İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

DIRECT AND SENSITIZED PHOTOINITIATED CATIONIC POLYMERIZATION BY USING PHENACYL ANILINIUM SALTS

M. Sc. Thesis by

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Department : **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

JANUARY 2003

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JANUARY 2003

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FENAÇİL ANİLİNYUM TUZLARININ KULLANILMASIYLA DOĞRUDAN VE UYARILMIS OLARAK BAŞLATILAN KATYONİK FOTOPOLİMERİZASYON

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OCAK 2003

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January 2003 Fatmanur Kasapoğlu

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LIST OF ABBREVIATIONS

^{1}H-NMR	**:** Proton Nuclear Magnetic Resonance Spectrospin
BVE	**:** Butyl vinylether
CHO	**:** Cyclohexene oxide
DPS	**:** Dialkylphenacylsulfonium salts
E_S	**:** Singlet energy
E_T	**:** Triplet energy
GC-MS	**:** Gas Chromatography-Mass Spectrum
GPC	**:** Gel Permeation Chromotography
M_n	**:** Number Average Molecular Weight
NVC	**:** N-vinyl carbazole
On^+	**:** Onium Salt
$PDA^+SbF_6^-$	**:** *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoroantimonate
PS	**:** Photosensitizer
UV	**:** Ultra violet

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DIRECT AND SENSITIZED PHOTOINITIATED CATIONIC POLYMERIZATION BY USING PHENACYL ANILINIUM SALTS

SUMMARY

Photoinitiated cationic polymerization is receiving more interest than the corresponding free radical polymerization in recent years. A novel phenacyl anilinium salt, *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoroantimonate, (PDA), was synthesized and used as photoinitiator for cationic polymerization of cyclohexene oxide (CHO), butyl vinyl ether (BVE) and N-vinylcarbazol (NVC). Plausable mechanism of the photoinitiation involves the decay of the excited PDA via both heterolytic and homolytic cleavages of carbon-nitrogen bond. Thus, phenacylium cations form directly or subsequent intermolecular electron transfer, respectively, initiate the polymerization. Further support for the mechanism was obtained by polymerizing CHO in a system containing 2,6-di-*t*-butyl-4-methyl pyridine, which is known to act as a proton scavenger, the rate of polymerization was not affected.

For the photosensitized systems, the mechanism of the initiation is even more complex. The results showed that polyaromatic photosensitizers such as perylene, anthracene, and certain aromatic carbonyl compounds such as benzophenone successfully activated the anilinium salt at the wavelengths where light is absorbed only by the photosensitizers. The plausible mechanism for the initiation was based on the electron transfer within the complex formed between photosensitizer and the salt. The thermodynamical calculations using redox potentials and excitation energies also favoured the proposed mechanism. Direct energy transfer seemed to be unlikely to occur.

FENAÇİL ANİLİNYUM TUZLARININ KULLANILMASIYLA DOĞRUDAN VE UYARILMIS OLARAK BAŞLATILAN KATYONİK FOTOPOLİMERİZASYON

ÖZET

Son yıllarda endüstriyel alanda geniş uygulamaları olan fotokimyasal katyonik polimerizasyon, serbest radikal polimerizasyondan daha cok ilgi görmektedir. Bu çalışmada yeni bir fenaçilanilinyum tuzu, *N*-fenaçil, *N*,*N*-dimetilanilinyum hekzafloroantimonat, (PDA), sentezlendi ve bu tuz siklohegzen oksit (CHO), butil vinil eter (BVE) ve N-vinilkarbazol (NVC) gibi katyonik polimerleşebilen monomerler için fotobaşlatıcı olarak kullanıldı. Başlama mekanizması, *N*-fenaçil, *N*,*N*-dimetilanilinyum hekzafloroantimonatın ışığı absorplayarak uyarılmış hale gelmesi ve bunun sonucunda C-N bağının hem homolitik hem de heterolitik olarak bölünmesini içermektedir. Doğrudan veya moleküller arası elektron transferi sonucu oluşan fenaçilyum katyonları polimerizasyonu başlatmaktadır. Ayrıca proton tutucu olarak 2,6-di-*t*-butil-4-metil piridin varlığında CHO monomerinin polimerleşmesi incelenerek mekanizma aydınlatıldı.

Fotouyarılmış sistemler için, başlama mekanizmasi oldukça kompekstir. Sonuçlar gösterdi ki, sadece fotouyarıcıların ışığı absorpladığı dalga boyunda; perilen, antrasen gibi poliaromatik fotouyarıcılar ve benzofenon gibi aromatik karbonil bileşikleri anilinyum tuzlarını aktive eder. Başlama için önerilen mekanizma, fotouyarıcı ile tuz arasında oluşan komplekse elektron transferi şeklindedir. Redoks potansiyeli ve uyarılma enerjileri kullanılarak yapılan hesaplamalar da önerilen mekanizmayı desteklemektedir. Doğrudan enerji transferinin gerçekleşdiği gözlenmemiştir.

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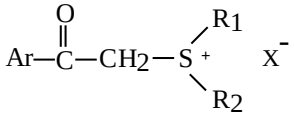
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1. INTRODUCTION

In recent years, photoinitiated cationic polymerization received more interest than the corresponding free radical polymerization [1]. The vast majority of photoinduced polymerization and crosslinking reactions, used in industrial applications for various techniques, e.g. those concerning surface coating and microlithography, involve a free radical mechanism [2]. A wide range of free radical photoinitiating systems, fulfilling requirements for industrial applications e.g., wavelength selectivity, solubility etc., are now available and their chemistry is well established [3]. The free radical photopolymerization has, therefore, reached an advanced level. On the contrary, the corresponding cationic polymerization, by which commercially important monomers such as epoxides and vinylethers are polymerized, has gained importance after the pioneering work of Crivello et al. who introduced sulphonium and iodonium salts as efficient photoinitiators for cationic polymerization [4-6]. Later on a number of other photoinitiating systems based on ionic and non-ionic compounds were describe [6-17].

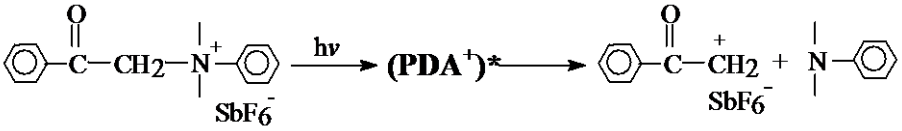
A large portion of todays relavant research concerns photoinitiators, i.e., introduction of new initiators or improving solubility, particularly in commercially important monomers, or modifying the spectral sensitivity of existing ones. In this respect the recent work of Crivello is noticable [18]. These authors described the facile synthesis of a novel series of second generation of dialkylphenacyl sulphonium salts (DPS) of the following structure.



Significant features of the DPSs involve the possibility to design of the compatibility with commercially important monomers and also spectral sensitivity [19].

It was shown by Nakano and Endo that certain anilinium salts act as latent thermal inititors for cationic polymerization [20]. On the other hand, these compounds do not undergo light induced reactions and can not be used as cationic photoinitiators. However, specially designed allyl anilinium salts were shown to be highly appropriate for the thermal and photochemical initiation of cationic polymerization [21]. In this case photoinitiation is achived by the added free radical photoinitiators via addition-fragmentation reactions.

Many photoinitiators are known and their photochemistry has been studied in detail. Among them the onium type photoinitators such as iodonium [22], sulphonium [23] and alkoxy pyridinium [9] salts occupy an important place due to their thermal stability, solubility in most of the cationically polymerizable monomers and efficiency in generating reactive species upon photolysis. Moreover, they can be photochemically activated in a broad wavelength range with the aid of various sensitizer and free radical photoinitiators [24-28]. We have recently reported [29] that *N*-phenacyl, *N, N*-dimethylanilinium hexafluorantimonate ($PDA^+SbF_6^-$) initiates cationic polymerization of appropriate monomers efficiently upon irradiation. Interestingly, the initiation mechanism by using this salt is quite different than with that of the sulphonium analogous [19,30]. It was proposed [29] that the phenacyl anilinium salts undergo an irreversible photolysis leading to fragmentation of the photoinitiator as depicted in reaction 1.1. Polymerization and spectroscopic investigations revealed that the benzylic cations, formed either by heterolytic cleavage or homolytic cleavage followed by electron transfer, are responsible for the initiation.



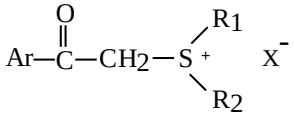
(PDA+) (1.1)

This study describes the activity of *N*-phenacyl, *N,N*-dimethylanilinium hexafluoro antimonate ($PDA^+SbF_6^-$) as a photoinitiator for cationic polymerization and also further investigations concerning the possibility of photosensitization of this compound by polynuclear aromatic compounds such as perylene, anthracene and phenothiazine and aromatic carbonyl compounds such as benzophenone and thioxanthone.

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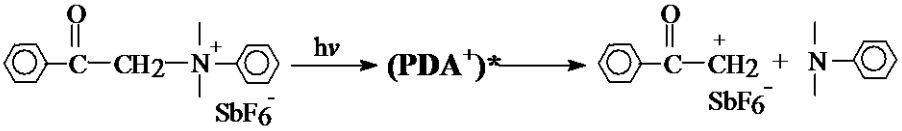
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2. THEORY

2.1. Photopolymerization

Photopolymerization, the utilization of electromagnetic radiation (or light) as the energy source for polymerization of functional monomers, oligomers and polymers is the basis of important commercial processes with broad applicability, including photoimaging and UV curing of coatings and inks. These processes require that light is absorbed by the system and utilized to effect the formation of new chemical bonds. Photopolymerization may be achieved by the utilization of photoinitiators, photocross-linking agents and photocrosslinkable polymers.

2.1.1. Photoinitiators

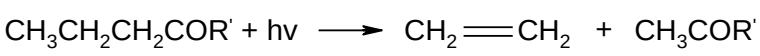
Photoinitiators for free-radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals.

2.1.1.1. Photoinitiation by intramolecular bond cleavage

Most peroxy initiators yield radicals on photolysis and benzoyl peroxide has frequently been used as a photoinitiator [32,33]. They require shorter wavelengths than azo compounds (<300nm), a disadvantage since many monomers absorb in this region. The same remark applies to many simple ketones which photodissociate according to the Norrish type I mechanism [34].

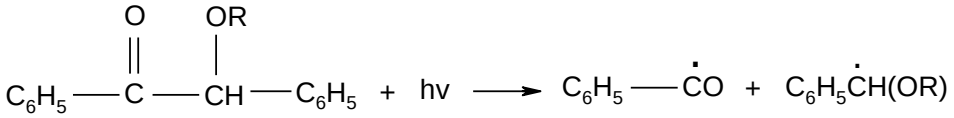
$$RCOR' + h\nu \longrightarrow RC\dot{O} + \dot{R}' \qquad (2.1)$$

Ketones carrying alkyl chains three or more carbon atoms long may undergo the essentially nonradical Norrish type II fission:



(2.2)

Benzoin is a well-known photoinitiator [35,36]. Benzoin ethers (a) which are much used in photocuring process, undergo a type I photodissociation into two different radicals. It has been reported that both types of radicals can initiate the polymerization.



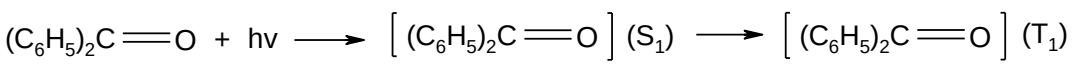
(a) (b) (c)

(2.3)

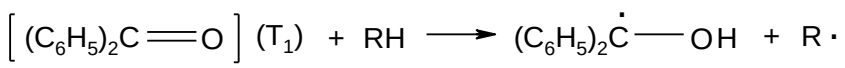
2.1.1.2. Photoinitiation by hydrogen abstraction

Photoinitiators of this group are generally aromatic ketones and include benzophenone, benzyl, quinones, Michler's ketone, and thioxanthanes. When photoexcited these compounds do not dissociate but enter into bimolecular abstraction reactions with hydrogen donors such as alcohols, ethers, tertiary amines, and so on.

The classical example is benzophenone, of which the photochemistry is well known [37]. The lowest excited singlet (S_1) is of $n \rightarrow \pi^*$ character and yields by intersystem crossing the lowest excited triplet (T_1). In the presence of a hydrogen donor RH the following reaction occurs:



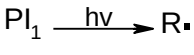
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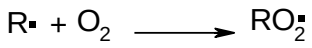
(2.5)

2.1.1.3.Type 1 and Type 2 combinations

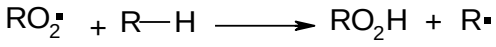
Mixtures of type 1-PI1 and type 2-PI2 are used to reduced air inhibition in the absence of amines [38]. A possible explanation for the synergistic effect is outlined below.



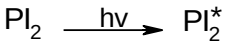
(2.6)



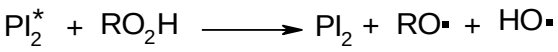
(2.7)



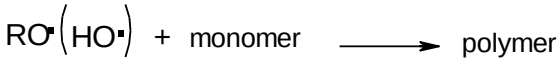
(2.8)



(2.9)



(2.10)



(2.11)

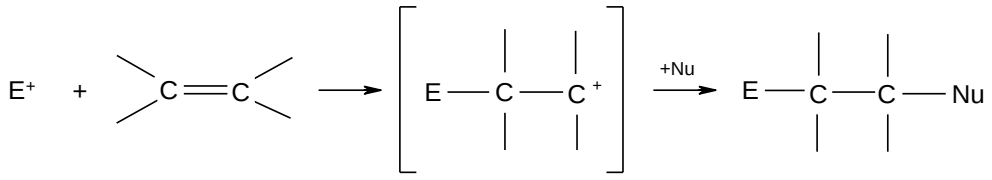
2.2. Cationic Polymerization

Within the context of polyaddition, cationic polymerization refers to chain growth reactions promoted by active species possessing electrophilic character: carbenium, carbonium, oxonium, sulfonium, ammonium and phosphonium ions, but also molecular chain carriers, i.e., mostly esters, which are sufficiently polarized to induce propagation. In these systems, the intrinsic structure and reactivity of the active species are maintained throughout the growth of a polymer molecule. Typical examples of such polyadditions are the cationic polymerizations of alkenyl

monomers through the opening of the C=C double bond and of saturated heterocyclic monomers through ring-opening. The two systems differ in that the active species in the polymerization of alkenes are carbenium ions, whereas onium ions are the active species in the polymerization of heterocycles [39].

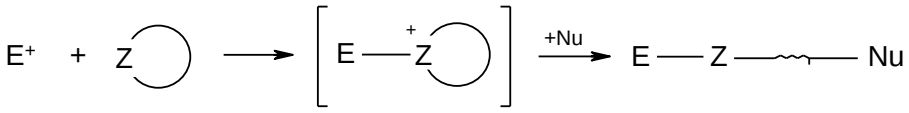
2.2.1. Electrophilic addition mechanism and monomers

All polyadditions can be viewed as special cases of specific physical organic reactions in which the intermediate species manages to survive long enough to ensure the growth of a macromolecule instead of rapidly collapsing into inactive products. A cationic polymerization is a special case of electrophilic addition. Classical electrophilic additions to the two types of common monomers in cationic polymerization, i.e., to the olefinic bond in alkenyl compounds and to the heteroatom in saturated heterocyclic compounds, can be represented as



(1)

(2.12)



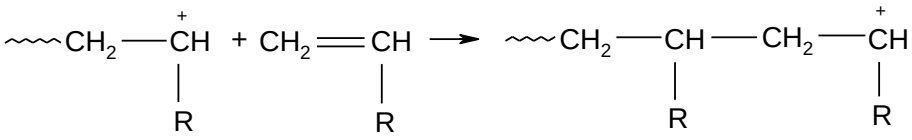
(2)

(2.13)

where Z = O, S, N—, P— etc. In cationic polymerization, the intermediates (1) and (2), shown as positively charged species must be prevented from collapsing through the reaction with an anion for long enough to allow them a large number of successive monomer additions.

2.2.1.1. Cationic polymerization of vinyl monomers

The monomers fitted for cationic polymerization include all those with electron donating substituents, in which the polarization of the double bond makes them sensitive to electrophilic attack by carbenium site.

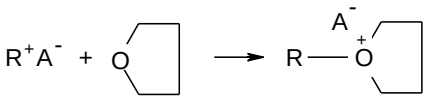


(2.14)

Solvents used in cationic polymerization should be stable towards acids and unable to react with electrophiles. Preferred are halogenated solvents such as methylene chloride, methyl chloride, ethylene chloride, carbon tetrachloride, nitro compounds such as nitromethane or nitrobenzene and also dioxane.

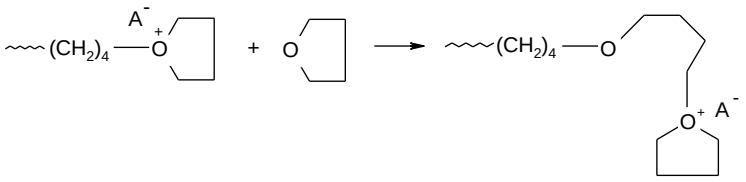
2.2.1.2. Cationic polymerization of heterocycles

The ring opening polymerization of several heterocycles proceeds by cationic initiation via oxonium sites that are formed upon alkylation (or protonation) of the monomer:



(2.15)

The mechanism of chain growth involves nucleophilic attack of the oxygen of an incoming monomer onto carbon atom in α-position with respect to the oxonium site, whereby the cycle opens and the active site is reformed on the attacking unit.



(2.16)

2.3. Photolatent Systems in Cationic Polymerization

Several vinyl and cyclic monomers, like alkyl vinyl ethers or the industrially important epoxides, may not be polymerized by a radical mechanism. The initiation has to be performed using an ionic initiator. Classical initiators dissociate in the reaction mixture into one initiating cation and a counter anion. The cation is therefore present almost immediately after adding the initiator. Externally stimulated initiators, on the other hand, liberate reacting cations only after stimulations such as heat or light. Thus, the time between adding the initiator and the actual initiation can be chosen from seconds up to several weeks. This circumstance enables externally stimulated initiators to be applied for curing formulations, where the curing (polymerization or crosslinking) of a coating may be initiated at exactly the time desired and with the curing rate intended. Notably, the counter anion does play a role in polymerization too. The anion has to be nonnucleophilic in order to prevent the termination of a growing chain by anion-cation combination. In general, for photoinitiated cationic polymerizations with both onium [40-42] and metal salts [43], molecular weights and percentage conversions increase in the order BF_4^- << PF_6^-< AsF_6^-< SbF_6^-.

Classical cationic initiators lack the following two disadvantages:

1. Since, usually all the initiator is added in the solid form or in a concentrated solution at the beginning of the polymerization and it initiates immediately, the concentration of the initiator at the beginning of the polymerization is not constant throughout the reaction mixture.

2. Due to the instantaneous initiation, upon adding the initiator an extensive evolution of heat is often observed. Therefore, one has to work at relatively low temperatures, what finally leads to relatively low polymerization rates.

Externally stimulated initiator systems do overcome these problems. By stimulations such as irradiation or heating, a controllable amount of initiating cations is formed. The concentration of initiating cations and finally of growing polymer chains may

conveniently be adjusted by choosing appropriate light intensities and temperatures for photo and thermolatent systems, respectively.

The polymers formed upon initiation by classical or externally stimulated initiators do often differ in molecular weight distribution. Since in externally stimulated polymerizations initiating cations are generated continuously, growing polymer chains with large differences in chain lengths are present at the same time. Therefore, polymers usually have a relatively broad molecular weight distribution. In case of classical initiators, all chains start to grow directly with adding the initiator. At the moment of termination, they are of almost the same lengths giving rise to polydispersities of nearly 1, provided that chain-breaking side reactions are of minor importance in the polymerization of the monomer involved.

What type of stimulation is applicable to generate cations depends on the chemical constitution of the system used. In some cases, such as benzylsulphonium or phosphonium salts, initiating cations may be formed by both heat and light. In many photolatent cationically polymerizing systems, moderate warming can be applied simultaneously with irradiation in order to enhance the polymerization rate.

Regarding onium salts, which are the most prominent latent cationic initiators, direct and indirect acting systems will be differentiated; this strict differentiation is reasonable because the initiating species produced by either of both systems are often not the same. In direct acting systems, the energy is absorbed by the onium salt and leads to its decomposition. In contrast to this, in indirect acting systems, the energy is absorbed by an additional component. After absorbing the energy, the additives can either react with the onium salt thus producing initiating species, or transfer their energy to the onium salt molecules. With changing the additives, one can often easily adjust to various temperature ranges or wavelengths for thermo- and photolabile systems, respectively.

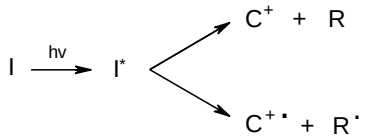
2.3.1. Onium salts

Onium salts are the most widely used cationic photoinitiators. These salts are compounds containing heteroatoms, with a cationic center on the heteroatom. As counter ions, mostly inorganic metal complex anions are used.

The polymerization by onium salts does generally start only after an external stimulation such as irradiation or heating. However, in a few cases dark polymerizations at room temperature have been observed [44].

2.3.2. Direct photoinitiation

If onium salt initiators, I , absorb light, electronically excited initiator, I^*, species are produced. The latter undergo a heterolytical or homolytical bond rupture leading to cations C^+ or $C^{+\cdot}$, respectively.

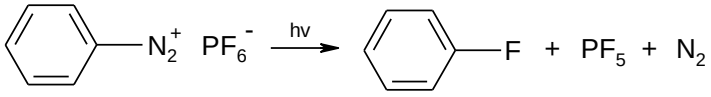


(2.17)

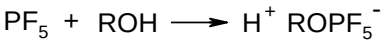
In some cases, these entities are able to react directly with monomer molecules starting a cationic polymerization. Frequently, C^+ or $C^{+\cdot}$ is inert towards the cationically polymerizable monomer in the manner necessary for initiating the polymerization. This often observed lack in reactivity is mostly explainable in terms of bulkiness of the species C^+ and $C^{+\cdot}$ produced in the primary reaction. However, both C^+ and $C^{+\cdot}$ are often able to react with the monomer or solvent molecules thus releasing the Bronsted acid H^+. Being highly reactive to all sorts of cationically polymerizable monomers, protons will act as initiating species in these circumstances.

Aryldiazonium Salts

Aryldiazonium salts are prepared by a treatment of aniline derivatives with sodium nitrite and a Bronsted acid, the latter one giving the counter anion. Upon irradiation, these salts with complex metal anions undergo a fragmentation generating a Lewis acid, which can initiate cationic polymerizations directly or react with a hydrogen donating constituent of the polymerization mixture yielding photons.



(2.18)



(2.19)

Simple benzyldiazonium salts absorb light only below 300 nm. By substituting the benzene ring, salts absorbing near UV and even visible light could be obtained. The decomposition quantum yields of aryldiazonium salts are relatively high, being usually between 0.3 and 0.6 [45]. However, these salts were, due to their thermal instability, scarcely used for practical applications. The salt's instability prevents long term storage; the initiation of the polymerization has to be started shortly after preparing the formulation. Another disadvantage derives from the evolution of nitrogen. The evolved gas leads to gas bubbles in the hardening coatings, thus making the material porous.

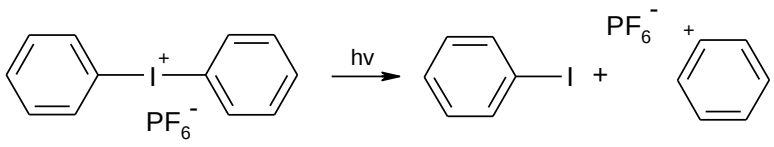
Diaryliodonium Salts

Among halonium salts, diaryl iodonium compounds are most prominent due to the fact that they are easy to prepare and very reactive. Symmetrical diarylsulphonium salts are obtained by a reaction of aromatic compounds with potassium iodate in the presence of sulphuric acid and acetic anhydride [22,46]. Since the products possess nucleophilic counter anions, the anion has to be changed for a less nucleophilic one.

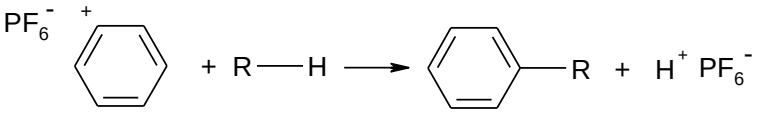
The spectral sensitivity of diaryliodonium salts is relatively poor. For example, the simplest salt, diphenyl iodonium, possesses an absorption maximum at 227 nm. Diphenyl iodonium salts substituted with electron donating groups show absorption maxima at lower energies. However, in most applications various additives are applied in order to exploit the emission wavelengths of common light sources.

Upon UV irradiation of diphenyl iodonium salts, the Ar-I bonds are ruptured, both hetero- and homolytically. While the heterolytic pathway generates a phenyl cation and an iodobenzene molecule (2.20), a phenyl radical and an iodobenzene radical cation are formed by homolytic cleavage (2.22). Both mechanisms involve the

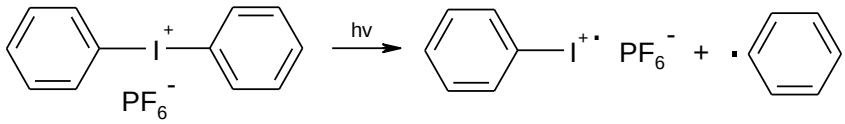
interaction with hydrogen donating solvent or monomer yielding Bronsted acid that initiates the polymerization. Besides, the reaction of escaping phenyl cations or phenyl radicals with neighboring iodobenzenes also produces protons and additionally various phenyliodobenzene derivatives.



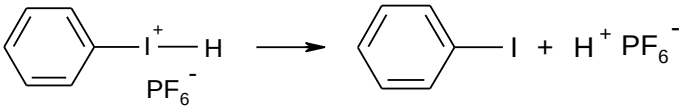
(2.20)



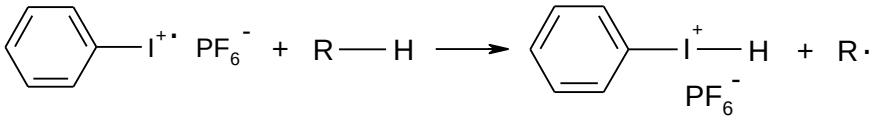
(2.21)



(2.22)



(2.23)



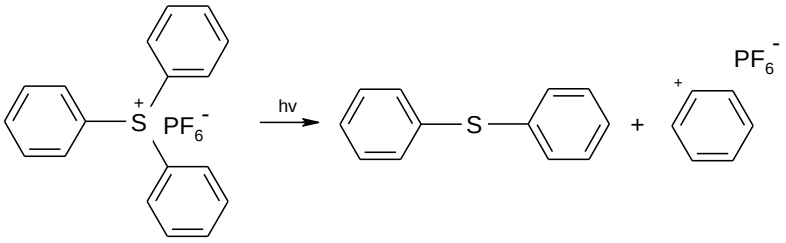
(2.24)

The photolytical formation of phenyliodonium radical cations has been evidenced by its transient absorption spectrum with maxima at 660 and 310 nm [47,48]. The heterolytic bond cleavage is the dominating reaction pathway for the direct irradiation of diaryliodonium salts [49,50]. Bronsted acid, formed upon the direct irradiation of diphenyliodonium salts has been used for the polymerization of many monomers.

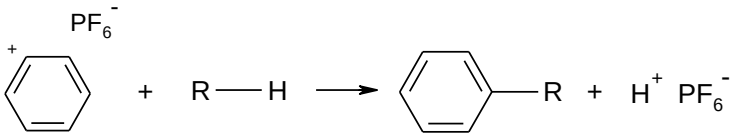
Sulphonium Salts

Regarding cationic photo polymerization, triaryl and alkylaryl sulphonium salts play the predominant role among all sulphonium salts [51]. Trialkyl sulphonium salts are less stable and initiate the polymerization of reactive monomers spontaneously [52].

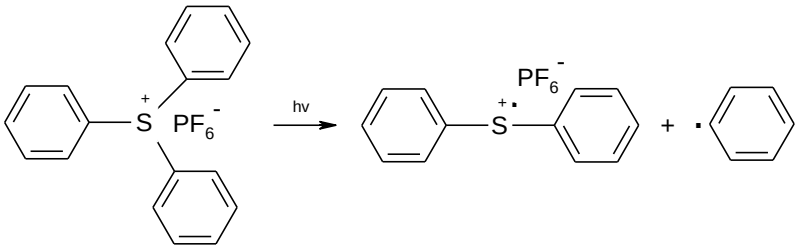
Regarding the photolysis mechanism of triarylsulphonium salts, both heterolytic (2.25, 2.26) and homolytic (2.27, 2.29) bond rupture of one sulfur-carbon bond is evidenced. In direct irradiation of triphenylsulphonium salts, the heterolytic bond cleavage starting from the excited singlet state is the preferred reaction pathway [53]. As in the case of diaryliodonium salts, in secondary reactions strong electrophilic Bronsted acid is produced. This acid initiates the cationic polymerization.



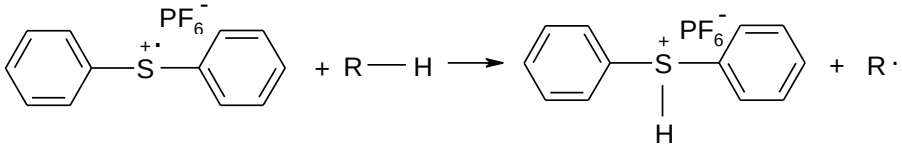
(2.25)



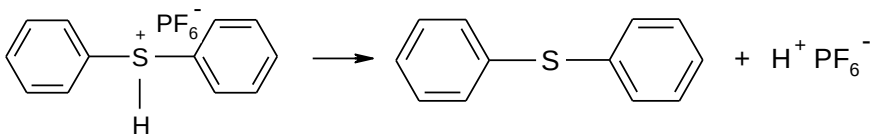
(2.26)



(2.27)

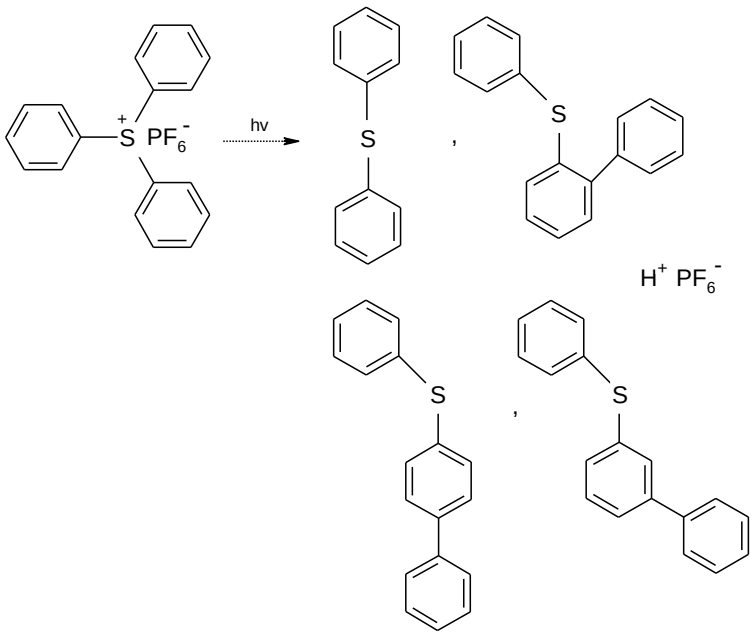


(2.28)



(2.29)

Mechanistic studies based on product analysis [54,55] have shown that both phenyl cations and phenyl radicals formed by either homolysis or heterolysis may add to neighboring sulfur bond aromatic rings, thus generating various biphenylthiophenyl isomers (2.30). The selectivity ortho > metha > para observed for these solvent cage products shows that the phenyl cations or phenyl radicals tend to react with the closest available site. In this addition reaction, protons are released.



(2.30)

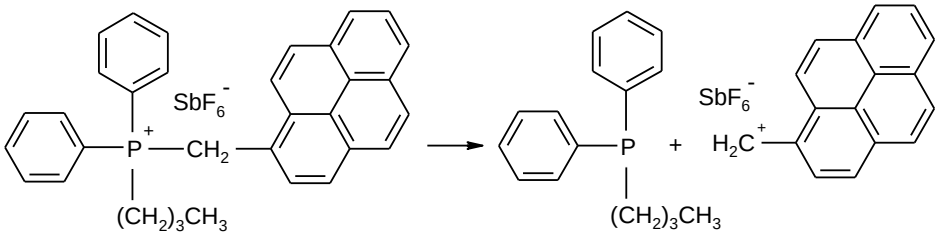
Cationic polymerizations following the direct photolysis of triarylsulphonium salts have been used for the industrially important UV curing of epoxy coatings [56]. Moreover, they were used in a number of investigations with reactive monomers with either epoxide [57-59] or vinyl groups [60].

Phosphonium Salts

The preparation of phosphonium salts is based on the reaction of chloromethylated or bromomethylated aryl compounds with the corresponding phosphines [61-63]. Phosphonium salts with absorptions acceptable for the direct photolysis have been synthesized.

Benzyl or pyrenylmethyl group containing phosphonium salts produce the respective carbon centered cations after a heterolytic bond rupture according to the reaction

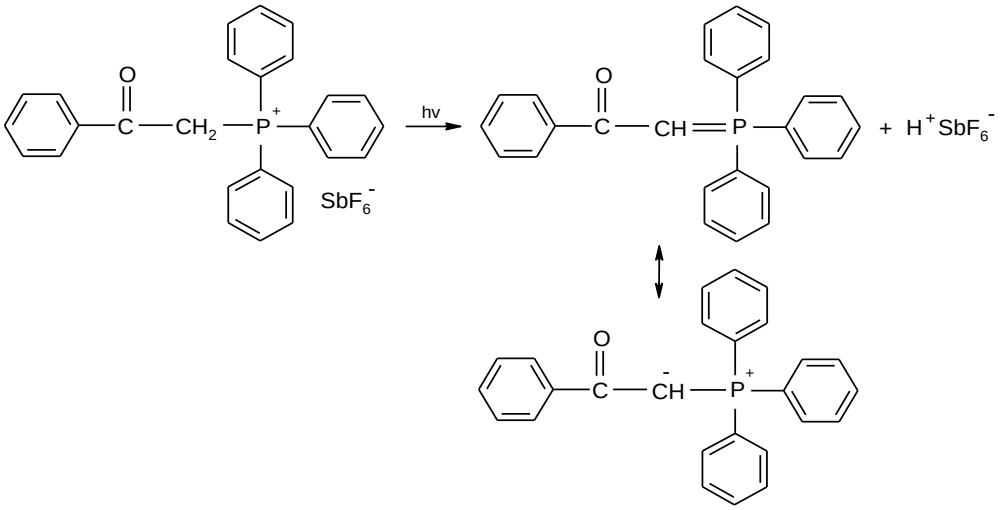
(2.31) [64-66]. These cations are assumed the initiating species in cationic polymerization.



(2.31)

The excellent initiating ability of phosphonium salts containing pyrenylmethyl groups has been demonstrated for epoxides and vinyl monomers [67,68]. In the polymerization of butylvinyl ether, conversions of 100 % were achieved. UV-VIS and ^{1}H-NMR spectra of the polymers obtained gave a clear evidence for the presence of aromatic groups thus providing that, indeed carbocations with aromatic substituents start the chain reaction.

In the case of phenacyltriphenyl phosphonium salts, however, Bronsted acid is expected to initiate cationic polymerizations. They are used in the cationic polymerization of cyclohexene oxide, styrene and *p*-methyl styrene [63-69] .



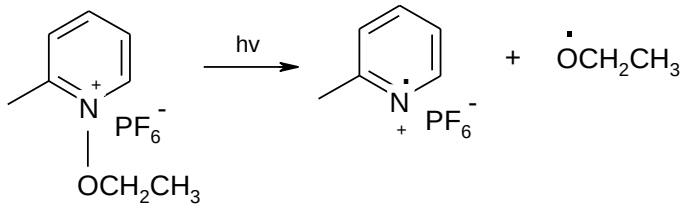
(2.32)

N-Alkoxy Pyridinium Salts

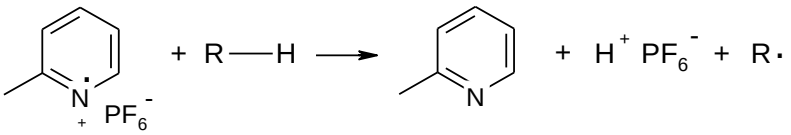
N-Alkoxy pyridinium salts are obtained with relatively high yields by a reaction of pyridine N-oxides with a triethyloxonium salt in methylene chloride or chloroform [9]. Quinolinium salts can also be prepared from the corresponding N-oxides [70]. In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions.

The absorption of the pyridinium based photoinitiator lies in the far UV region. Phenyl substituents shift the absorption maximum towards higher wavelengths by 40 nm.

When absorbing UV light in the presence of a cationically polymerizable monomer, pyridinium type salts do readily initiate the polymerization [9,70,71]. The two initiation mechanisms described are depicted in (2.33-2.34) on the example of N-ethoxy-2-methylpyridinium hexafluorophosphate (EMP $^{+}$ PF_6^{-}).



(2.33)



(2.34)

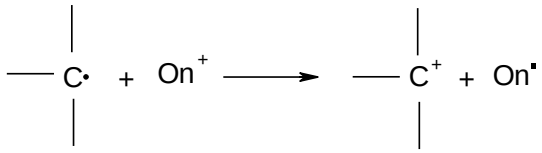
Upon photolysis, the initiator's nitrogen-oxygen bond is ruptured forming a pyridinium type radical cation and an alkoxy radical. Detected by laser flash photolysis, the former were found to be highly reactive towards various nucleophilic monomers. Bronsted acid formed in the presence of hydrogen donors (monomer, solvent) may initiate the polymerization, as illustrated in (2.34).

2.3.3. Indirect photoinitiation

Several systems were developed to extend the applicability of the onium salt photoinitiators towards longer wavelengths. In these cases, additives are present which participate in the reaction sequences to yield reactive species capable of initiating the cationic polymerization.

2.3.3.1. Free radical promoted cationic polymerization

Many photochemically formed radicals can be oxidized by onium salts according to the following reaction:

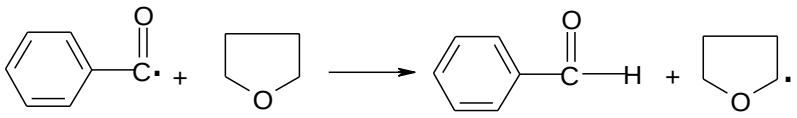


(2.35)

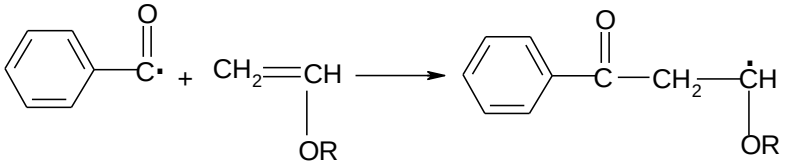
The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as the free radical promoted cationic polymerization.

This so-called free radical promoted cationic polymerization is an elegant and flexible type of externally stimulated cationic polymerization [72,73]. Free radicals may be produced by various modes; photochemically, thermally or by irradiating the system with high-energy rays. Suitable radical sources for all modes of stimulation are available. The photochemical generation of radicals can be applied even at low temperatures. In order to exploit the photon energy efficiently, a photolabile compound with an absorbency matching with the emission spectrum of the lamp has to be chosen. Usually, one works at a wavelength's region, where the onium salt itself is transparent.Being photolized with high quantum yields (0.41 for benzoin [28]); benzoin derivatives are so far the most effective photoinitiators. The photolysis of benzoin salts results in the generation of strong electron donor radicals. The influence of factors, such as light intensity, onium salt concentration or the type of radical source onto the rate of radical induced cationic polymerization with benzoin derivative/onium salt systems has been carefully investigated [74]. In addition, to direct generation of electron donating radicals, non-nucleophilic radicals, like $PhCO^{\cdot}$, $(R_1R_2)\ PO^{\cdot}$ and $Ph^{\cdot}$ Formed upon photolysis of the photolabile compound may react

with monomer molecules producing electron donating radicals, as described on the examples of $PhCO^{\cdot}$ in reaction (2.36) and (2.37).



(2.36)



(2.37)

Thus formed, these radicals can easily be oxidized by onium salts yielding initiating species. The efficiency of onium salts as oxidizing agents is related to their electron affinity. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{red}^{1/2}$ (On^{+}).

The efficiency of onium salts in this mode of polymerization rises in order of trialkyl sulfonium salts ($E_{red}^{1/2}$ = -1.2 V) < alkoxy pyridinium salts ($E_{red}^{1/2}$ = -0.7 V) < diaryliodonium salts ($E_{red}^{1/2}$ = -0.2 V) <aryldiazonium salts ($E_{red}^{1/2}$ = 0.3 V) [73].

Aryldiazonium salts are most suitable for the oxidation of radicals. However, their practical application is hampered by the lack of thermal stability. Diphenyliodonium salts have also a relativley high reduction potential. Being very suitable for the oxidation of free radicals, these salts have been most frequently used for the oxidation of photogenerated free radicals [74-78]. On the other hand, triphenylsulphonium salts have only limited potential for radical induced cationic polymerizations due to their low reduction potential. However, some highly nucleophilic radicals could be oxidized with sulphonium salts [79,80].

Provided the oxidation and reduction potentials of the free radical and the onium ion, respectively, are known, it can be estimated on the bases of the Rehm-Weller equation (2.38) whether a radical can be oxidized by a given onium salt or not.

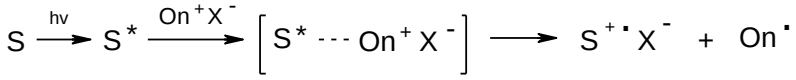
$$\Delta G = F\,[E_{ox}^{1/2}(R^{\bullet}) - E_{red}^{1/2}(On^{+})] \quad (2.38)$$

F: Faraday constant

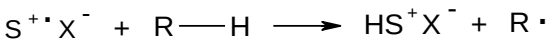
However, the calculation of ΔG is usually not feasible since the exact oxidation potentials $E_{ox}^{1/2}(R^{\bullet})$ of most radicals involved in radical promoted polymerizations are unknown.

2.3.3.2. Photoinitiation by electron transfer

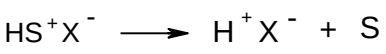
Many aromatic hydrocarbons are able to sensitize the decomposition of onium salts via electron transfer in an excited complex referred to as exciplex [25,27]. For this type of cationic initiation, the following general scheme holds:



(2.39)

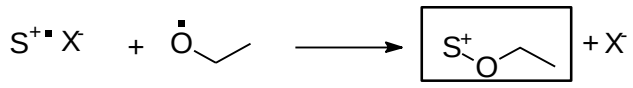


(2.40)



(2.41)

The excitation of the sensitizer is followed by the formation of a complex between excited sensitizer molecules and ground state onium salt. In this complex, one electron is transferred from the sensitizer to the onium salt giving rise to the generation of sensitizer radical cations. These can by themselves initiate the polymerization of appropriate polymers or, alternatively, interact with hydrogen containing constituents of the polymerization mixture (solvent, monomer) resulting in the release of Bronsted acid. In the case of alkoxy pyridinium salts, an additional mechanism has to be taken into account. Alkoxy radicals, which are generated by the decomposition of alkoxy pyridinium salts, react with sensitizer radical cations yielding initiating sulfur centered cations [81].



(2.42)

The electron transfer (2.39) is energetically allowed, if ΔG calculated by (2.43) (extended Rehm-Weller equation) is negative.

$$\Delta G = F\,[E_{ox}^{1/2}(S) - E_{red}^{1/2}(On^{+})] - E(S^{*}) \qquad (2.43)$$

F: Faraday constant

E (S*): Excitation energy of the sensitizer (singlet or triplet)

Since the oxidation potentials of sensitizers, $E_{ox}^{1/2}$ (S), are easy to determine (in contrast to that of radicals), the calculation of ΔG can indeed be applied in order to predict whether or not an oxidation would take place. The half wave oxidation potentials ($E_{ox}^{1/2}$) and absorption characteristics of sensitizers used most frequently in conjunction with onium salts are summarized in Table 2.1.

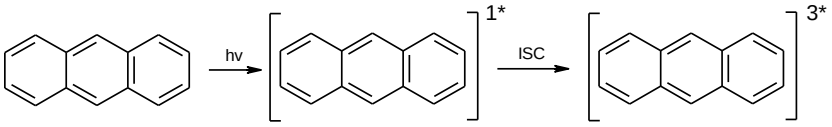
Table 2.1. Triplet or singlet excitation energies (E_{PS}^{*}), half wave oxidation potentials ($E_{ox}^{1/2}$)

sensitizer	$E_{(PS^{*})}$ (kJ.mol^{-1})	$E^{ox}_{1/2}$ (V)
Perylene	277	0.9
Anthracene	319	1.1
Phenothiazine	239	0.6
Benzophenone	290	2.7
Thioxanthone	277	1.7

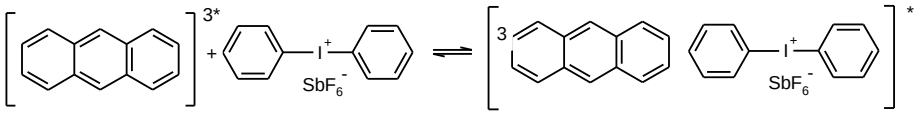
However, not all sensitizers are suitable in conjunction with onium salts. According to (2.43), the requirements are low oxidation potentials, $E_{ox}^{1/2}$ (S), and relativley high excitation energies, E (S*), of the sensitizer. Besides that, only onium salts with high (low negative) reduction potentials $E_{red}^{1/2}(On^{+})$, such as diphenyliodonium or alkoxy pyridinium salts are easily reduced by the sensitizer.

In the case of sensitization of onium salts (especially diphenyliodonium and triphenylsulphonium salts) by anthracene, exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer

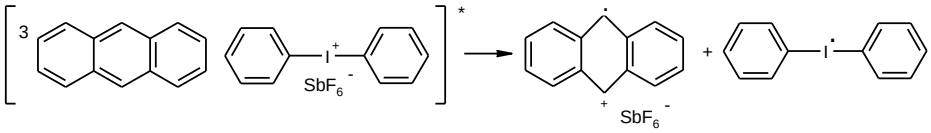
fluorescence. The reactions are illustrated below on the example of diphenyliodonium salt.



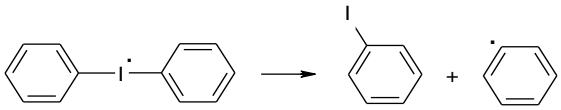
(2.44)



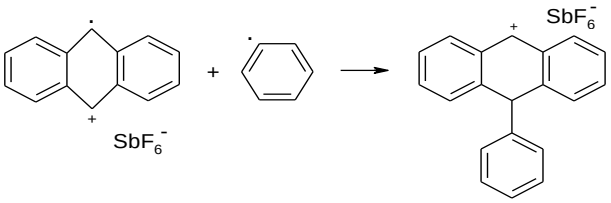
(2.45)



(2.46)



(2.47)

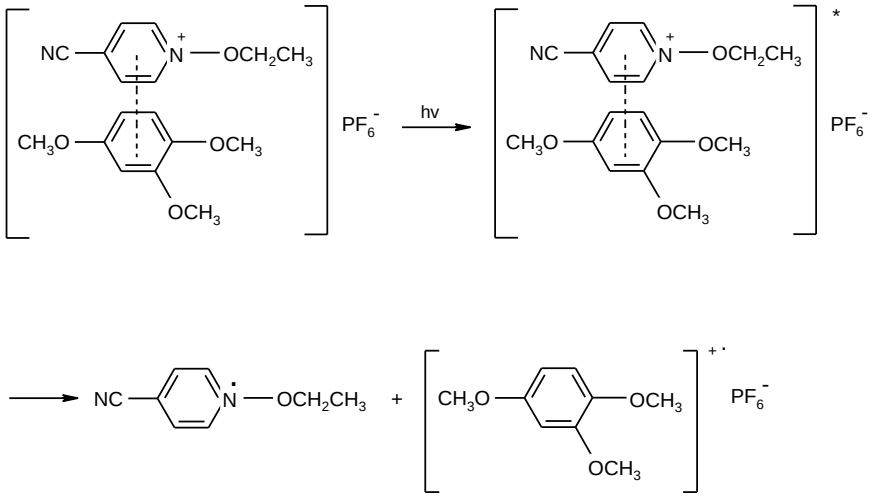


(2.48)

2.3.3.3. Photoinitiation by charge transfer complexes

Pyridinium salts are capable of forming ground state CT complexes with electron-rich donors such as methyl- and methoxy-substituted benzene [82]. Notably, these complexes absorb at relativley high wavelengths, where the components are virtually transparent. For example, the complex formed between N-ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2,4-trimethoxybenzene possesses an absorption maximum at 420 nm. The absorption maxima of the two constituents are 270 nm and 265 nm for the pyridinium salt and trimethoxybenzene, respectively. It was found that the CT complexes formed between pyridinium salts and methyl- and

methoxy-substituted benzene act as photoinitiators for the cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide [82]. The following mechanism for the initiation of the cationic polymerization has been suggested:

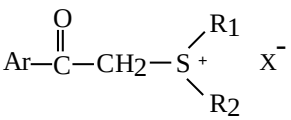


(2.49)

Since the proton scavenger 2,6-di-tert-butylpyridine did not noticeably influence the polymerization, the initiation by Brønsted acid that could be formed after an interaction with hydrogen containing components can be excluded. Notably, the CT complexes described above are applicable for the photoinitiation of epoxide monomers but not for the photoinitiation of vinyl ethers and N-vinyl carbazol. The latter monomers are already polymerized in a dark reaction upon addition of these complexes.

2.4. Phenacylsulfonium Salts

Dialkylphenacylsulfonium salts, (I), in which the anions,



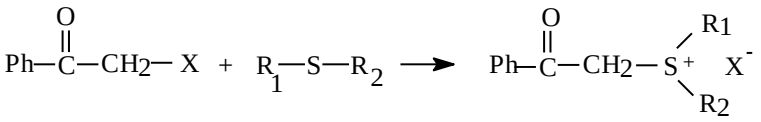
(I)

X^-, are of poor nucleophilic character, as, for example, BF_4^-, AsF_6^-, SbF_6^-, PF_6^-, etc., were reported by Crivello to be a new class of useful photoinitiators for cationic polymerization [23]. Crivello and co-workers described the development of photosensitizers for these compounds that permit the extension of their photoresponse into the long wavelength region of the ultraviolet spectrum [26]. The

excellent photosensitivity of these photoinitiators together with their very good thermal stability makes them ideal photoinitiators for the polymerization of many types of cationically polymerizable monomers.

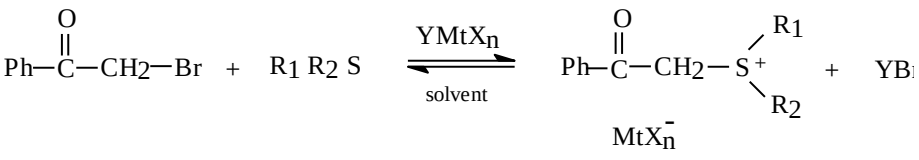
2.4.1. Synthesis of phenacylsulfonium salts

Dialkylphenacylsulfonium salts can be readily prepared in yields generally above 80% by the method of Bohme and Krause [83] that involves the condensation of phenacyl halides with dialkylsulphides (2.50).



(2.50)

As in the case of other sulphonium salts, the above simple halide containing salts are not directly suitable for use as photoinitiators because of the tendency of these anions to act as terminating agent in cationic polymerizations. Direct metathesis of the sulphonium halides with the appropriate acid or alkali metal salts of such nonnucleophilic anions as PF_6^-, SbF_6^- and AsF_6^- suffices to convert them to the active photoinitiators. In a following work, the same group has described a new simplified synthetic procedure for the preparation of dialkylphenacylsulfonium salts. As shown in (2.51), the synthesis involves a one-pot reaction of phenacylbromides (2-bromoacetophenones) or their aryl counter parts with the appropriate dialkyl sulfides in the presence of an alkali metal salt of the desired nonnucleophilic anion.

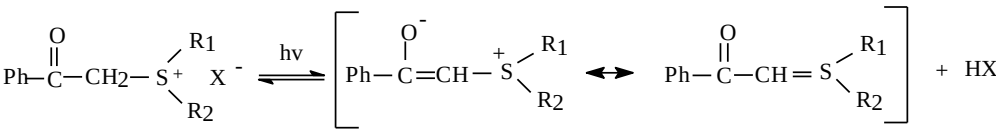


(2.51)

This way, dialkylphenacylsulfonium salts possessing a wide variation in the length and structure of the alkyl chains and photochromophoric groups were sucessivley synthesized.

2.4.2. Photolysis of phenacylsulphonium salts

The overall mechanism described for the sulphonium salts is essentially reversible and in the absence of monomers the ylides rapidly react with the protonic acid to afford the starting salt (2.52).



(II) (2.52)

The former compounds reversibly photodissociate to form the resonance stabilized ylids (II) and protonic acid, HX.

The thermal back reaction competes with the forward photolysis and results in an overall steady-state concentration of ylid and acid. While sulphonium ylids are in general highly reactive fleeting species, resonance stabilized ylids (II) has been prepared and isolated as stable compounds [84,85]. It is interesting to note that among related sulphonium salts, only those that can give similar resonance stabilized ylids are useful photoinitiators.

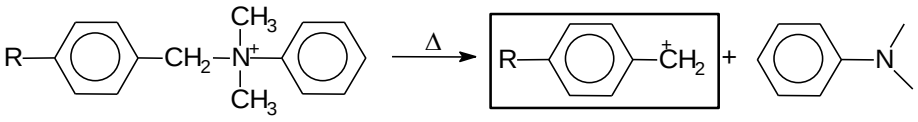
The protonic acids, HX, formed during the photolysis of dialkylphenacyl sulphonium salts are strongly solvated species. Further, the possibility that solvents may be involved in the formation of the acids by assisting in the removal of a proton from the excited sulphonium salts cannot be ruled out.

The reversibilty of the photoinduced process will be discussed in the results and discussion section in order to provide comperasion with the photoinitiaon mechanism of the phenacylanilinium salts.

2.5. Anilinium Salts

Previously, it was established that anilinium salts initiate the cationic polymerization in two different mechanisms depending on the structure of the salt used. First, Endo and co-workers investigated the thermal initiation by benzyl ammonium salts [20].

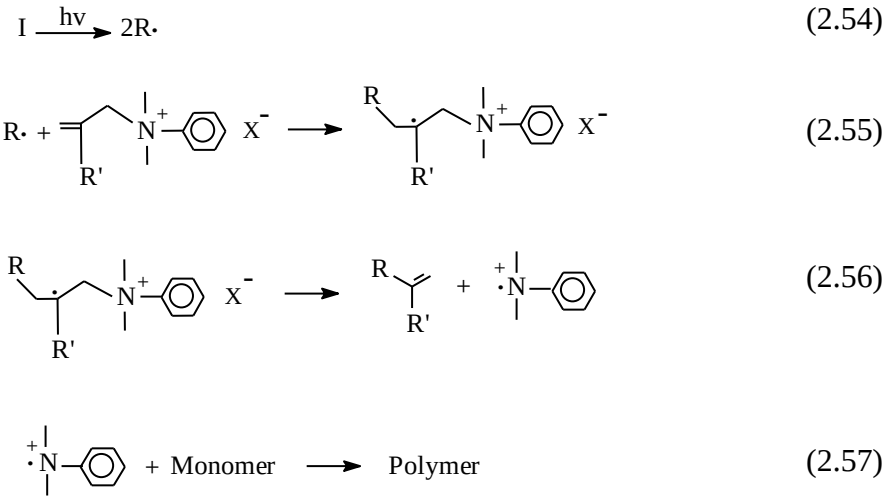
The thermolysis of these salts gives dimethyl aniline and benzyl cations, the latter being very efficient in initiating cationic polymerizations.



(2.53)

Polymerization of a typical cationic monomer gycdylphenylether (GPE) proceeded homogeneously because the initiator is soluble in the monomer. It was also pointed out by the same authors that *N*,*N*-dimethyl aniline formed concominantly terminates the polymerization. Thus polymer chain ends contain terminal amino groups.

Specially designed allyl anilinium salts were shown to be highly appropriate for the thermal and photochemical initiation of cationic polymerization [21]. In this case photoinitiation is achived by the added free radical photoinitiators via addition-fragmentation reactions.



(2.54)

(2.55)

(2.56)

(2.57)

Phenacylanilinium salts with non-nucleophilic counter anions are expected to act as latent photoinitiors, because the phenacyl moiety can be photochemically excited and *N*,*N*-dimethylaniline would behave as a good leaving group due to its weak basicity.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Cyclohexene oxide (CHO) (Fluka)

It was vacuum distilled from calcium hydride (CaH_2) before use.

Butyl vinyl ether (BVE) (Fluka)

It was extracted with water, dried with sodium and distilled.

N-Vinyl carbazole (NVC) (Fluka)

It was recrystallized from ethanol.

3.1.2 Solvents

Methylene chloride (CH_2Cl_2) (Lab-scan)

It was used as solvent in polymerization, dilution of polymer solutions and in UV measurements. It was first extracted with sulphuric acid, washed with water, then extracted with 5 % NaOH solution, and again washed with water. It was dried over calcium chloride and distilled by fractionation column.

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

Tetrahydrofuran (THF) (J.T. Baker)

It was used as eluent for choromatography as received (HPLC grade).

Acetone (Merck)

It used as solvent in the synthesis of $PDA^+SbF_6^-$.

3.1.3. Sensitizers

Perylene (Aldrich)

It was recrystallized from toluene.

Benzophenone (Merck)

It was recrystallized from heptane.

Phenothiazine (Aldrich)

It was recrystallized from toluene.

Thioxanthone (Fluka)

It was recrystallized from hexane.

Anthracene (Aldrich)

It was used as received.

3.1.4. Initiators and Other Chemicals

Benzoin (Aldrich)

It was recrystalized from ethanol prior to use, and used as a photoinitiator.

Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) (Fluka)

It was used as received.

Triphenylsulfonium hexafluorophosphate ($Ph_3S^+PF_6^-$) (Fluka)

It was used as received.

***N,N*-dimethylaniline (Fluka, 98%)**

It was distilled prior to use.

Bromoacetophenone (Fluka)

It was used as received.

Sodium hexafluoroantimonate (Aldrich)

It was used as anion exchanger in the synthesis of $PDA^{+}SbF_6^{-}$. It was used without further purification.

2,6-di-*t*-butyl-4-methyl pyridine (Aldrich)

It was used as a proton scavenger in the polymerization. It was used without further purification.

3.2. Equipments

3.2.1. Photoreactors

A merry-go-round type photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

For photoirradiations at monochromatic wavelength, AMKO LTI photoreactor equipped with a XBO 75 W xenon lamp and monochromator.

3.2.2. UV Spectrophotometer

UV-Visible spectra were recorded on a Perkin Elmer Lambda 2 spectrometer.

3.2.3. Elemental Analysis

Elemental analysis measurements were performed by a CHNS-932 (LECO) instrument.

3.2.4. Nuclear Magnetic Resonance Spectra

^{1}H-NMR spectra were recorded on a Bruker 250 MHz instrument.

3.2.5. Gel Permeation Chromatography (GPC)

GPC analyses were performed via set-up consisting of a Waters pump and three styragel HR3, HR4, HR4E columns with THF as the eluent, at a flow rate of 1 ml min^{-1} and detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3.2.6. Gas Chromatography-Mass Spectrum (GC-MS)

GC-MS analysis was performed with Varian 3700 GC equipped with quartz capillary column, permaphase PVMS/54, length 25 m, i.d.0.3 mm connected to a Varian MAT-44 mass spectrometer.

3.3. Synthesis of *N*-phenacyl *N,N*-dimethylanilinium hexafluoroantimonate ($PDA^+SbF_6^-$)

Into a 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 1.5 g (7.54 x 10^{-3} mol) of bromoacetophenone, 0.914g (7.54 x 10^{-3} mol) *N,N*-dimethylaniline and 1.951 g (7.54 x 10^{-3} mol) $NaSbF_6$ and 50 ml of acetone. The reaction mixture was brought to reflux and held at this temperature for 15 min. The dark pink solution was filtered to remove NaBr that was formed during the reaction. Then, the solvent was removed on a rotary evaporator, leaving *N*-phenacyl, *N,N*-dimethylanilinium hexafluoroantimonate ($PDA^+SbF_6^-$) as a tan solid. The product was recrystallized twice from ethanol solution and dried at vacuum, (mp.122 ^oC, yield 54 %). The structure was confirmed by elemental analysis (Table 3.1.) and ^{1}H-NMR spectra (Figure 3.1).

^{1}H-NMR (δ in ppm): 7.5-8, $C_6\mathbf{H}_5$; 6.12, N^+-C$\mathbf{H}_2$-; 3.77, N^+-(C$\mathbf{H}_3$)$_2$.

UV: λ_{max}= 255 nm, $\varepsilon_{255\ nm}$ =21615 mol^{-1} cm^{-1}.

Table 3.1. Elemental analysis results of $PDA^+SbF_6^-$

Elements %	Calculated	Found
C	40,36	40,14
H	3,78	3,98
N	2,94	2,27

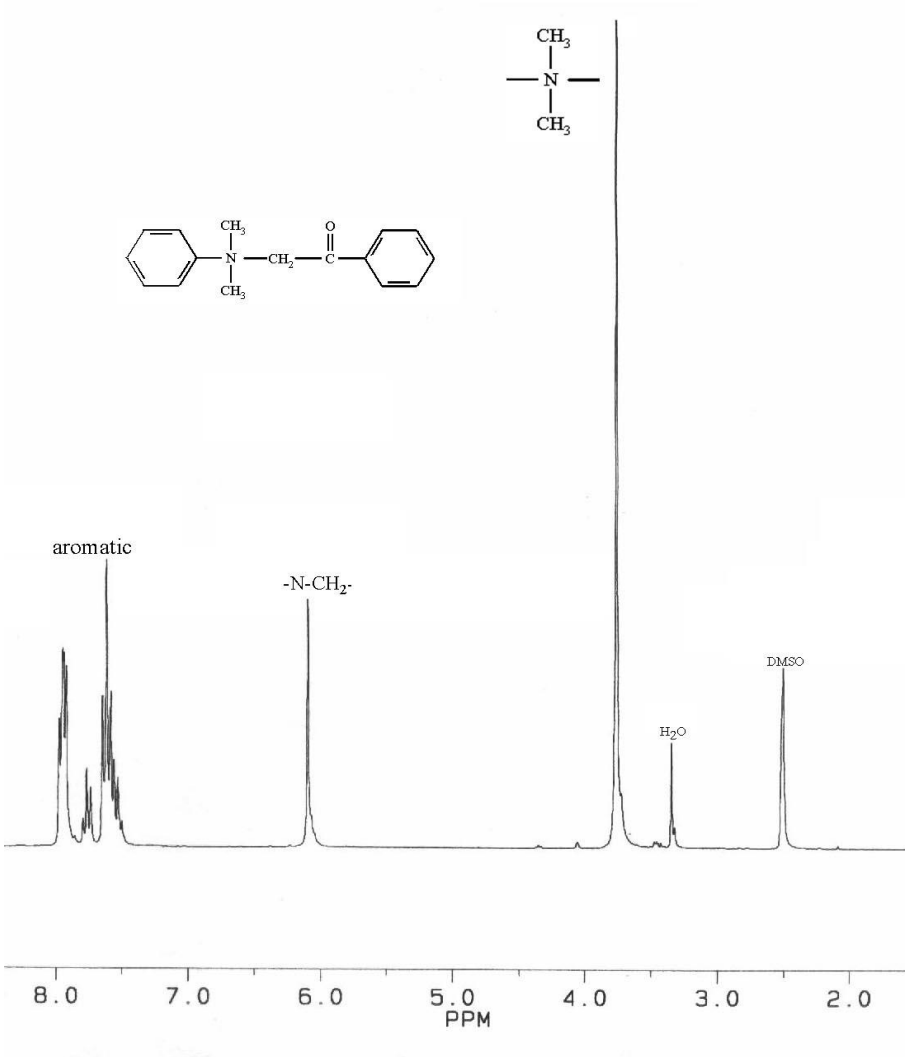


Figure 3.1. ^{1}H-NMR spectrum of *N*-phenacyl *N*,*N*-dimethylanilinium hexafluoroantimonate in DMSO

3.4. Polymerization Techniques

3.4.1. Photopolymerization

Appropriate solutions of monomer and $PDA^{+}SbF_6^{-}$ were mixed in pyrex tubes and degassed with nitrogen prior to irradiation by a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at λ>300 nm. At the end of a given time, polymers were precipitated into methanol, filtered, dried in vacuum oven and weighed. Conversion percentages were calculated according to the equations indicated below:

$$\text{Conversion \%} = (W / M) \times 100$$

where: W = amount of polymer obtained

M = amount of monomer used

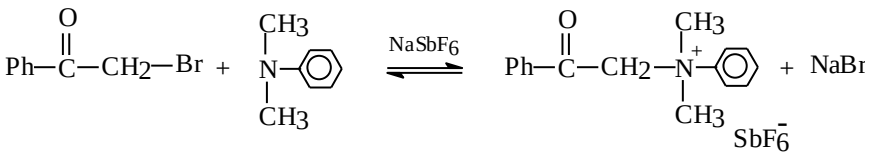
3.4.2. Photosensitization

Appropriate solutions of monomers $PDA^{+}SbF_6^{-}$ and photosensitizer were degassed with dry nitrogen prior to irradiation by an AMKO LTI photoreactor equipped with a XBO 75W xenon lamp and monochromator. At the end, irradiated polymers were precipitated into methanol, filtered, dried in vacuum oven and weighed. Conversion percentages were calculated according to the equations indicated above.

4. RESULTS AND DISCUSSION

4.1. Synthesis

Simplified one-pot reaction, described for the preparation of DPS, was used for the synthesis of the phenacyl anilinium salt, $PDA^{+}SbF_6^{-}$ [18]. Accordingly, phenacylbromide was reacted with *N,N*-dimethylaniline in the presence of sodium hexafluoroantimonate.



(4.1)

The precipitation of insoluble NaBr strongly favors the two simultaneous equilibrium reaction towards the desired final product. The structure of the salt was confirmed by elemental analysis (Table 3.1.) and ^{1}H-NMR spectrum (Figure 3.1).

Simple anilinium salts are photochemically stable. Therefore, using these compounds no polymerization takes place upon photolysis. However, incorporation of chromophoric phenacyl moiety introduces a photochemical activity to the salt. As can be seen from Figure 4.1, the absorption spectrum of $PDA^{+}SbF_6^{-}$, exhibits an n-π^* absorption with a maximum at about 300 nm, characteristic of acetophenone derivatives.

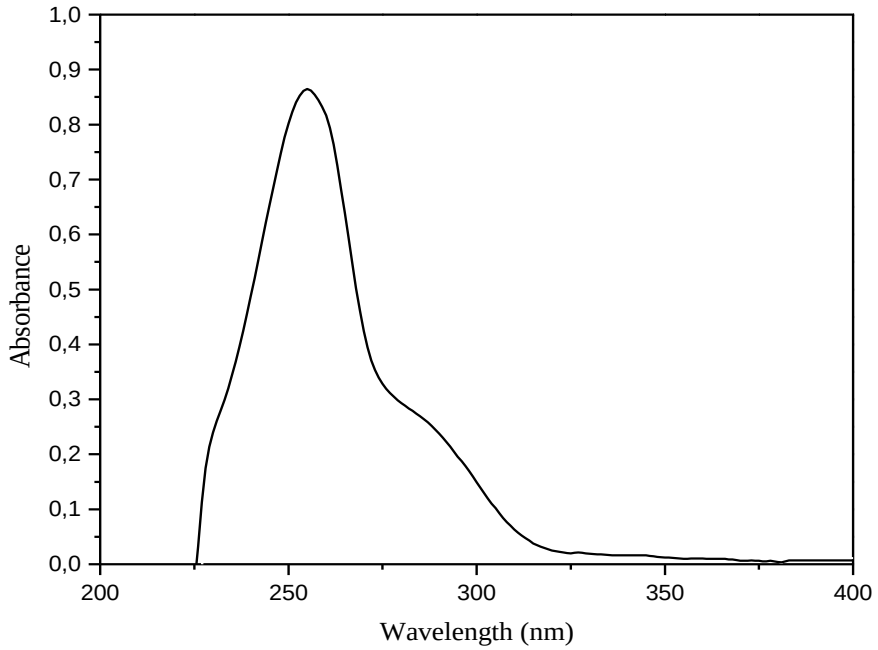


Figure 4.1. Absorption spectrum of $PDA^{+}SbF_6^{-}$ (4 x 10^{-5} mol l^{-1}) in CH_2Cl_2

4.2. Polymerization

The utilization of phenacyl anilinium salt as photoinitiator for cationic polymerization of several monomers was tested. As can be seen from Table 4.1, run1, CHO readily polymerized upon irradiation of the monomer solution containing $PDA^{+}SbF_6^{-}$ at λ>300 nm. Conversion to poly(cyclohexene oxide) increases and reaches to a limiting conversion after about 3 h irradiation (Figure 4.2).

When the polymerization of CHO initiated by $PDA^{+}SbF_6^{-}$ was carried out in the presence of 2,6-di-*t*-butyl-4-methyl pyridine, which is known to act as a proton scavenger, the polymerization was not affected (Table 4.1, runs 1 and 2).

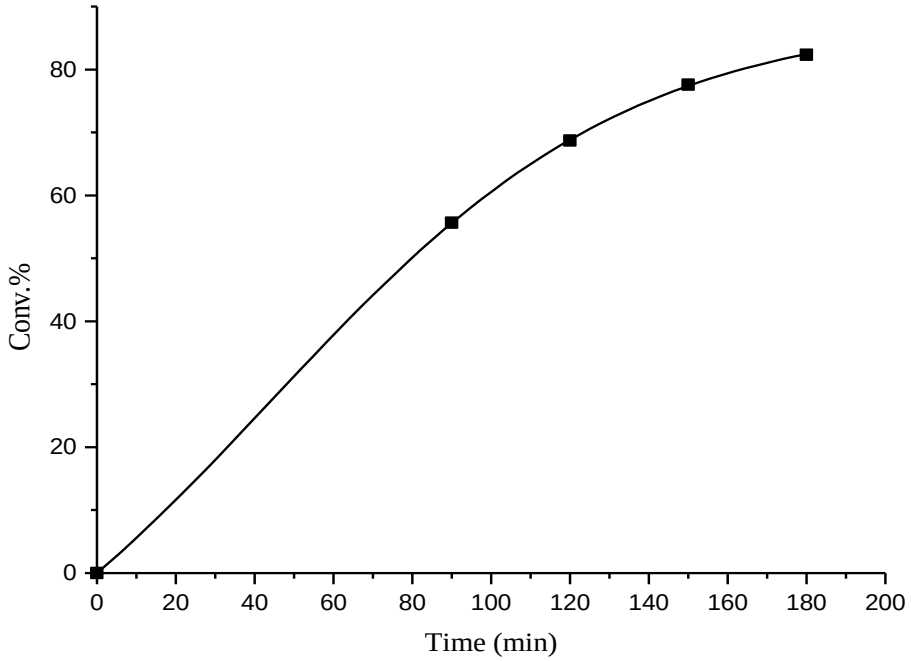


Figure 4.2. Photopolymerization of CHO by using $PDA^+SbF_6^-$ at λ>300 nm. $[PDA^+SbF_6^-]= 5x10^{-3}M$

Apart from CHO, *N*-vinyl carbazole (NVC) and butyl vinyl ether (BVE) were also polymerized (Table 4.1, runs 3 and 4). Notably, strong electron donating monomer, NVC, polymerizes more efficiently.

Table 4.1. Photopolymerization of various monomers in the presence of $PDA^+SbF_6^-$ at room temperature. λ >300 nm, $[PDA^+SbF_6^-]= 5x10^{-3}$ mol L^{-1}.

Run	Monomer (mol l^{-1})	Time (min)	Conversion (%)	M_n[a] x 10^{-3}
1	CHO (9.88)	180	82.4	3.7
2	CHO[b] (9.88)	180	75.4	5.0
3	NVC[c] (2.07)	30	87.9	47.9
4	BVE (7.72)	150	30.0	11.7

[a] Determined by GPC
[b] in the presence of 2,6-di-*t*-butyl-4-methyl pyridine
[c] in CH_2Cl_2

It should be pointed out that $PDA^+SbF_6^-$ is thermally stable. A control experiment under identical conditions did not produce any precipitable polymer after heating monomer solution containing $PDA^+SbF_6^-$ at 70°C for 3 h.

Polymerization of CHO initiated by $PDA^+SbF_6^-$ in the presence of various free radical photoinitiators was also studied. As can be seen from Table 4.2, when TMBPO was used as a free radical photoinitiator in the system the apparent conversion was significantly lower. In the case benzoin, however, the polymerization rate was almost same as in the absence of added free radical initiator. By spectroscopic and cyclic voltagramic investigations, $PDA^+SbF_6^-$ does not participate in redox reactions. Therefore, the different reactivity of benzoin and TMBPO cannot be related to the direct oxidation of radicals generated from the respective photoinitiator by $PDA^+SbF_6^-$. However, at the irradiation wavelength both the salt and the photoinitiator absorb the light. Thus, radicals from the photoinitiator and ammonium radical cations from $PDA^+SbF_6^-$ are formed concomitantly. While hydroxybenzyl radical (from benzoin) can undergo redox reactions with the ammonium radical cation, both phosphonyl and benzoyl radicals are inert towards strong oxidants such as iodonium and alkoxy pyridinium salts.

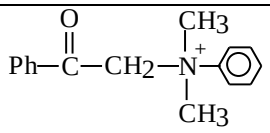
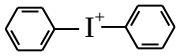
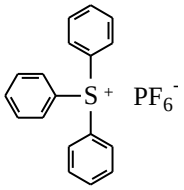
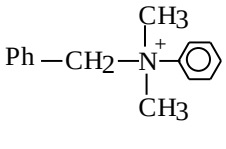
Table 4.2. The effect of free radical photoinitiators on the polymerization of CHO initiated by $PDA^+SbF_6^-$. time =180 min, $[PDA^+SbF_6^-] = 5x10^{-3}$ mol L^{-1}

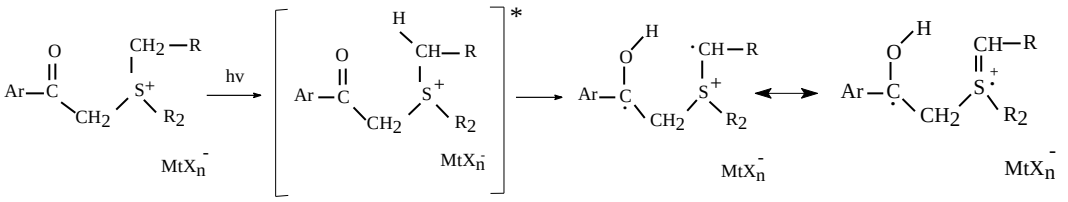
Free Radical Photoinitiator	[Photoinitiator] ($mol.l^{-1}$)	Conversion %
Benzoin	5.10^{-3}	80.84
TMBPO	$1.7.10^{-3}$	15.05
no initiator	0	82.35

For the sake of comparison, results obtained with triphenylsulphonium salt, diphenyliodonium salt and structurally related benzyl anilinium salt are shown in Table 4.3. Notably, diphenyl iodonium salt also initiated the polymerization of CHO, but at a much lower rate due to the weak absorption at λ>300 nm. On the other hand, triphenylsulfonium salt is inefficient since it does not absorb light at the irradiation wavelength. It is also interesting to note the inefficiency of benzyl anilinium salt indicating the importance of chromophoric phenacyl moiety for successful

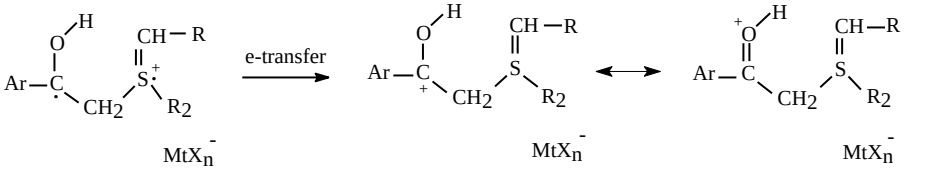
polymerization. These results indicate that $PDA^{+}SbF_6^{-}$ is manifestly superior to the commercially available onium type photoinitiators as far as initiation efficiency at wavelengths above 300 nm where commercial lamp emits light is concerned.

Table 4.3. Photopolymerization of CHO by using various salts at room temperature. λ>300 nm, [salt]= $5x10^{-3}$ mol L^{-1}, time=180 min

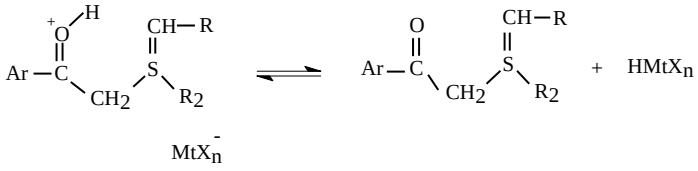
Salt	Conversion (%)	M_n^a x 10^{-3}
	82.4	3.7
	46.6	11.4
	0	-
	0	-



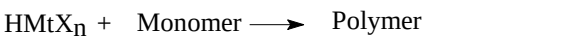
(4.2)



(4.3)



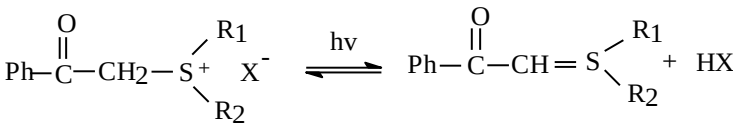
(4.4)



(4.5)

Scheme 1

First, we considered that the same mechanism also implies for the initiation by the anilinium salt since it is structurally similar and there are available hydrogen atoms adjacent to positively charged nitrogen atom for the hydrogen abstraction by the excited carbonyl. In our case, when the irradiation was carried out in the presence of 2,6-di-*t*-butyl-4-methyl pyridine, which is known to act as a proton scavenger, the rate of polymerization was not affected (Table 4.1, runs 1 and 2). As mentioned before the overall mechanism described for the sulfonium salts is essentially reversible and in the absence of monomers, the ylides rapidly react with the protonic acid to afford the starting salt (reaction 4.6).



(4.6)

Whereas the phenacyl anilinium salt undergo an irreversible photolysis leading to fragmentation of the photoinitiator (Figure 4.3.b, scheme 2).

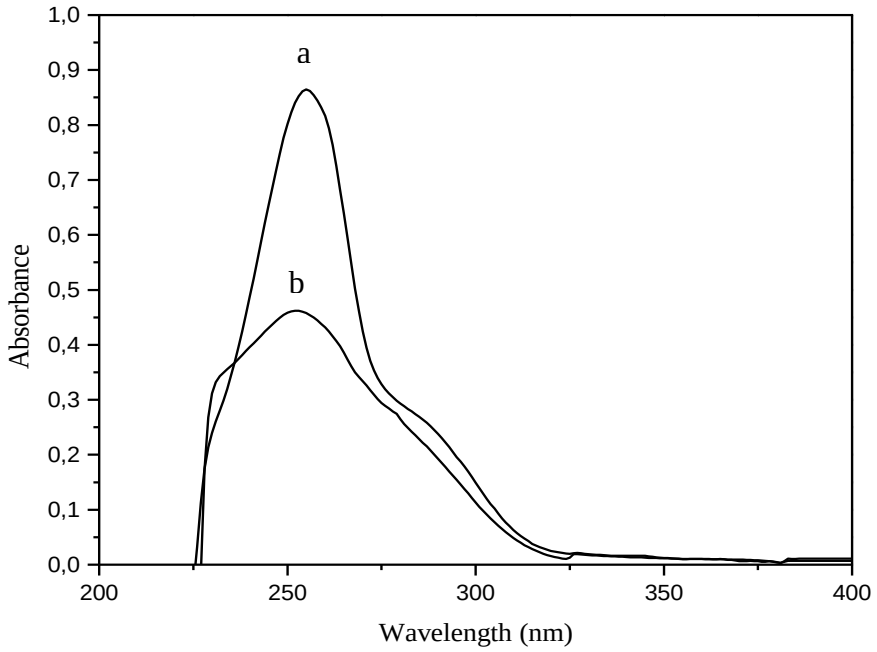
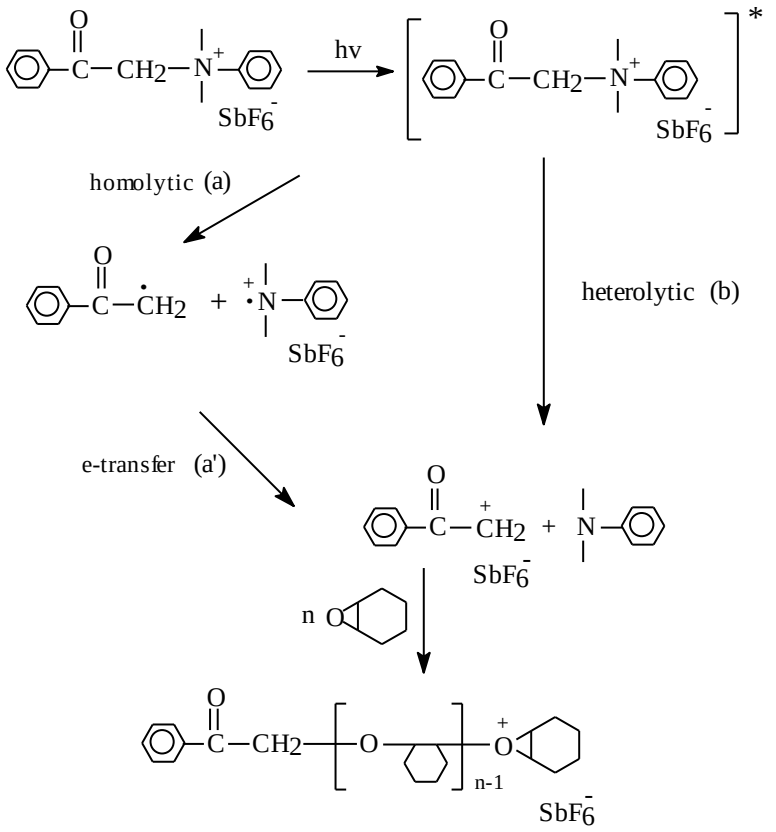


Figure 4.3. Absorption spectra of $PDA^{+}SbF_6^{-}$ (4 x 10^{-5} mol L^{-1}) in CH_2Cl_2 before (a) and after 15 min irradiation (b).

Based on these results, the following mechanism for the initiation of the polymerization by the phenacyl anilinium salts is suggested (Scheme 2).

Electronically excited $PDA^{+}SbF_6^{-}$ may undergo heterolytic cleavage (reaction 4.8.b) resulting in the formation of phenacylium cations capable of initiating cationic polymerization. It is also feasible that homolytic cleavage (reaction 4.8.a) followed by the intermolecular electron transfer (reaction 4.8.a') essentially yields the same species. A reaction mechanism considering both possibilities is proposed in Scheme 2. It should be also noted that termination could occur by the reaction of the growing chain with dimethylaniline.



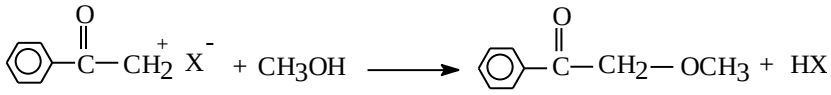
(4.7)

(4.8)

(4.9)

Scheme 2

Further support for the initiation by phenacylium cations was obtained by analysizing photolysis products in methanol in the absence of a monomer. Notably, GC-Ms detection of *N*,*N*-dimethylaniline (m/z=121) and phenacylmethyl ether (m/z=150) formed according to reaction (4.10) and its deprotonated product (m/z=149) confirms the proposed mechanism.



(4.10)

4.3. Photosensitization

Photosensitization with the aid of various sensitizers absorbing light at longer wavelengths (λ>350 nm) can help to extend the applicability of the phenacylanilinium salt, *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoroantimonate, ($PDA^+SbF_6^-$), as photoinitiator. For this purpose, the reactions of $PDA^+SbF_6^-$ with

excited states of perylene, anthracene, phenothiazine, benzophenone and thioxanthone were studied. In the ground state, these compounds absorb light between 350 and 400 nm (Figure 4.4).

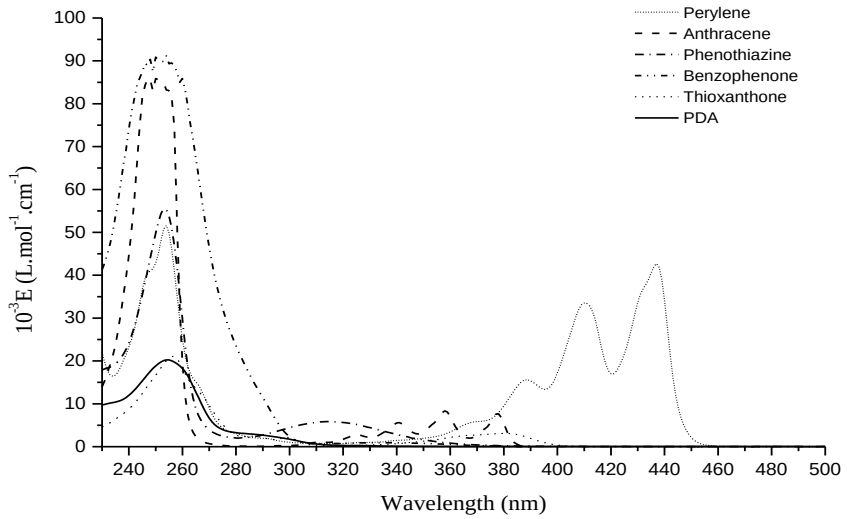


Figure 4.4. Optical absorption spectra of perylene, anthracene, phenothiazine, benzophenone, thioxanthone and $PDA^+SbF_6^-$ in CH_2Cl_2 solution

The polymerization of cyclohexene oxide served as a probe for the conversion of $PDA^+SbF_6^-$ into species capable of initiating cationic polymerizations. Monochromatic irradiations are employed which permit the selection of bands absorbed by the photosensitizer, except benzophenone, and not by $PDA^+SbF_6^-$. In the case of benzophenone, the incident light was absorbed both by benzophenone and $PDA^+SbF_6^-$. Typical results are presented in Table 4.4. It should be pointed out that all sensitizers are ineffective for initiating cationic polymerizations in the absence of $PDA^+SbF_6^-$. Notably, all compounds except thioxanthone and benzophenone act as sensitizers. Some but little polymerization observed with benzophenone is due to the tail absorption of $PDA^+SbF_6^-$ at the irradiation wavelength.

Table 4.4. Sensitized photopolymerization of cyclohexene oxide with $PDA^+SbF_6^-$, $[PDA^+SbF_6^-] = 5x10^{-3}$ mol L^{-1}, irradiation time = 180 min.

Sensitizer	[Sensitizer] (10^{-3}mol.L^{-1})	λ (nm)	Conversion (%)	$M_n^c x10^{-3}$ (g.mol^{-1})	M_w/M_n
Perylene[a]	5	440	52	7	1.8
Anthracene[a]	5	360	13	5	1.6
Phenothiazine[a]	5	415	11.6	3	1.4
Benzophenone[b]	5	340	9	3	1.3
Thioxanthone[b]	5	300	0	-	-

[a] Aromatic hydrocarbon photosensitizer
[b] Aromatic ketone photosensitizer
[c] Determined by GPC against polystyrene standards

To compare the photosensitization activity of each sensitizer, we have performed polymerization experiments at the same wavelength, 380 nm. The results are collected in Table 4.5. As can be seen that phenothiazine seemed to be the most effective photosensitizer owing to its high extinction coefficient at this particular wavelength.

Table 4.5. Sensitized photopolymerization of cyclohexene oxide with $PDA^+SbF_6^-$, $[PDA^+SbF_6^-]=5x10^{-3}$ mol L^{-1}, λ=380 nm, irradiation time=180 min

Sensitizer	[sensitizer] (10^{-3} mol.l^{-1})	Conversion (%)	M_n^c x 10^{-3} (g mol^{-1})	M_w/M_n
Perylene[a]	5	21.3	4.0	1.5
Anthracene[a]	5	18.5	3.5	1.4
Phenothiazine[a]	5	28.4	5.0	1.8
Benzophenone[b]	5	1.1	5.0	1.7
Thioxanthone[b]	5	0	-	-

[a] Aromatic hydrocarbon photosensitizer
[b] Aromatic ketone photosensitizer
[c] Determined by GPC against polystyrene standarts

The observation that, the phenacylanilinium salt, *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoroantimonate, ($PDA^+SbF_6^-$), was found to quench the emission from the sensitizer indicates an interaction between $PDA^+SbF_6^-$ and excited state of the photosensitizer. Quenching of photoexcited perylene by $PDA^+SbF_6^-$ is demonstrated in Figure 4.5 where fluorescence emission of perylene is reduced by the addition of $PDA^+SbF_6^-$.

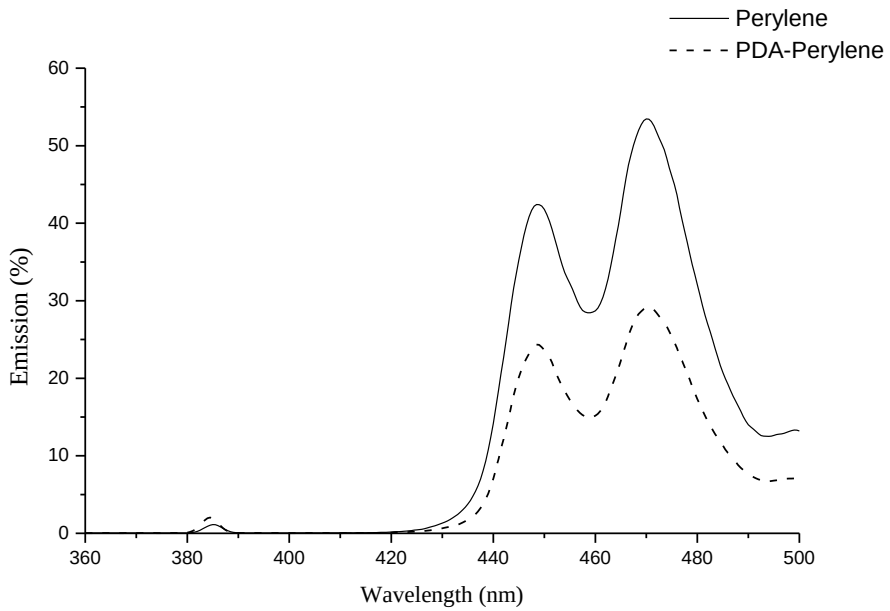


Figure 4.5. Quenching of perylene fluorescence emission at λ_{ex}=386 nm by $PDA^{+}SbF_6^{-}$ in CH_2Cl_2, [PDA]=1x10^{-4} mol L^{-1}, [perylene]=1x10^{-4} mol L^{-1}

Although at lower rate there is also some change in the absorption spectrum of perylene by the addition of the salt indicating some ground state interaction (Figure 4.6).

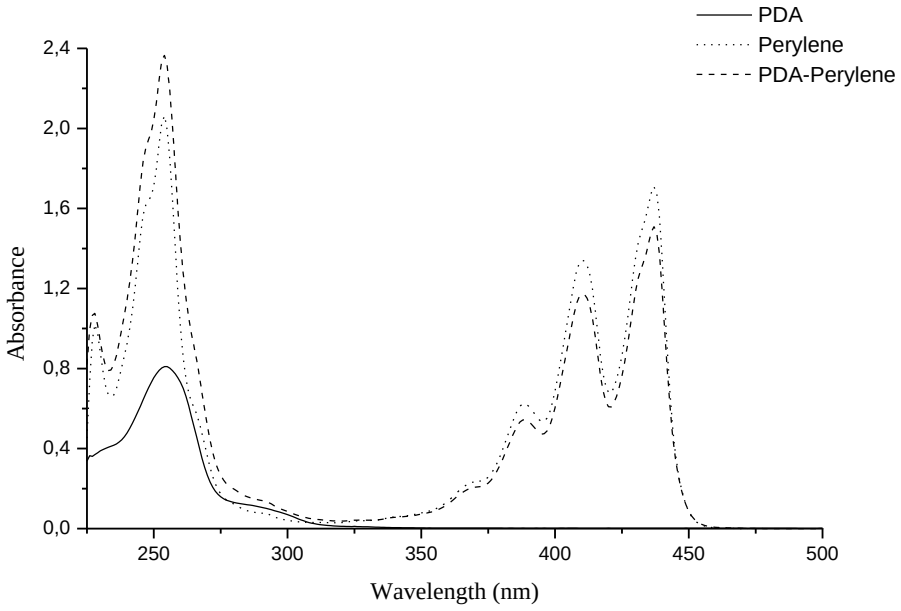


Figure 4.6. Absorption spectra of $PDA^{+}SbF_6^{-}$, perylene, $PDA^{+}SbF_6^{-}$+perylene (4x10^{-5} mol L^{-1}) in CH_2Cl_2 solution

Indeed the differences in absorption spectra become more significant after the photolysis (Figure 4.7).

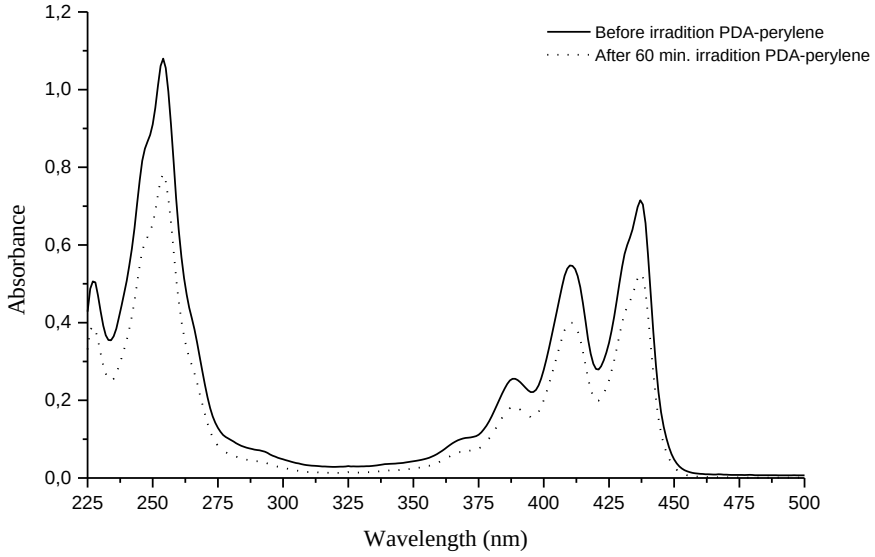


Figure 4.7. Absorption spectra of $PDA^{+}SbF_6^{-}$ ($8x10^{-6}$mol L^{-1}) and perylene ($8x10^{-6}$mol L^{-1}) in CH_2Cl_2 before (—) and after 60 min. irradiation (···) at λ = 440 nm

There are two possibilities for the sensitizing mechanism of the compounds used in this work, (i) energy transfer from the electronically excited sensitizer, PS*, to $PDA^{+}SbF_6^{-}$ followed by the decomposition of the excited salt according to the equation 4.11:

$$PS^* + PDA^+ \longrightarrow PS + (PDA^+)^* \qquad (4.11)$$

and (ii) electron transfer between the excited state photosensitizer and PDA^{+} ions resulting in the formation of the radical cation of the sensitizer according to the equation 4.12:

$$PS^* + PDA^+ \longrightarrow PS^{\cdot +} + PDA^{\cdot} \qquad (4.12)$$

As far as energy transfer is concerned, singlet-singlet routes can be excluded, because the singlet energies of all sensitizers studied in this work are lower than that of $PDA^{+}SbF_6^{-}$ (*E*s = 382 kJ mol^{-1} = 65.74 kcal mol^{-1}, as determined from fluorescence spectrum, Figure 4.8). Regarding triplet energy transfer, conclusions cannot be drawn because the triplet energy of $PDA^{+}SbF_6^{-}$ is unknown.

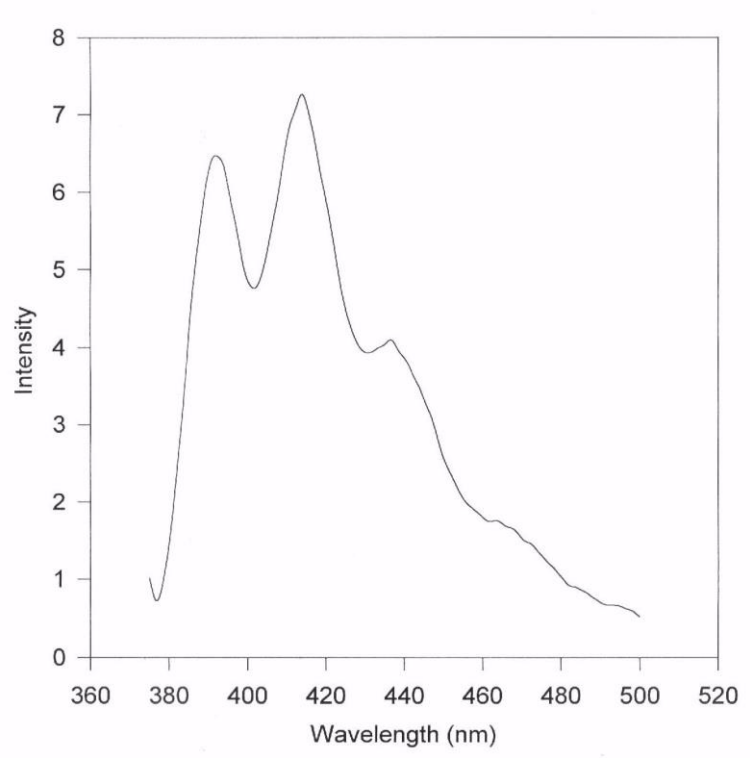


Figure 4.8. Fluorescence spectrum of $PDA^+SbF_6^-$ at room temperature.
$\lambda_{excitation}$=366 nm, $[PDA^+SbF_6^-]$ =2.5x10^{-2} mol L^{-1}, in CH_2Cl_2 solution

Table 4.6 gives the related values for various photosensitizers, which were used in the photosensitization of $PDA^+SbF_6^-$.

Table 4.6. Singlet and triplet energies for photosensitizers

Photosensitizer	E_S (kcal/mol)	E_T (kcal/mol)
Perylene[a]	65.8	35.1
Anthracene[a]	76.3	42.0
Phenothiazine[a]	--	57.0
Benzophenone[b]	75.4	68.6
Thioxanthone[b]	80.5	65.5

[a] Aromatic hydrocarbon photosensitizer
[b] Aromatic ketone photosensitizer

According to the Rehm-Weller equation (Eq. 4.13), electron transfer from sensitizer to PDA^+ ion is feasible if the change in free energy is negative:

$$\Delta G = fc\,[E^{ox}_{1/2} - E^{red}_{1/2}] - E_{(PS^*)} \qquad (4.13)$$

Here $E^{ox}_{1/2}$ and $E^{red}_{1/2}$ are the half-wave oxidation and reduction potentials of sensitizer and $PDA^{+}SbF_6^{-}$ ($E^{red}_{1/2}$ = -1,1 V), respectively, conversion factor f_c =97 kJ mol^{-1} V^{-1}; and E(PS*) is the excitation energy of the sensitizer.

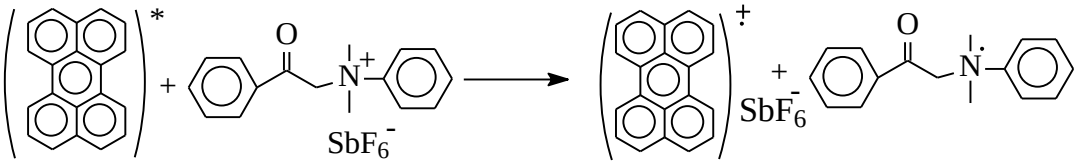
The ΔG values listed in Table 4.7 suggest that electron transfer from triplet or singlet excited states of sensitizers to PDA^{+} ions are favourable in the cases of perylene, antracene and phenothiazine.

Table 4.7. Triplet and singlet energies $E_{(PS^*)}$ and half-wave oxidation potentials $E^{ox}_{1/2}$ (vs. saturated calomel electrode, SCE) of sensitizers

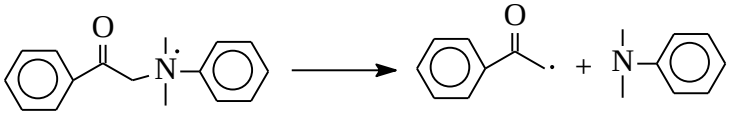
Sensitizer	$E_{(PS^*)}$ (kJ mol^{-1})	$E^{ox}_{1/2}$ (V)	ΔG^a (kJ mol^{-1})	Photosensitization
Perylene	277 (E_s)	0.9	-83	Yes
Anthracene	319 (E_s)	1.1	-63.6	Yes
Phenothiazine	239 (E_t)	0.6	-112.1	Yes
Benzophenone	290 (E_t)	2.7	91.6	No
Thioxanthone	277 (E_t)	1.7	-5.4	No

[a] Calculated according to the equation (4.13)

Notably, thioxanthone and benzophenone do not take part in this redox reaction due to the unfavourable thermodynamic conditions. A mechanism based on electron transfer is described below for the case of perylene and $PDA^{+}SbF_6^{-}$ in equation 4.14 and 4.15.



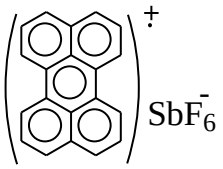
(4.14)



(4.15)

Excited perylene is oxidized to perylene radical cation; while PDA^{+} ion is reduced to the corresponding nitrogen centered radical that undergoes irreversible fragmentation to yield the resonance stabilized phenacyl radical and dimethylaniline. The proposed mechanism was further supported by photolysis studies in the absence of a monomer (equation 4.16). When solutions of $1x10^{-3}$ mol L^{-1} perylene and $1x10^{-3}$ mol L^{-1} $PDA^{+}SbF_6^{-}$ were irradiated in CH_2Cl_2 for 60 min at 440 nm, a deep blue solution, attributed to perylene radical cation [9], was produced. Interestingly, upon addition of

monomer CHO the deep blue color was immediately discharged and extremely vigorous polymerization occurred. The direct initiation of cationic polymerization by perylene radical cations is a well-established process and described by several authors [9, 19].



+ Monomer ⟶ Polymer (4.16)

These results indicate that $PDA^{+}SbF_6^{-}$ proceeds via irreversible process.

5. CONCLUSIONS AND SUGGESTIONS

In conclusion, the preliminary results show that, upon irradiation, phenacyl anilinium salt is capable of initiating cationic polymerization of appropriate monomers such as CHO, BVE and NVC. Although the present state of knowledge does not permit any conclusions on the exact nature of the initiation mechanism, it is clear that UV irradiation of $PDA^{+}SbF_6^{-}$ yields reactive phenacylium cations, which might be responsible for the initiation.

These results indicate that $PDA^{+}SbF_6^{-}$ is manifestly superior to the commercially available onium type photoinitiators as far as initiation efficiency at wavelengths above 300 nm where commercial lamp emits light is concerned.

It has been shown that the decomposition of $PDA^{+}SbF_6^{-}$ can be photosensitized by anthracene, perylene and phenothiazine that absorb strongly between 350 and 400 nm. This was evidenced by means of polymerization and spectroscopic studies.

It was also shown that interaction of electronically excited sensitizer with PDA^{+} ions proceeds via electron transfer mechanism and results in the formation of ionic species capable of reacting with CHO molecules.

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2. Photosensitized Cationic Polymerization of Cyclohexene Oxide Using Phenacyl Anilinium Salt

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3. Photoinitiated Polymerization of Methyl Methacrylate by Phenacyl Type Salts

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