearly enhanced the efficiency of the photoreaction and also induced the unusual evolution of quantum efficiency at pH > 7 not observed in PVA systems.

E-SPEEK seemed a more effective sensitizer than V-SPEEK for formate-containing solutions given that a maximum $\Phi(Cl^-)$ of 2.2 is immediately obvious in Figure 4.6b. Such a high $\Phi(Cl^-)$ value constituted unequivocal evidence that the CCl_4 photoreduction proceeded through a chain process. Furthermore, a steeper increase in $\Phi(Cl^-)$ from 0.6 to 1.3 was noticed within 5 ≤ pH ≤ 7 in Figure 4.6b as compared with the data of Figure 4.6a. While the pH of the maximum remained unchanged, the subsequent decrease in reaction efficiency at higher $[OH^-]$ was less drastic than the one for solutions with V-SPEEK. A possible origin for the divergent quantum efficiencies obtained with the different SPEEK polymers was the different temperatures during the experiments: 23 °C for the data shown in Figure 4.6a versus 29 °C for the results of Figure 4.6b.

Arrhenius parameters ($\log k = 8.63 - 9.1/\theta$ in $M^{-1}\ s^{-1}$, $\theta = 2.303RT$ in kcal/mol) have been obtained for the rate-determining step of the CCl_4 chain reduction involving H-atom abstraction by the $\bullet CCl_3$ radical.[3] Evaluation of the ratio of quantum yields resulting at different temperatures seemed feasible assuming that the CCl_4 photoreduction initiated by SPEEK included an analogous rate-determining step with similar Arrhenius parameters.

Utilization of the procedure outlined above produced a ratio of $\phi(Cl^-,296K)/\phi(Cl^-,302K) = 0.725$ and the resulting quantum yields at 23 °C for solutions of E-SPEEK were included in Figure 4.6b. An additional experiment was conducted to test the trustworthiness of the assumptions behind the calculation procedure. For this purpose a solution containing E-SPEEK, HCO_2^- ions at pH = 7.3 was placed in a photoreactor equipped with a water jacket, enabling to maintain a temperature of 23 °C during photolysis inside the Rayonet illuminator. The resulting $\Phi(Cl^-)$ of 1.7 coincided well with the estimated value of 1.6 and confirmed the soundness of the calculations. Both quantum yields agreed as well, within experimental uncertainty, with the maximum of 1.4 found for the V-SPEEK system. However, only at pH values of 7.1 and 7.3 were the calculated quantum efficiencies close to the experimental data for V-SPEEK solutions (Figure 6a). Outside that narrow pH range the calculated efficiencies were generally larger by a factor of 2 than the corresponding experimental values.

Obviously, no significant difference in photochemical activity existed between the two polyketones within the pH region of the $\Phi(Cl^-)$ maximum. This means that both sensitizers were equally efficient at producing the triplet excited state and, therefore, at generating SPEEK•. Efforts to verify such conclusion involved determinations of (SPEEK•) for E-SPEEK and for V-SPEEK in neutral solutions of HCO_2^- via detection of the radical absorption with $\lambda_{max} = 565$ nm.[24] These were challenging experiments given the low photon fluxes utilized; problems due to scavenging of SPEEK• by traces of O_2 left after degassing were circumvented via photolyzing the solutions repeatedly and monitoring the decay of photogenerated radicals spectrophotometrically. Complete O_2 consumption became evident when SPEEK• decayed via a clean second–order process;[24] ϕ(SPEEK•) amounted to 0.03 for V-SPEEK solutions at pH = 7.3 while a value of 0.02 resulted in the case of E-SPEEK at a pH of 7.



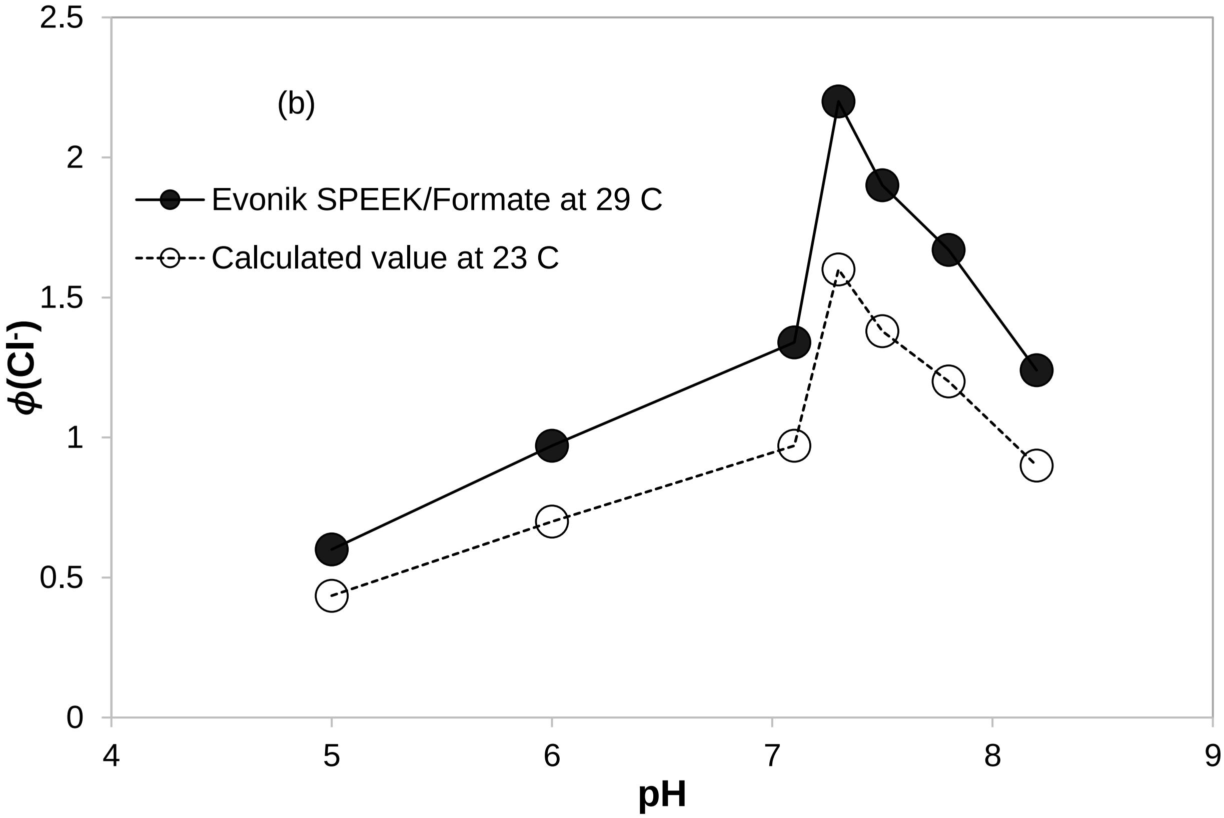


Figure 4.6. (a) Efficiencies of Cl^- ion formation as a function of pH during photolysis of degassed solutions containing 1 mL CCl_4, 0.018 M V-SPEEK and 0.36 M formate buffer (●), or [PVA] = 0.36 M and 0.1 M $NaClO_4$ (□), T = 23 °C and $I_0 = 9 \times 10^{-7}$ M(hν)/s. The quantum yields from experiments with PVA and $NaClO_4$ were multiplied by a factor of 10. (b) Results from (●) air-free solutions containing 1 mL CCl_4, 0.018 M E-SPEEK and 0.36 M formate buffer, $I_0 = 2.2 \times 10^{-7}$ M(hν)/s and T = 29 °C; (○) calculated ø(Cl^-) values at T = 23 °C using the activation parameters from reference 3.

Comparison of these results with the available ϕ(SPEEK•) values for neutral solutions revealed that very similar efficiencies were obtained in the present and previous studies.[22,24] Thus, generation of SPEEK• was equally efficient in neutral solutions independent of the nature of the H-atom donor or of the SPEEK precursor. Quantum yields similar to ϕ(SPEEK•) were reported for alkanes and polyesters containing isolated carbonyl groups in their backbones and their low efficiencies were attributed to either primary or secondary cage recombination of photogenerated radicals.[53] SPEEK/PVA films exhibited reduction yields about 10 times higher than solutions because radical recombination via diffusional processes was severely restricted due to polymer crosslinking.[21,22] SPEEK• losses originating from radical diffusional processes including secondary cage recombinations can account for the lower reaction yields of SPEEK solutions. $CHCl_3$ and CO_2 were the only volatile products detected via GC/MS analysis of headspace samples from photolyzed neutral solutions. Efforts to detect oxalate ions originating from dimerization of $\bullet CO_2^-$ radicals with ion chromatography, and also of products from the addition of $\bullet CCl_3$ to the benzene rings of SPEEK with NMR, were unsuccessful. Furthermore, no changes in solution refractive index, heat capacity or SPEEK phosphoresence were noticed in the neutral pH range characterized by a large increase in $\Phi(Cl^-)$. SPEEK solutions displayed a non-ideal behavior most probably because formation of aggregates influenced the properties of the polyelectrolyte systems.[26] Despite of the heterogeneous nature of the solutions several photochemical results obtained in the presence of HCO_2^- ions constituted firm evidence that the photoreduction of CCl_4 comprised a chain process. The following simple mechanism can account for these findings:

$$\{R'RC{=}O\}_z + h\nu \rightarrow {}^3\{R'RC{=}O\}_z^* \tag{1}$$

$${}^3\{R'RC{=}O\}_z^* + HCO_2^- \rightarrow \{R'RC\bullet OH\}_z + \bullet CO_2^- \tag{2}$$

$$\{R'RC{=}O\}_z + \bullet CO_2^- \rightarrow \{R'RC\bullet O^-\}_z + CO_2 \tag{3}$$

$$\{R'RC\bullet O^-\}_z + H^+ \leftrightarrows \{R'RC\bullet OH\}_z \tag{4}$$

$$\{R'RC\bullet OH\}_z + CCl_4 \rightarrow \bullet CCl_3 + Cl^- + H^+ + \{R'RC{=}O\}_z \tag{5}$$

$$\bullet CCl_3 + HCO_2^- \rightarrow CHCl_3 + \bullet CO_2^- \tag{6}$$

$$\bullet CCl_3 + \{R'RC\bullet OH\}_z \rightarrow Cl^- + H^+ + \{R'RC{=}O\}_z + :CCl_2 \tag{7}$$

$$:CCl_2C + 2H_2O \rightarrow 2HCl + HCO_2H \tag{8}$$

For simplicity all elementary steps were written as if occurring in homogeneous solution; the simplified notation utilized $\{R'RC{=}O\}_z$ to represent SPEEK while $^3\{R'RC{=}O\}_z^*$ corresponded to the triplet excited state of the polyketone. SPEEK• was symbolized by $\{R'RC{\bullet}OH\}_z$ whereas $\{R'RC{\bullet}O^-\}_z$ represents the deprotonated form; both formulas imply that on average one unpaired electron is present per polymer chain.

Quenching of $^3BP^*$ by HCO_2^- in homogeneous solutions is fast ($k_q = 1 \times 10^8\ M^{-1}\ s^{-1}$) leading to $\bullet CO_2^-$ formation.[37] An analogous quenching of $^3\{R'RC{=}O\}_z^*$ by HCO_2^- is represented by step 2 but the rate constant of this reaction is probably somewhat lower due to electrostatic repulsions between formate ions and the highly charged SPEEK. The large polymer charge arises because the polyelectrolyte chains contain on average about 156 SO_3^- and Na^+ ions for V-SPEEK, or 198 in the case of E-SPEEK. Counterion condensation is an established phenomenon that accounts for the behavior of ionic species in polyelectrolyte solutions;[54] a recent model is able to provide a pathway for the $\bullet CO_2^-$ formation.[55] According to this model, solutions of SPEEK and $NaHCO_2$ consisted of negatively charged macromolecules each surrounded by a cloud of Na^+ ions located in close proximity. The strong interaction between the anionic macromolecules and the condensed counterions induced partial screening of the SO_3^- groups from SPEEK, enabling Na^+-HCO_2^- ion pairs to migrate into the cation cloud. In this scenario step 2 was facilitated by the presence of Na^+-HCO_2^- ion pairs very near the polyelectrolyte. The resulting $\bullet CO_2^-$ radicals participated in step 3 after evading geminate recombination via diffusion as Na^+-$\bullet CO_2^-$ ion pairs.[56]

Reduction of SPEEK via step 3 probably occurred in a way analogous to the slow reaction of the negatively charged 4-carboxybenzophenone (4-CB) with $\bullet CO_2^-$ ($k = 3 \times 10^7\ M^{-1}\ s^{-1}$) due to electrostatic repulsions.[57] Competition between step 3 and the reduction of CCl_4 by $\bullet CO_2^-$ seemed possible but an earlier study found no evidence for such reaction.[4] In contrast, support for the scavenging of $\bullet CO_2^-$ by CCl_4 was provided by a more recent investigation.[16] Relevant kinetic data is only available for the reduction of CCl_3F by $\bullet CO_2^-$ where $k = 7 \times 10^4\ M^{-1}\ s^{-1}$.[35] The rate constants for the reductions of 4-CB and CCl_3F, together with the fact that [SPEEK] >> [CCl_4], implied that reduction of the halomethane by $\bullet CO_2^-$ was unable to compete with step 3 in SPEEK solutions. Chain propagation involved steps 5 and 6 whereas termination took place via the radical-radical reaction step 8. Dihalocarbene intermediates were formed via cross-reaction of the chain carriers during the photoreductions of CCl_4 and CCl_3F.[35,58] An analogous termination step seemed reasonable in the present case, followed by hydrolysis of the resulting carbene. The proposed mechanism accounted for all the reaction products and the steady-state approximation predicted a linear dependence of $\Phi(Cl^-)$ with $I_0^{-1/2}$ consistent with the trend shown in Figure 4.4. Evaluation of the kinetic chain length (kcl) from the results of Figure 6 employed the quantum yield of SPEEK• formation derived from the previously determined $\phi(H_2O_2)$, equal to 0.04.[22] Such procedure was adopted in order to provide more realistic yield of initiating radicals and resulted in kcl values of 55 and 35 for the $\phi(Cl^-)$ maxima. On the other hand, the rate law derived from the simple mechanism included reaction orders of ½ for [SPEEK] and [HCO_2^-], which were inconsistent with the results of Figures 4.2 and 4.3. Perhaps the most serious limitation of the simplistic mechanism was the failure to account for the sharp $\Phi(Cl^-)$ maxima observed at pH > 7.

An interesting feature of the mechanism is that step 3 produced the anionic form of SPEEK•, which was found to predominate at pH values above 9.[22] The α-hydroxy radical from BP behaved similarly (pK_a of 9.2); protonation of the conjugate base $(Ph)_2C\bullet O^-$ was found to be diffusion controlled.[59] Using $(Ph)_2C\bullet O^-$ as a model for $\{R'RC\bullet O^-\}_z$ then a rate constant of about $10^{10}\ M^{-1}\ s^{-1}$ seemed reasonable for the forward reaction of equilibrium 4, yielding a pseudofirst-order rate constant $\leq 10^4\ s^{-1}$ at pH $\geq$ 6 for this step. On the other hand, $(CH_3)_2C\bullet OH$ reduced CCl_4 with a rate constant of 1×10^8 M^{-1} s^{-1},[4] and a similar rate constant appeared feasible when $\{R'RC\bullet O^-\}_z$ was the reductant. In this scenario CCl_4 was reduced with a pseudofirst-order rate constant of 5×10^5 s^{-1}, predominating over the radical protonation step at pH ≥ 6. Another route for protonating $\{R'RC\bullet O^-\}_z$ involved direct H^+ abstraction from HCO_2H; relevant deprotonation rate constants of acids induced by OH^- range between 10^9-10^{10} M^{-1} s^{-1}.[60] Even when such high protonation rate constants are considered, the reduction of CCl_4 by $\{R'RC\bullet O^-\}_z$ remained competitive at pH ≥ 7 because $[HCO_2H] \leq 2 \times 10^{-4}$ M in that range of acidities.

At a first sight, participation of $\{R'RC\bullet O^-\}_z$ in the reduction process was a tempting rationalization for the sudden increase in $\phi(Cl^-)$ at pH > 7. Reduction of CCl_4 was anticipated to be faster for $\{R'RC\bullet O^-\}_z$ as compared with SPEEK• because the anionic conjugates of α-hydroxy radicals are stronger reductants (by about 0.4 V) than the protonated forms.[31] A mechanism involving $\{R'RC\bullet O^-\}_z$ both in the reduction of CCl_4 and the termination step with $\bullet CCl_3$ also yielded a linear dependence of $\phi(Cl^-)$ with $I_0^{-1/2}$ under steady-state conditions. However, the mechanism that considers $\{R'RC\bullet O^-\}_z$ as the main polymeric chain carrier failed to explain the decline in $\phi(Cl^-)$ at pH > 7.3 illustrated in Figure 6. Furthermore, no simple rate law resulted upon including the combined contributions of SPEEK• and the conjugate radical anion. Participation of SPEEK aggregates in the photochemical processes is another obvious possibility but the impact of such multi-chain domains is hard to assess since their characterization has not been possible thus far.[26]

Another interesting result was the possibility of inducing extended CCl_4 photoreductions via zero-order kinetics generating $[Cl^-]$ in the mM range without much interference from the halide ions. This finding indicates that Cl^- was not an efficient quencher of $^3\{R'RC{=}O\}_z^*$, similar to the case of $^3BP^*$.[61] In addition, the data shown in the inset of Figure 4.1 indicates that efficient reduction of CCl_4 is also feasible in air-containing solutions although no chain processes were observed under such conditions.

4.4 Conclusions

Reduction of CCl_4 induced by photolysis of SPEEK was shown to occur in aqueous solutions containing either PVA or HCO_2H/HCO_2^- as H-atom donors. The concentration of the generated Cl^- ions increased linearly with time, indicating that reaction was controlled by the initial photochemical process of radical formation in a way similar to the reduction of O_2.[22] Only low $\Phi(Cl^-)$ values were obtained in PVA solutions indicating that the polyol was significantly less effective at sustaining the CCl_4 reduction than the formate buffer. Similarly low quantum yields were determined previously for the reductions of O_2 and several metal ions,[22,24] further supporting the notion that fast radical-radical decay processes dominated in the heavily entangled SPEEK/PVA solutions and limited their reaction efficiencies. In contrast, conditions were identified that enabled SPEEK to initiate a chain photoreduction of CCl_4 to form $CHCl_3$ in air-free solutions containing the formate buffer. Such conditions were similar to those identified during the photoreductions of CCl_3F and CCl_2FCClF_2 in TiO_2 suspensions,[35,36] and involved a high concentration of the H-atom donor and an amount of CCl_4 beyond the solubility limit in H_2O. The photoreaction was characterized by a peculiar pH dependence and occurrence of a chain process was most evident at pH = 7.3 where $\Phi(Cl^-)$ exhibited a sharp maximum irrespective of the SPEEK sensitizer used. Outside the neutral pH range E-SPEEK induced more effective photoreductions than polyketone samples derived from the Victrex precursor. A plausible origin for such difference involves extensive coiling of V-SPEEK chains, or the presence of crosslinks/branches in the macromolecules, that enhanced self-quenching of the excited polymer thereby decreasing the photoreaction efficiency.

Studies with colored dissolved natural organic matter (CDOM, such as humic materials) have shown that they can induce oxidative degradation of several organic toxins upon exposure to light.[62] Experiments with model compounds, including BP, pointed to carbonyl functionalities present in the CDOM as possible photoinitiators of the oxidations. The results presented in the inset of Figure 4.1 indicate that photoreduction of CCl_4 is also feasible in the presence of air provided that efficient H-atom donors are available. This, in turn, suggests that reductive pathways induced via photolysis of CDOM may provide a route for the degradation of halogenated compounds if natural compounds containing H-atom donor groups (such as alcohols and amines) are also present.

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Chapter V

Radical Chain Reduction of CCl_4 Initiated by Illumination of SPEEK/PVA Film

5.1 Introduction

CCl_4 has been identified as an important pollutant in a wide range of sites exhibiting large underground plumes of toxic chemicals.[1] Contamination of water results when the underground pools of the pollutants establish contact with aquifers. Reductive dehalogenation seems to offer a potential avenue for the remediation of pollution consisting of stable and persistent chlorinated fluids that are refractory toward oxidation. Reduction of CCl_4 by means of strongly reducing α-hydroxy radicals of simple alcohols or $\bullet CO_2^-$ proceeds in the absence of air to form $CHCl_3$ via efficient chain reactions.[2-4] Light-induced reductions of halocarbons have always been of interest as the energy required for such transformations are provided by electromagnetic radiation that is available from sunlight. Photolysis of particles of semiconducting oxides (called photocatalysts) suspended in water can induce transformations of halogenated compounds including CCl_4.[5-8] Light-initiated reduction of this chemical using homogeneous systems has also been reported but the efficiencies of such systems vary considerably.[9-13]

A previous report has shown that CCl_4 can be efficiently photoreduced in air-free solutions of the Na^+ salt of sulfonated poly(ether-etherketone), or SPEEK also containing poly(vinyl alcohol), PVA, or HCO_2^- ions.[14] SPEEK is a polymeric analogue of benzophenone (BP, $(Ph)_2C{=}O$), which upon illumination with 350 nm photons in the presence of 2-propanol is able to generate α-hydroxy radicals, $(Ph)_2C\bullet OH$, with 100% efficiency.[15] SPEEK acts as a sensitizer analogous to BP whereas PVA or HCO_2^- play the role of H-atom donors. In analogy to BP, absorption of a photon by SPEEK results in a triplet excited state, $^3\{SPEEK\}^*$, able to abstract a H-atom from the donors forming an α-hydroxy radical of the polyketone, SPEEK•.[14,16-18] A radical of the H-atom donor is simultaneously formed (PVA• or $\bullet CO_2^-$), which may react with another BP group from SPEEK forming additional SPEEK•. Thus, two α-hydroxy radicals of SPEEK can, in principle, be generated via absorption of one photon.

The oxidation potential of SPEEK• has been estimated to be about 1.3 V,[17] which explains the ability of this species to induce the reduction a variety of species such as metal ions (Ag^+, Cu^{2+} and Au^{3+}), O_2, CCl_4 and $CHCl_3$,[14,16-21] see also Chapter II. The reduction of $CHCl_3$ by SPEEK• resulting from exposure to light of cross-linked SPEEK/PVA films swollen in aqueous solutions was described in Chapter III. Studies with films are of particular interest since such systems may be of practical use as protective barriers able to inactivate toxins and pathogens by means of light-generated reactive species. Previous work has shown that SPEEK/PVA films can photoreduce O_2 to H_2O_2, a chemical suitable as antibacterial and oxidizer.[21] The ability of these polymer films to reductively dehalogenate $CHCl_3$ was demonstrated in Chapter III.

In the present chapter evidence is presented that SPEEK• generated by illumination of cross-linked SPEEK/PVA films is able to induce highly efficient reductive chain dehalogenations of CCl_4. Quantum yield higher than 10^3 have been obtained in solutions that initially contained air, although O_2 is an efficient scavenger of reducing radicals. Hence, SPEEK/PVA films may be of interest for the photochemical reduction of CCl_4 present in heavily contaminated sites.

5.2 Experimental

Samples of poly(ether etherketone), PEEK, were provided as gifts by Evonik, USA (L5000G powder, average $M_n = 5.7 \times 10^4$ g/mol) or by Solvay, USA (Ketaspire KT-880 FP powder, average $M_n = 4 \times 10^4$ g/mol). These materials were converted to the sodium salt of SPEEK, via sulfonation in H_2SO_4 as described before.[21] Poly(vinyl alcohol), 99 % hydrolyzed, average M_n of 8.9-9.8 x 10^4 g/mol as well as CCl_4 were obtained from Sigma Aldrich. KCl, NaOH, $NaClO_4$, $NaCO_2H$, HCO_2H, H_2SO_4 and $HClO_4$ were purchased from VWR. The method for the preparation of cross-linked SPEEK/PVA films have been outlined in detail.[18,21] Recent small improvements were presented in Chapter III, which also included thorough descriptions of the illumination procedures and images of the photoreactor as well as of the analytical methods. Unless otherwise stated, irradiations were carried out with solutions containing 1 mL of CCl_4 after cleaning the chloromethane repeatedly with H_2O to extract the stabilizer. Identical results were obtained from experiments using CCl_4 with and without stabilizer. Two liquid phases formed due to the low solubility of carbon tetrachloride in H_2O (5.1×10^{-3} M or 27 μL CCl_4 in 54 mL of aqueous solution),[22] but under constant stirring the excess CCl_4 was present as small droplets. Irradiations were performed, at least, twice always using air-saturated solutions. All aqueous solutions were prepared with water purified using a Millipore Milli-Q Biocel system. Potentiometric determinations of [Cl^-] were characterized by an error of < 5% whereas the photochemical data obtained with SPEEK/PVA films exhibited deviations of about 20%, which are typical of these rather heterogeneous polymer systems.[21]

5.3 Results and Discussion

Illuminations of SPEEK/PVA films immersed in air-saturated aqueous HCO_2^- solutions containing CCl_4 were conducted under experimental conditions identified previously in Chapter III as those favorable for inducing an efficient photoreduction of $CHCl_3$. Depicted Figure 5.1(a) is the evolution of [Cl^-] as a result of exposure to light of films containing SPEEK derived from the

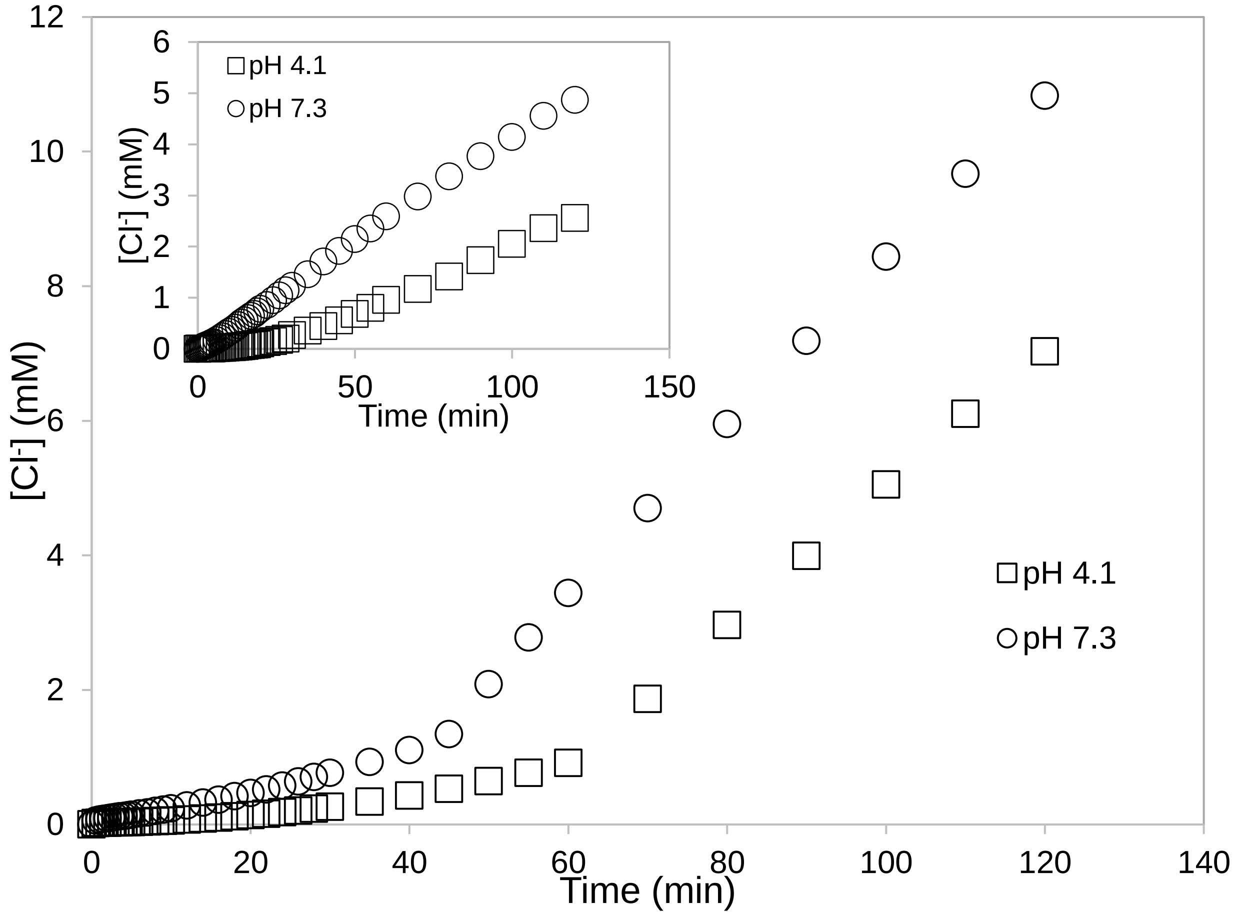

Figure 5.1(a). Evolution of [Cl$^-$] with time during illumination of an SPEEK/PVA film (S-SPEEK, average film thickness = 66 μm) immersed in an air-saturated 0.36 M HCO_2^- solution containing 1 mL CCl_4 with at: (□) pH = 4.1 and (O) pH = 7.3, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s. Inset: data obtained from experiments with E-SPEEK under same condition as in the main figure.

Solvay precursor denoted as S-SPEEK. The fact that Cl$^-$ ions were photogenerated demonstrated unequivocally that CCl_4 experienced a reductive transformation. Two sets of results from experiments conducted at pH = 4.1 and pH = 7.3 are shown in the main figure. In general the evolution of [Cl$^-$] as a function of time consisted of two steps, including an initial process of slow and somewhat inconsistent Cl^- formation that lasted between 5-60 min. The time associated with the initial process is known as the induction period, exhibiting an erratic length and irreproducible kinetics. Not much chemical change occurs during induction periods and they are typically observed when O_2 interferes with reactions involving reducing species. An example is the reduction of CCl_3F by $\bullet CO_2^-$, which exhibited induction periods that scaled in a non-linear fashion with the concentration of oxygen present in the system.[23]

The induction periods noticed in Figure 5.1(a) are surprisingly long as compared with those presented in Chapter III (3-14 min) for the film-induced photoreduction of $CHCl_3$. A second step is also evident in Figure 5.1(a) involving a linear increase in $[Cl^-]$ with time. Thus, product formation followed a zero-order rate law because the transformation was controlled by the photoprocess that generated the reducing radicals, which depended only on the light intensity, I_0. Included in the inset are analogous sets of data for the CCl_4 photoreduction initiated by polymer films containing SPEEK prepared from the Evonik precursor, or E-SPEEK. The photoreactions initiated using those films also exhibited an initial induction period of slow and irreproducible change but that lasted only between 1-17 min. At longer times the phototransformation proceeded faster and exhibited a linear temporal evolution of $[Cl^-]$.

For both SPEEK materials the CCl_4 photodehalogenation was faster at pH = 7.3 than at pH = 4.1 and the induction periods were shorter for reductions that proceeded at a higher pace. Although the reactions initiated by films containing S-SPEEK exhibited longer induction periods, they also took place faster than those induced by solid polymer matrices with E-SPEEK. The second step of the photoreaction enabled evaluation of the rate of Cl^- photogeneration, $r(Cl^-) = d[Cl^-]/dt$, from the slope of the linear increase in $[Cl^-]$ with illumination time. However, the resulting rates required some correction because the halide ions were generated by the SPEEK/PVA films but migrated swiftly into the solution bulk driven by the continuous extraction method employed in the experiments.[21] The resulting dilution of Cl^- is corrected using D_f = V(solution)/V(film), where V(solution) corresponds to the solution volume and V(film) represents the volume of the swollen film.[21] Thus, a rate of Cl^- formation corrected for dilution, $r_c(Cl^-)$, can be evaluated using: $r_c(Cl^-) = D_f\, r(Cl^-)$.

A further correction was needed given that the polymer film captured only a fraction of the photon flux entering the photoreactor, which is determined with the actinometer. This mean that the amount of photons absorbed by the polymer film (I_c) can be estimated from the relationship: $I_c = I_o \times SA_f$, where SA_f corresponds to the ratio of surface area of swollen film and vessel.[21] The efficiency of chloride ion formation, $\phi(Cl^-)$, is then evaluated from: $\phi(Cl^-) = r_c(Cl^-)/I_c$.

Presented in Figure 5.1(b) are results obtained from illuminations at different pH values after the above-mentioned corrections. The most significant finding was that very large $\phi(Cl^-)$ values approaching 500 in neutral solutions were obtained during the photoreduction of CCl_4. Such high efficiencies are not frequently found during reductions of chlorocarbons, particularly in systems containing air. The results of Figure 5.1(b) also imply that the CCl_4 photoreduction by SPEEK/PVA films occurred, at least, 10 times more efficiently than $CHCl_3$. A similar, but not as pronounced, difference between reduction efficiencies was established in Chapter II for air-free aqueous solutions of SPEEK/PVA. Films based on S-SPEEK exhibited quantum yields that remained fairly constant throughout the studied pH range. The lack of any $\phi(Cl^-)$ drop in acidic medium suggested that the films were insensitive to quenching of the SPEEK triplet excited state, $^3\{SPEEK\}^*$, by H_3O^+ ions. This was another surprising finding and seems to suggest that BP group from S-SPEEK are less accessible to hydronium ions than those from E-SPEEK, making the excited state of the fomer polyketones less susceptible to pH changes. The near

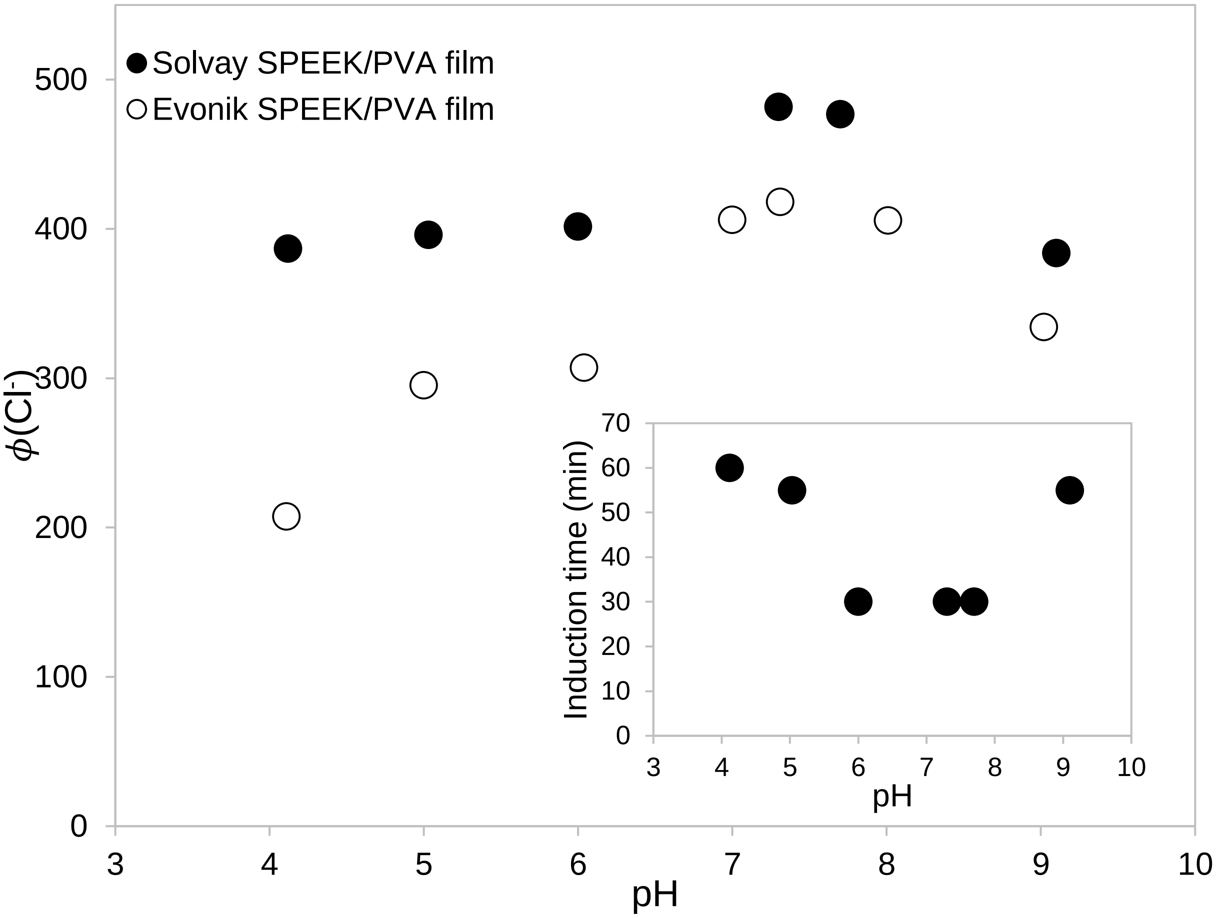

Figure 5.1(b.) Efficiency of Cl^- ion formation as a function of pH during illumination of SPEEK/PVA films (average thickness = 65 μm) in a 0.36 M HCO_2^- solution containing 1 mL of CCl_4, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s; ○ = S-SPEEK, ● = E-SPEEK. Inset: length of induction period as a function of pH for experiments with S-SPEEK.

independence of $\phi(Cl^-)$ on pH shown in Figure 5.1(b) for films with S-SPEEK is in stark contrast with the efficiency change, by a factor of 2, when the pH lowered from 7 to 4 during the film-initiated $CHCl_3$ photoreduction described in Chapter III.

On the other hand, the efficiencies of films containing E-SPEEK were similar to those based on S-SPEEK only in neutral and slightly basic solutions. According to Figure 5.1(b), such films exhibited decreases in $\phi(Cl^-)$ by a factor of 2 when the acidity was increased up to a pH of 3. These findings indicate SPEEK• formation in E-SPEEK was susceptible to acidic environments as found previously for the reductions of O_2 and $CHCl_3$ in solutions/films of SPEEK/PVA,[19-21] and for CCl_4 in polymer solutions,[14] see previous chapters of this dissertation.

The data shown in the inset established a strong correlation between speed of reduction and induction period but only for films containing S-SPEEK. As shown in previous chapters, the general trend is that conditions leading to slow chlorocarbon reductions also lengthened the induction periods. However, in the case of systems with S-SPEEK changes in pH that only induced small variations (≤ 20%) in $\phi(Cl^-)$ increased the induction periods by 100%. A possible explanation is H_2O_2, generated during the induction period by the O_2 reduction, interfered with the SPEEK• formation perhaps via quenching of $^3\{SPEEK\}^*$. In fact, excited polyketones are known to experience quenching by peroxides and hydroperoxides.[24] Furthermore, the photoreduction of $CHCl_3$ in SPEEK/PVA solutions containing air was severely retarded upon introduction of 0.1 mM peroxide.[20] Quenching of $^3\{SPEEK\}^*$ by H_2O_2 may have contributed to retarding that photoreaction as well as to extending the induction periods in the case of films containing S-SPEEK. However, the possible effect of H_2O_2 on the photochemical properties of S-SPEEK fails to provide a rationalization for the extreme variability in the length of the induction periods noticed for this polymer but not for E-SPEEK.

The unusual results achieved with S-SPEEK, including the very large efficiencies for the CCl_4 reduction, were intriguing and motivated a continuous effort on photoreduction experiments centered exclusively on this polyketone.

The $CHCl_3$ photoreduction data from experiments using both SPEEK/PVA solutions and films of presented in Chapters II & III showed that $\phi(Cl^-)$ increased upon utilization of chlorocarbon amounts higher than the solubility limit in water.[20] Similar findings were made during the CCl_3F reduction induced by photogenerated $\bullet CO_2^-$.[25] Such observations prompted experiments that probed the effect of CCl_4 volume on the reaction rate; shown in Figure 5.2 are the corresponding results. Included in the inset are results of experiments with increasing CCl_4 amounts added but restricted to the low range of concentrations. The results of the main figure were collected using CCl_4 volumes much higher than the solubility limit.

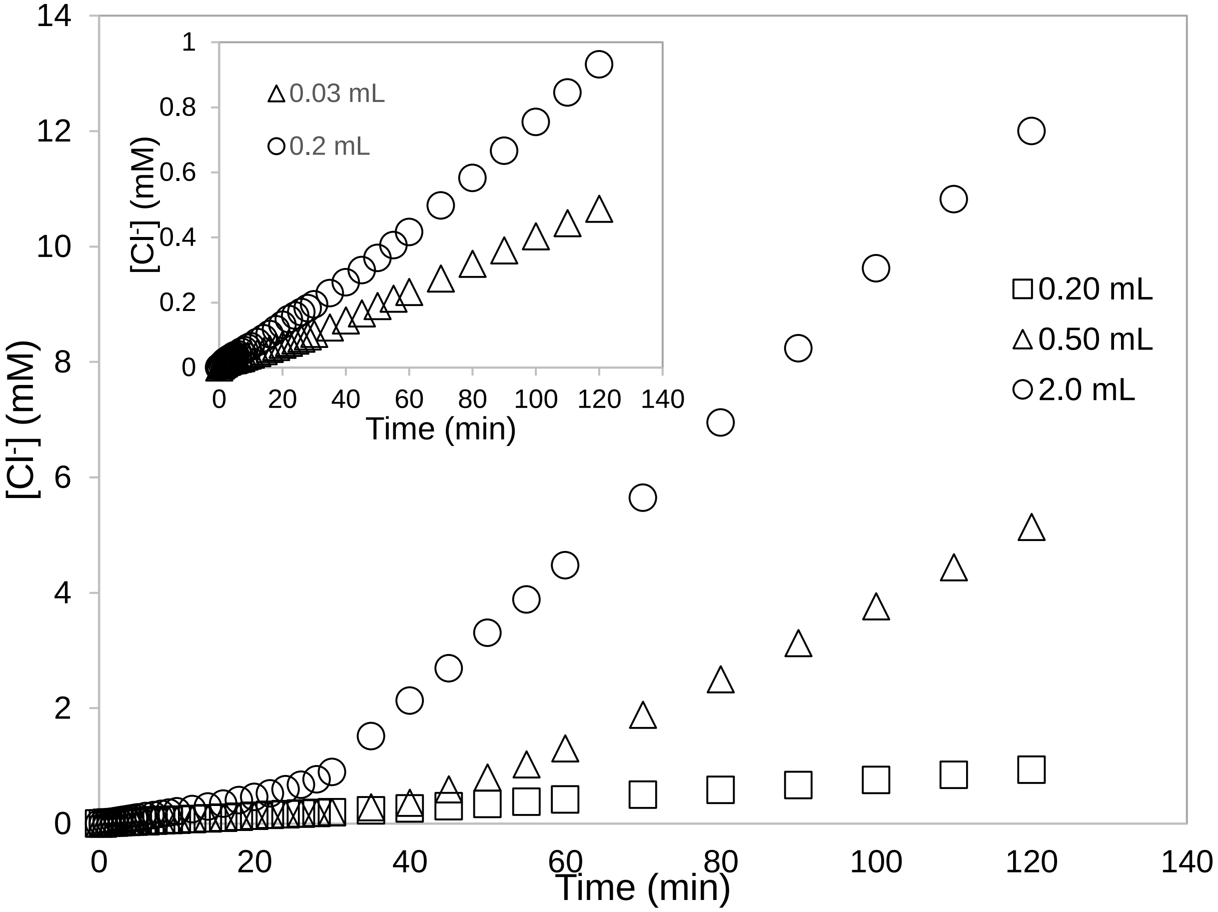

Figure 5.2. Evolution of [Cl^-] during the illumination of S-SPEEK/PVA films (average thickness = 71 μm) in 0.36 M HCO_2^- solutions at pH 7.3 containing: (O) 2 mL, (Δ) 0.5 mL and (☐) 0.2 mL of CCl_4, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s. Inset: data for: (O) 0.2 mL and (Δ) 0.03 mL CCl_4; these amounts are below where [CCl_4] is in the range of solubility limit in water.

According to the data shown in the inset, low CCl_4 concentrations yielded were fairly short and constant (~ 5 min) induction periods, as well as reduction rates that were similar. However, a different picture emerged at the higher end of added CCl_4, provided by the data displayed in the main figure. Longer induction period of 25-30 min were noticed at CCl_4 volumes between 0.2 - 2 mL, and the reaction rate was raised vastly with increasing amounts of chlorocarbon added. These results clearly showed that the length of the induction was affected by the presence of the organic compound. The solubility of O_2 in SPEEK/PVA solutions equilibrated with air is 0.26 mM,[19] whereas 4 to 8 times higher values are typical of organic solvents. Hence, addition of large CCl_4 volumes introduced further O_2 into the aqueous solutions. This extra O_2 source may have contributed to extending the induction periods.

Figure 5.3 provided further confirmation that addition of excess CCl_4 beyond the solubility limit in H_2O boosted very significantly the quantum yield of Cl^- formation. Yet, the influence of excess chloromethane on the reaction rate was complex as no significant increase in reaction efficiency occurred for CCl_4 volumes of up to 0.2 mL, which is well above the solubility limit.[22] Excess CCl_4 in the form of small droplets accelerated the photoreaction as in the cases of $CHCl_3$ and CCl_3F.[20,25] However, an increase in efficiency by a factor of 14 was achieved at the highest CCl_4 volume added whereas increases by factors between 2 and 4 resulted for the other halomethanes. Obviously, molecules initially segregated in the CCl_4 droplets were eventually able to participate in the reduction process. Such contribution can be rationalized using the interfacial model previously employed to understand the effect of droplets in the photoreduction of CCl_3F.[25]

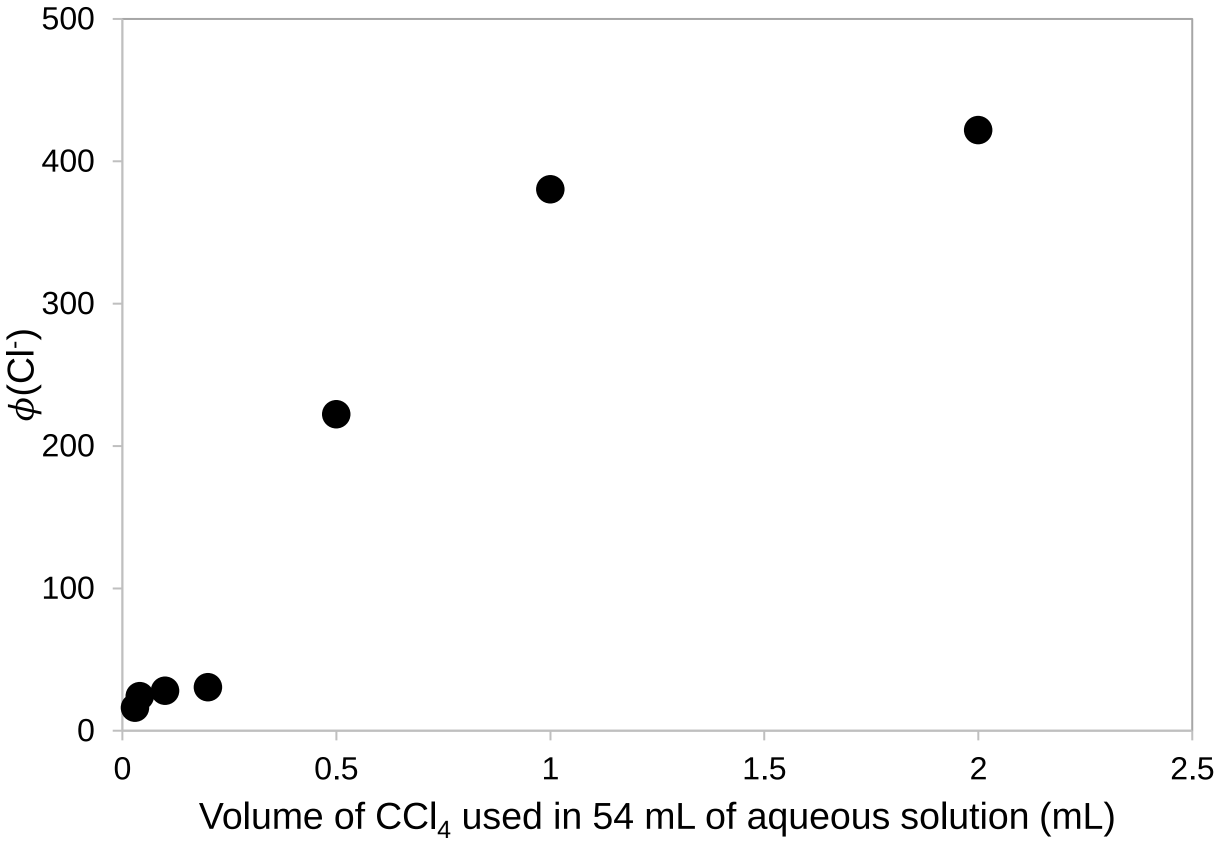

Figure 5.3. Quantum yield of Cl^- ion formation as a function of CCl_4 volume added to 0.36 M HCO_2^- solutions at pH 7.3, illuminated in the presence of SPEEK/PVA films (average thickness = 70 μm), $I_0 = 2.2 \times 10^{-6}$ M(hν)/s.

Figure 5.4 depicts the variation of $\phi(Cl^-)$ when $[HCO_2^-]$ was systematically changed between 0.18 and 0.9 M   Increasing the concentration of the H-atom donor improved the efficiency of the photoreaction drastically resulting in a highest $\phi(Cl^-)$ of 1.84×10^3 at the largest $[HCO_2^-]$ used. The increase in efficiency was not a simple function of formate concentration as $\phi(Cl^-)$ increased steeply until 0.36 M HCO_2^-, followed by a less pronounced change at higher concentrations. The results shown in the inset of Figure 5.4 demonstrated that a decrease by a factor of 2 in the

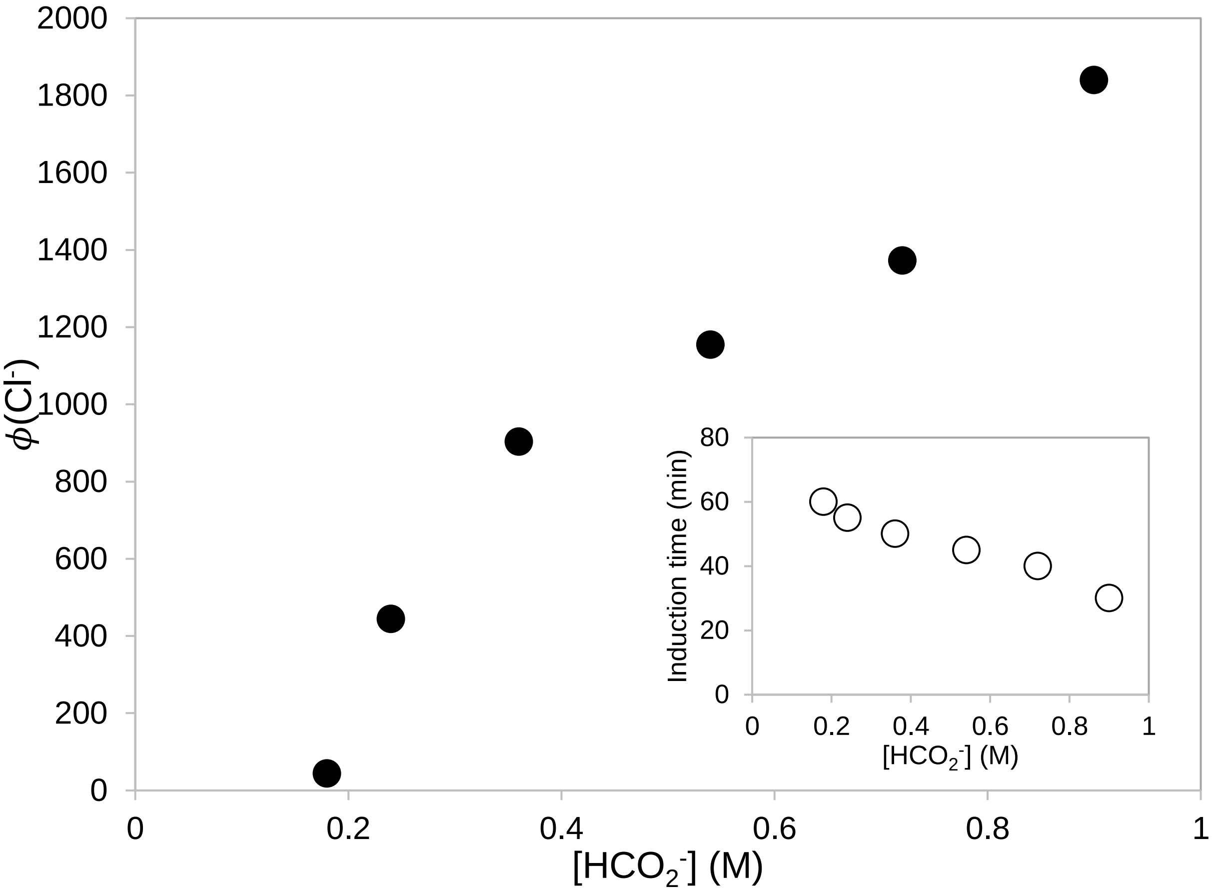

Figure 5.4. Efficiencies of Cl^- ion formation as a function of $[HCO_2^-]$ during the illumination of SPEEK/PVA films (average thickness = 48 μm) immersed in solutions at pH = 7.3 containing 1 mL of CCl_4, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s.

induction period was achievable by raising $[HCO_2^-]$ to 0.9 M. In fact, the length of the induction period appeared to decrease close to linearly with increasing $[HCO_2^-]$. These findings suggest that incorporation of formate into the swollen polymers was an important factor that influenced $\phi(Cl^-)$ as well as the length of the induction period. Strong electrostatic repulsions between HCO_2^- and SPEEK are anticipated as the polyelectrolyte contains between 150-200 SO_3^- groups and Na^+

counterions per chain. Diffusion of formate ions into the films will be facilitated if this process involves Na^+-HCO_2^- ion pairs, which exit mainly at high [HCO_2^-].

Efforts to optimize the performance of the CCl_4 photoreduction included tests about the influence exerted by SPEEK in the reaction rate. For that purpose the percent by weight of the polyketone was varied in a systematic fashion. While such procedure also altered the amount of PVA present in the films. Considering that the polyol remained in excess over the polyketone at all compositions studied, the changes observed were analyzed exclusively in terms of effects

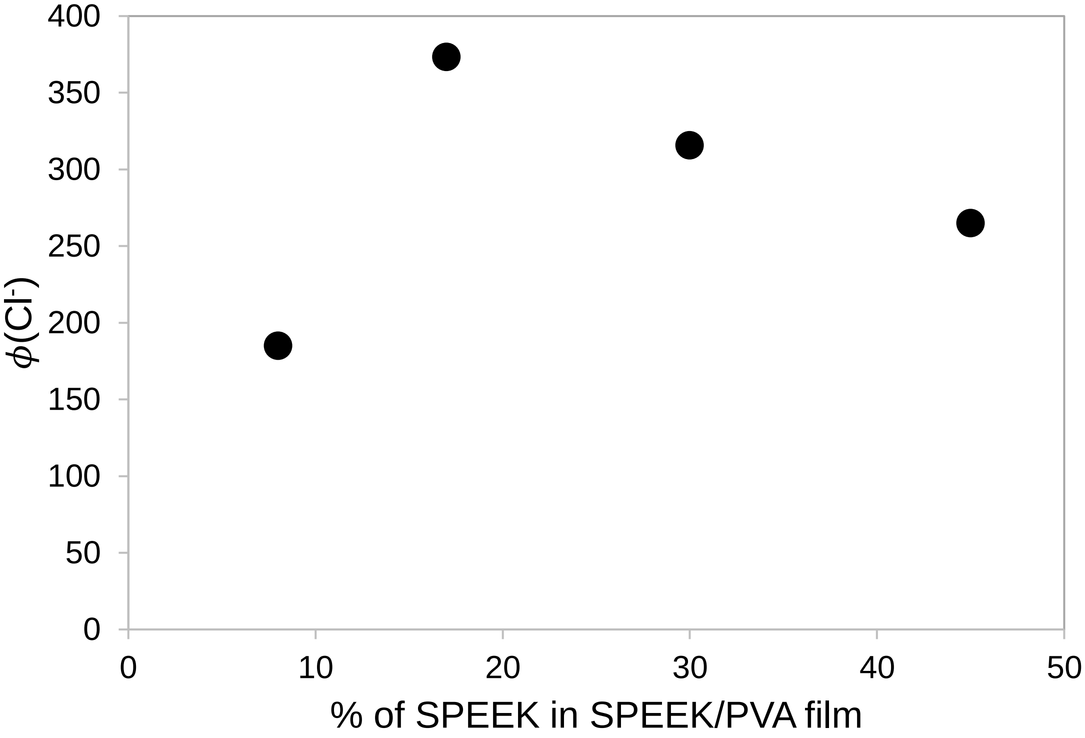

Figure 5.5. Dependence of Cl^- formation as a function of percent SPEEK present in SPEEK/PVA films (average thickness = 80 μm) photolyzed while immersed in 0.36 M HCO_2^- solutions at pH 7.3 containing 1 mL of CCl_4, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s.

originating from changes in SPEEK concentration. Earlier experiments employed films with a composition of 30/70 wt % SPEEK/PVA, which yielded efficient photoreduction of Ag^+.[16,18,20] The data presented in Figure 5.5 shows that the most efficient photoreaction occurred in films containing 17% SPEEK, which agreed exactly with the optimum composition determined for the $CHCl_3$ photoreduction induced by SPEEK/PVA films, see Chapter III.

A significant drop in $\phi(Cl^-)$ resulted at the lower SPEEK concentrations, which is not surprising given that this polymer is the material containing chromophoric BP functions that absorb electromagnetic radiation. Thus, less photons are absorbed at lower SPEEK concentrations, compromising the film efficiency to photogenerate SPEEK• and thereby reduce the halomethane. Less pronounced decreases were noticed at SPEEK amounts higher than 17%. Analogous decreases in $\phi(Cl^-)$ were presented in Chapter III for the $CHCl_3$ photoreduction by films, which were rationalized in terms of intermolecular quenching of $^3\{SPEEK\}^*$ by BP groups of adjacent macromolecules. Such effect became more predominant at high SPEEK concentrations, enabling closer proximity between the polyketone macromolecules.

Illustrated in Figure 5.6 is the evolution of $\phi(Cl^-)$ when the film thickness was varied between 48 - 82 μm. As was reported in Chapter II for the $CHCl_3$ photoreduction the reaction efficiency increased by a factor of about 3 upon decreasing the thickness of the films in this range. Only an improvement of 20% occurred in the range of 72 – 82 μm but larger changes were notice for thinner films. A possible explanation for such an effect assumed that the chain reduction of CCl_4 was confined mainly to the inner volume of the swollen film. However, some of the propagating radicals may migrate outside the film and initiate a different chain process in solution. Such rationalization could account for the fact that $\phi(Cl^-)$ increased for thinner films where the chances that propagating radical leave the swollen polymer matrices are higher.

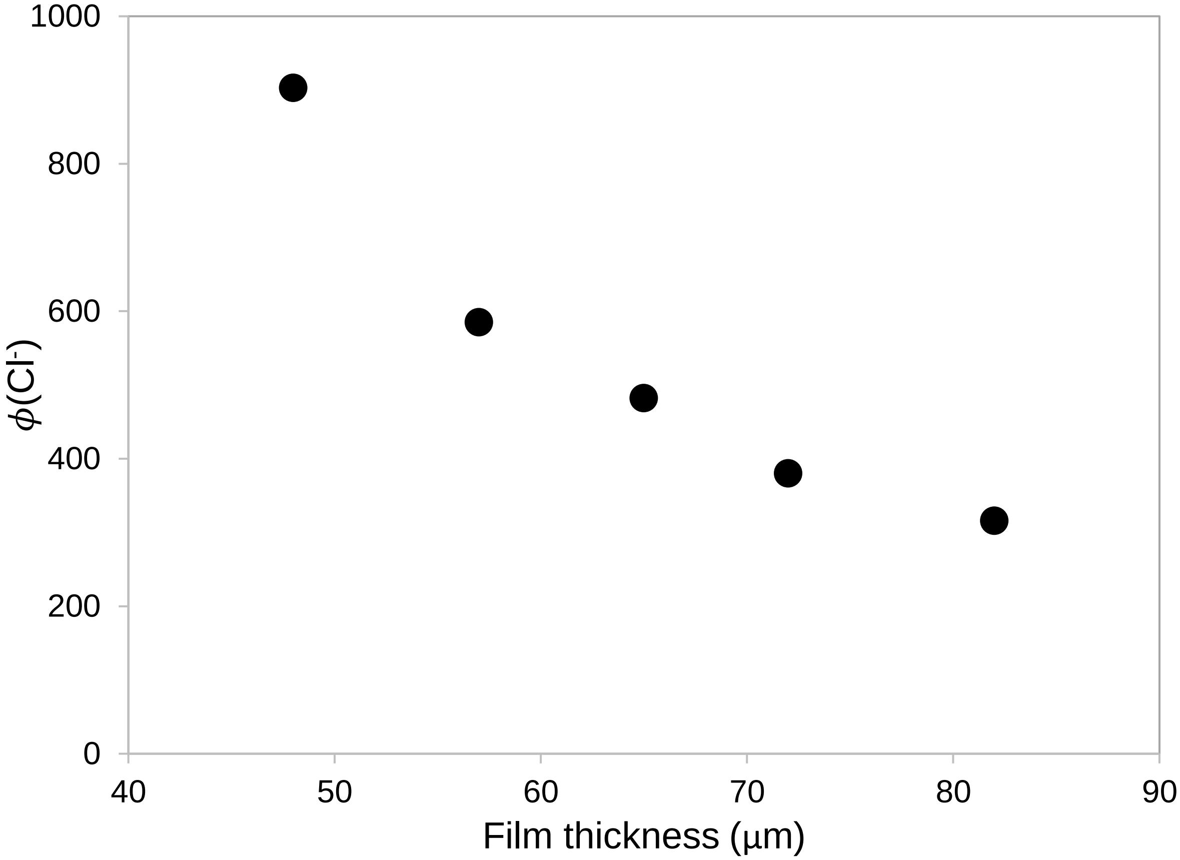

Figure 5.6. Dependence of reduction efficiencies on film thickness for illuminated SPEEK/PVA solid polymer blends immersed in 0.36 M HCO_2^- solutions at pH 7.3 containing 1 mL of CCl_4, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s.

Results presented in Chapter III demonstrated that the photoreduction of $CHCl_3$ induced by SPEEK/PVA films exhibited a marked non-linear increase in [Cl^-]. However, such behavior was noticeable mainly after long irradiation times. A simpler way to expose such behavior consisted in illuminating films repeatedly to assess their performance over long exposures. Given the potential utilization of such films for decontamination of sites polluted with CCl_4, testing of the films for repeated utilization seemed worth exploring long. Figure 3.7 displays data from analogous tests on the photoreduction of CCl_4, showing a linear decrease in quantum yield with increasing cycle of photolysis and film cleansing similar to those determined for the $CHCl_3$ reduction. While the effectiveness of the films decreased as noticed before, they still exhibited very large quantum yields of reduction even after 3 cycles. Hence, they remained highly

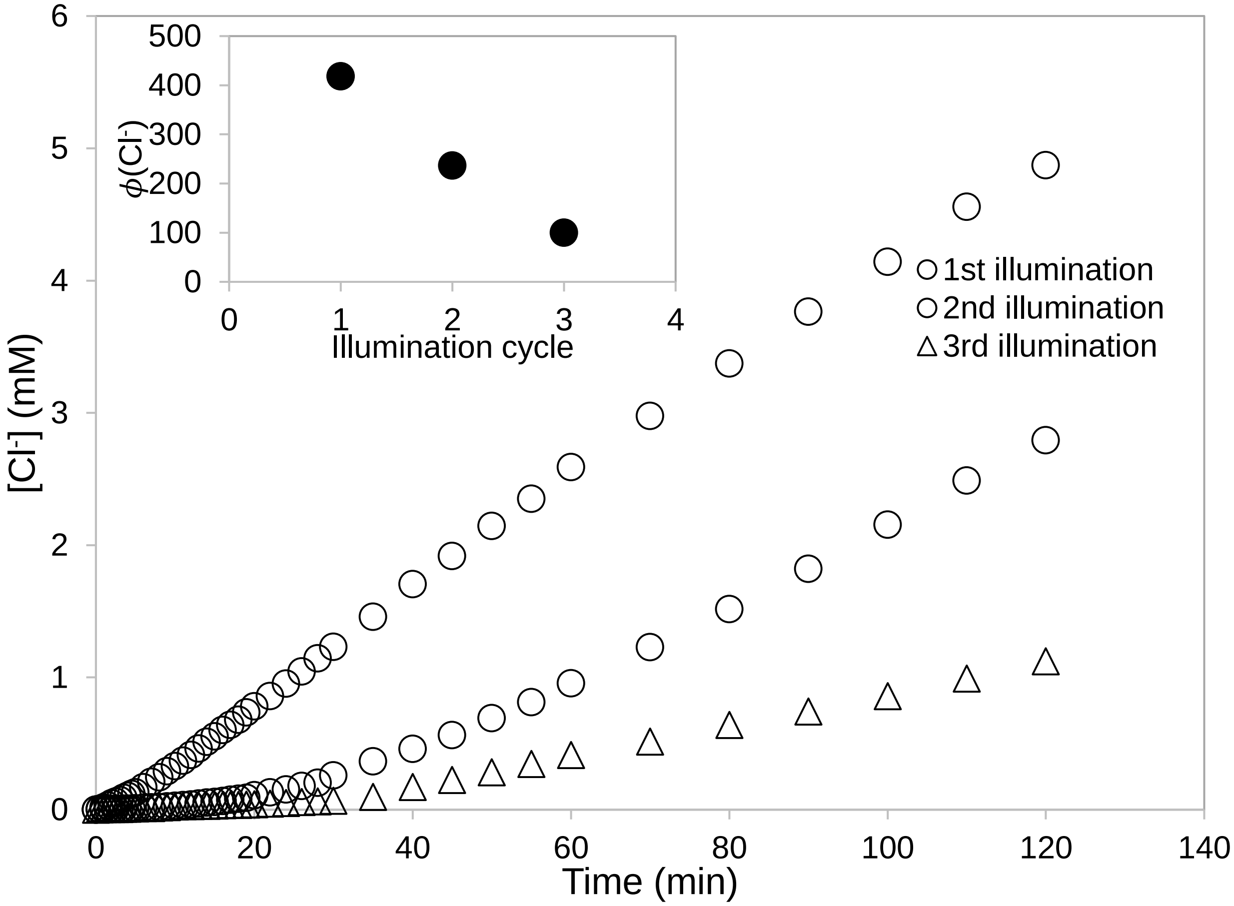

Figure 5.7. Formation of [Cl$^-$] during the repeating illuminations of a 66 μm thick SPEEK/PVA film in 0.36 M HCO_2^- solutions of pH 7.3 containing 1 mL CCl_4, $I_0 = 2.2 \times 10^{-6}$ M(hν)/s. Inset showing the dependence of quantum yield with illumination cycle.

capable of inducing photoreductions after 360 h of irradiation. Further efforts will be devoted to counter the decrease in photoactivity.

GC-MS determinations conducted on solutions photolyzed in the presence of films for extended times yielded only chloroform as a volatile product from the photoreaction while CO_2 was not found. The absence of CO_2 as a reaction product implies that most of the photogenerated $\bullet CO_2^-$ reacted either with SPEEK• to form LAT, or dimerized forming oxalate ions. The very large $\phi(Cl^-)$ values determined in the present investigation provided conclusive evidence that the photoreduction of CCl_4 took place via a chain process. However, such transformation may have involved $\bullet CCl_3$ and SPEEK• as chain carriers or via participation of the peroxyl $CCl_3O_2\bullet$ radical, which form by reaction of $\bullet CCl_3$ with O_2. Chain decompositions of CCl_4 involving $CCl_3O_2\bullet$ as a chain carrier have been identified but they take place either in organic solvents, or in mixtures of 50/50 water/alcohols.[26-28] Involvement of such processes is difficult to prove as they lead to complete dehalogenation of CCl_4 without formation of $CHCl_3$. A possibility is that both chain processes operated simultaneously. For that reason formulation of a reaction mechanism is, at the present time, not warranted. Further experiments employing very thin films are planned as they may reveal further mechanistic insight.

5.4 Conclusion

The results from this investigation agreed well those from an earlier study that reported a radical chain reduction of CCl_4 initiated by illumination of air-free SPEEK solutions. Important outcomes of the present work are the much higher efficiencies of reduction and the fact that the transformations can be initiated in the presence of air. Such characteristics makes utilization of SPEEK/PVA film an attractive possibility for their practical use for decontamination purposes. Further improvements of the photochemical properties of the films should be investigated.

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