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İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**PHOTOINITIATED CATIONIC RING OPENING
POLYMERIZATION OF THIOCARBONATES**

**M. Sc. Thesis by
Nihan YÖNET
(515021001)**

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Supervisor (Chairman): Prof. Dr. Yusuf YAĞCI

Members of the Examining Committee Prof. Dr. Nurseli UYANIK (İ.T.Ü.)

Assoc. Prof. Dr. Duygu AVCI (B. Ü.)

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**MONOTİOKARBONATLARIN
FOTOBAŞLATICILAR KULLANILARAK
KATYONİK POLİMERİZASYONU**

**YÜKSEK LİSANS TEZİ
Nihan YÖNET
(515021001)**

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Tez Danışmanı : Prof. Dr. Yusuf YAĞCI

Diğer Jüri Üyeleri Prof. Dr. Nurseli UYANIK (İ.T.Ü.)

Doç. Dr. Duygu AVCI (B. Ü.)

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LIST of ABBREVIATIONS

DDT	: 5,5-Dimethyl-1,3-dioxane-2-thione
UV	: Ultra Violet
Ph₂I⁺PF₆⁻	: Diphenyliodonium Hexafluorophosphate
Ph₃S⁺AsF₆⁻	: Triphenylsulfonium Hexafluoroarsenate
EMP⁺PF₆⁻	: <i>N</i> -Ethoxy-2-Methylpyridinium Hexafluorophosphate
DMPA	: 2,2-Dimethoxy-2-phenyl acetophenone
ETM⁺SbF₆⁻	: Ethyl- α -(tetrahydrothiophenium methyl) acrylate hexafluoroantimonate
NMR	: Nuclear Magnetic Resonance Spectroscopy
Ar	: Aryl Group
R	: Alkyl Group
On⁺	: Onium Salt
EPP⁺	: <i>N</i> -Ethoxy-4-cyanopyridinium
EIQ⁺	: <i>N</i> -ethoxyisoquinolinium
CT	: Charge Transfer
PS	: Photosensitizer
S	: Sensitizer
GPC	: Gel Permeation Chromatography
IR	: Infrared
M_n	: Number Average Molecular Weight

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PHOTOINITIATED CATIONIC RING-OPENING POLYMERIZATION OF MONOTHIOCARBONATES

SUMMARY

In this thesis, photoinitiated cationic polymerization of monothiocarbonate, namely 5,5-dimethyl-1,3-dioxane-2-thione (DDT), was investigated. Photocationic polymerization of DDT was achieved upon direct UV irradiation ($\lambda=300$ nm) of dichloromethane solutions containing onium salts such as diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$), triphenylsulfonium hexafluoroarsenate ($\text{Ph}_3\text{S}^+\text{AsF}_6^-$) and *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$) and indirect activation by UV irradiation ($\lambda=350$ nm) of dichloromethane solutions involving onium salt / free radical promoter, 2,2-dimethoxy-2-phenyl acetophenone (DMPA), and onium salt / sensitizer (perylene or anthracene) combinations. In direct photolysis, a proton released from the decomposition of the onium salts initiates the polymerization. However, onium salts oxidize DMPA yielding a carbocation that is capable of initiating the polymerization of DDT. Due to the differences in the redox potential of the onium salts, $\text{Ph}_2\text{I}^+\text{PF}_6^-$ salt was found to be more efficient than $\text{Ph}_3\text{S}^+\text{AsF}_6^-$ salt in indirectly activated photopolymerization. Moreover, perylene and anthracene were used to sensitize $\text{Ph}_2\text{I}^+\text{PF}_6^-$ salt. The applicability of onium salts as photoinitiator, thus, is extended to higher wavelengths. In agreement with the proposed mechanism, the sensitizers did not initiate the polymerization of DDT themselves while their organic complex formations with the onium salts, $\text{Ph}_2\text{I}^+\text{PF}_6^-$, initiated the polymerization of DDT. On the other hand, the effect of the reaction parameters such as concentration of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ salt and living property in dark medium were investigated.

MONOTİOKARBONATLARIN FOTOBASLATICILAR KULLANILARAK KATYONİK POLİMERİZASYONU

ÖZET

Bu tezde, monotiokarbonatların fotobaslatıcılar kullanılarak katyonik polimerizasyonu araştırılmıştır. Kullanılan monotiokarbonatın, 5,5-dimetil-1,3-diokzan-2-tion (DDT), doğrudan katyonik polimerizasyonu onyum tuzları (difeniliyodonyum hekzaflorofosfat ($\text{Ph}_2\text{I}^+\text{PF}_6^-$), trifenilsülfonyum hekzafloroarsenat ($\text{Ph}_3\text{S}^+\text{AsF}_6^-$) ve *N*-etoksi-2-metilpiridinyum hekzaflorofosfat ($\text{EMP}^+\text{PF}_6^-$)) içeren diklorometan çözeltilerinin UV ışığında ($\lambda=300$ nm) aydınlatılmasıyla, dolaylı polimerizasyonu ise onyum tuzu / serbest radikal foto başlatıcı ve onyum tuzu / uyarıcı bileşimlerini içeren diklorometan çözeltilerinin UV ışığında ($\lambda=350$ nm) aydınlatılmasıyla gerçekleştirilmiştir. Doğrudan polimerizasyon yönteminde, onyum tuzlarının bozunmasıyla oluşan proton polimerleşmeyi başlatır. Ancak dolaylı polimerizasyon yönteminde, onyum tuzları 2,2-dimetoksi-2-fenil asetofenonu (DMPA) oksitleyerek DDT polimerleşmesini başlatabilecek karbokatyonlar oluşturur. Bu sistemde onyum tuzlarının redoks potansiyelleri arasındaki farktan dolayı $\text{Ph}_2\text{I}^+\text{PF}_6^-$ tuzunun DDT'nin fotopolimerizasyonunda $\text{Ph}_3\text{S}^+\text{AsF}_6^-$ tuzundan daha etkili olduğu bulunmuştur. Ayrıca $\text{Ph}_2\text{I}^+\text{PF}_6^-$ tuzunun uyarılmasında perilen ve antrasen kullanılmıştır. Böylece onyum tuzlarının fotobaslatıcı olarak uygulanabilirliği daha büyük dalga boylarına genişletilmiştir. Önerilen mekanizma ile uyumlu olarak, uyarıcılar kendi başlarına DDT polimerizasyonunu başlatmadıkları halde onyum tuzlarıyla, $\text{Ph}_2\text{I}^+\text{PF}_6^-$, oluşturdukları organik kompleksler polimerizasyonu başlatmıştır. Bundan ayrı olarak, onyum tuzu konsantrasyonu ve karanlık ortamda yaşayan polimer özelliği gibi reaksiyon parametreleri de incelenmiştir.

1. INTRODUCTION

The chemistry of cyclic carbonates, which has been explored since the 1930s, has come to be a rich area of research within the past 20 years. Two main approaches for the use of cyclic carbonates have been investigated. Brunelle and the research group from General Electric have focussed on the synthesis of aromatic cyclic carbonate oligomers and their applications in the preparation of bisphenol A polycarbonates, copolymers, and composites [1]. At the same time Kricheldorf, Höcker and Heitz groups [2,3] from Germany and Endo [4] from Japan have been exploring aliphatic cyclic carbonates as useful monomers for the preparation of polycarbonates as well as copolymers with other heterocyclic monomers [5].

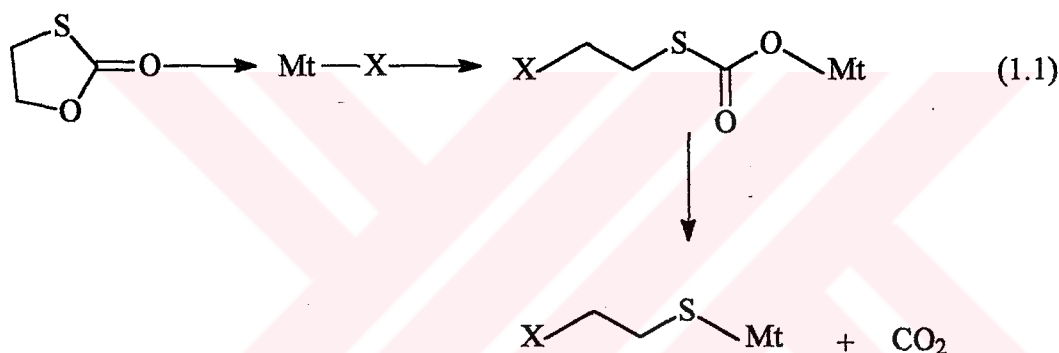
Synthetic biodegradable polymers have become interesting materials for a variety of biomedical applications. In those fields homopolymers and copolymers of five- (1,3-dioxolan-2-ones) and six membered carbonates (1,3-dioxan-2-ones) with cyclic esters (lactones and lactides) have been found to be good materials because of their biocompatibility, low toxicity and biodegradability.

Much of the interest in ring-opening polymerizations stems from the fact that the polymers formed may have lower densities than the monomers from which they are derived (volume expansion may accompany polymerization) [4,6-8]. This is in marked contrast with conventional polymerizations, which invariably involve a net volume contraction. Such polymerizations are therefore of particular interest in adhesive, mold filling, and other applications where volume contraction is undesirable. In relation to this, besides expandable spiroorthocarbonates known since the 1970s [9,10], cyclic carbonates (six- and seven-membered) also polymerize with volume expansion in which the degree of density reduction may reach 10% as was recently found by Endo et al [11,12,13].

The polymerization of ethylene monothiocarbonate (1,3-oxathiolan-2-one) was carried out in the presence of metal alkyls such as ZnEt_2 or CdEt_2 and metal alkoxides like $\text{Mg}(\text{OCH}_3)_2$, $\text{Al}(\text{OnBu})_3$ or $\text{Ti}(\text{OnBu})_4$. The polymerization with these catalysts was accompanied by carbon dioxide elimination and the polymers obtained

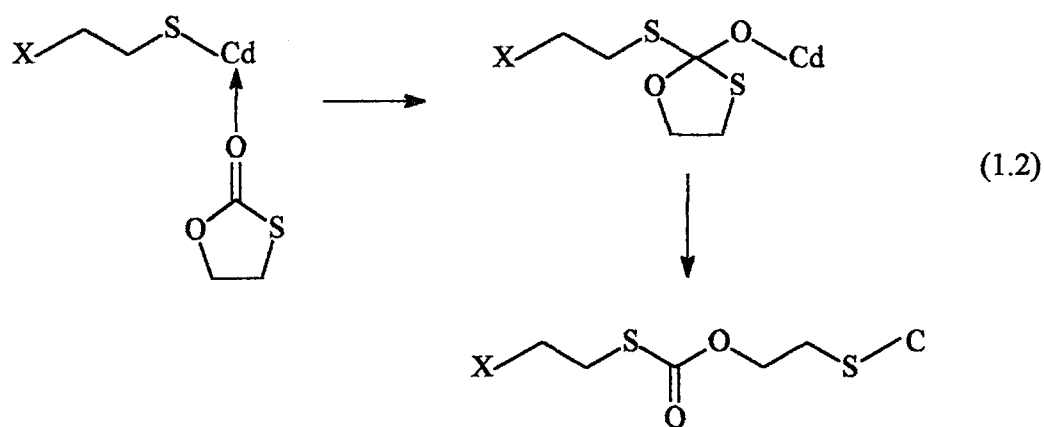
appeared to be poly(ethylene sulfide-monothiocarbonate)s. The content of ethylene monothiocarbonate (oxycarbonylthioethylene) units and ethylene sulfide (thioethylene) units in the polymers produced was dependent upon the catalysts used but all these polymers yielded from the ethylene monothiocarbonate polymerization at 80°C contained less than 50 mol % of monothiocarbonate units [14].

As compared with the ethylene carbonate polymerization, the ethylene monothiocarbonate polymerization with coordination catalysts proceeds easier and also may involve the decarboxylation to a lesser extent. The decarboxylation during the ethylene monothiocarbonate polymerization seems to involve the metal monothiocarbonate species that are analogous to those formed in the system with ethylene carbonate. But the ethylene monothiocarbonate decarboxylation leads to metal thiolate species, which may be outlined schematically as in (1.1).



The metal thiolate species are more reactive towards coordinating the monothiocarbonate monomer during the polymerization (1.1), than the corresponding metal alcoholate species operating in the ethylene carbonate polymerization.

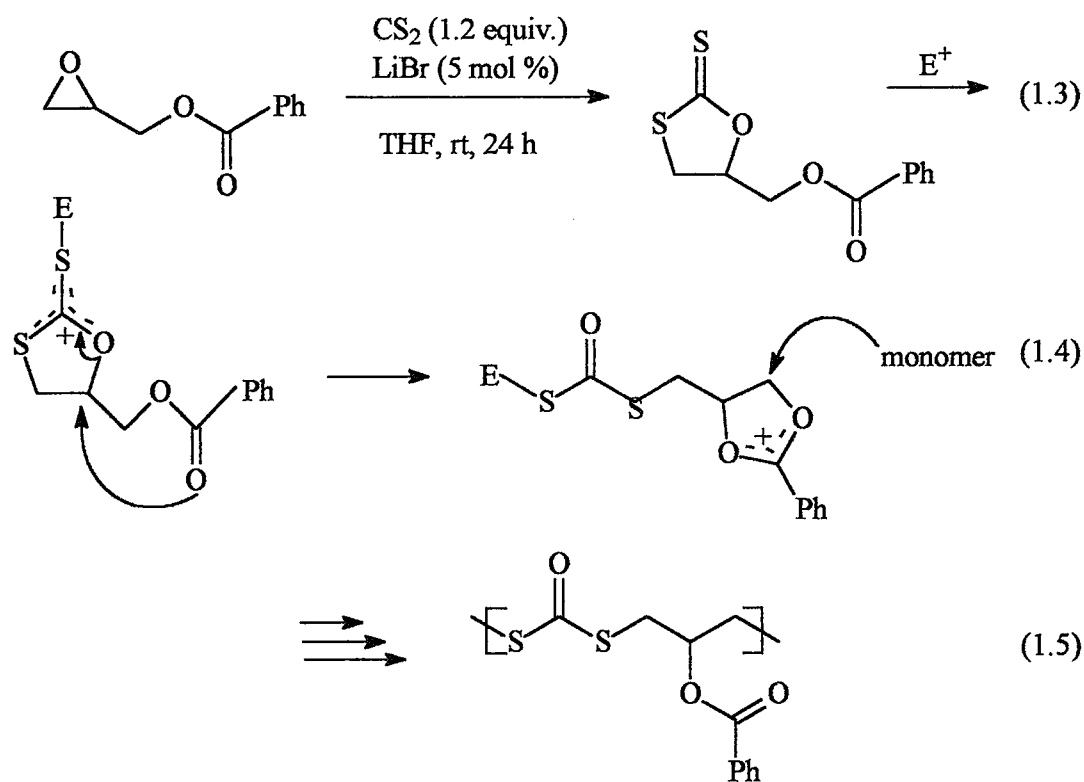
The relatively highest efficiency of the diethylcadmium catalyst in the ethylene monothiocarbonate polymerization (at 80°C), as regards the high content of ethylene monothiocarbonate units in the polymer obtained, results probably from the softness of both cadmium and sulfur atoms fitting one to the other, to participate in the covalent bonding. Thus, the decarboxylation occurs to the lowest extent. Moreover, the propagation according to (1.2), involving the formation of the cadmium-sulfur bond leading to the metal thiolate species of relatively high activity, occurs more likely than that which might involve the formation of the less reactive metal alkoxide species.



In contrast, five-membered cyclic dithiocarbonates undergo cationic ring-opening polymerization to afford corresponding poly(dithiocarbonate)s without evolution gaseous compounds [15].

A five-membered cyclic dithiocarbonate containing a benzyloxymethyl group exhibits interesting feature [16]. The monomer, 5-benzyloxymethyl-1,3-oxathiolane-2-thione subjected to cationic polymerization initiated by $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{CH}_3$ at 60°C afforded corresponding poly(dithiocarbonate)(1.3) with $M_n = 9000\text{--}25\ 000$ in 60–100 % yields. The narrow polydispersity of the poly(dithiocarbonate)s (1.09–1.29) and the M_n increase in direct proportion to monomer conversion indicates living cationic polymerization based on neighboring group participation.

The formation of a carbenium cation stabilized by neighboring benzyloxymethyl group participation, as observed by NMR spectroscopy, might result in the living polymerization [16].



During the past decade photoinitiated cationic polymerization have received considerable attention. Most of the existing photoinitiating systems for cationic polymerization are based on the use of certain onium salts, such as diphenyliodonium, triphenylsulfonium, and alkoxy pyridinium salts. These salts, however, do not absorb above 300 nm if additional chromophores are not incorporated into the salt structure. For that reason, free radical photoinitiators [17-20], singlet and triplet photosensitizers [21,22] are used to extend sensitivity range of onium salts to 350 nm. Thus, the wavelength flexibility of the photoinitiators is maintained by this indirect activation of onium salts.

In this thesis, photoinitiated cationic ring-opening polymerization of a six-membered monothiocarbonate, 5,5-dimethyl-1,3-dioxane-2-thione (DDT) by using onium salts is reported. Both direct and indirect photoactivation of onium salts are studied.

2. THEORETICAL PART

Photopolymerization is one of the most rapidly expanding processes for materials production. Applications of photopolymerization are being further developed and provide a number of economic advantages over the usual thermal operations: solvent-free formulations, low energy input, room temperature treatment and low costs [23,24]. During the past decade photopolymerization practically applied in variety of areas, including printing inks, adhesives, surface coating, microelectronics and printing plates [25-27]. Mainly, transformation of a monomer into polymer by chain reaction initiated by reactive species such as free radicals and ions generated by UV irradiation is called as photoinitiated polymerization. Photopolymerization differs from photocrosslinking where every chain propagation step requires the absorption of a photon.

A photochemical reaction cannot occur if a photon is not absorbed. In that sense, photoinitiators function by photons being absorbed and their energy being transferred to the electronic structure of the molecule. Ultimately, the excitation of the electrons can result in the formation of a free radical, a cation or of a base. An ideal commercial photoinitiator is expected to be easily synthesized, to exhibit low price, lack of toxicity and odor, excellent stability pot life when dissolved in monomers, high absorption of incident light. On the other hand, a photosensitizer is defined as a molecule that is capable of light absorption and can transfer the excitation to another molecule that will be used as photoinitiator.

Photopolymerization reactions fall into two categories: radical photopolymerization (e.g. of acrylates) and cationic photopolymerization (e.g. ring opening reaction of epoxides); for that reason, two different types of photoinitiators have to be used.

2.1 Photoinduced Cationic Polymerization:

Due to availability of a wide range photoinitiators and the great reactivity of acrylate-based monomers, much effort has been devoted to free radical systems [26,27] however, there are some drawbacks associated with this type polymerization such as the initiation effect of oxygen and post-cure limitations which may influence the properties of the final product. Photoinitiated cationic polymerization has received considerable attention particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations. Ring opening heterocycles as cyclic ethers, epoxides, lactones, cyclic sulphides, acetals, siloxanes and vinyl compounds as vinyl ethers are well-known cationically polymerisable monomers. The most important for industrial applications are epoxides, followed by vinyl ethers. Mainly, photoinitiated cationic polymerization differs from photoinduced radical polymerization in the following ways:

1. The initiating species either Brønsted or Lewis acid, is usually a chemically stable compounds, which in the absence of bases or nucleophiles has an unlimited lifetime, unlike free radicals which unless trapped have a very short lifetime.
2. The polymerization once initiated, continues for a long time in the absence of light. Generally, photoinduced free radical polymerization ceases shortly after exposure ceases.
3. Thermal activation is needed in addition to photochemical activation of the initiator to allow curing of all except the most reactive types of monomers. Free radicals, once generated, do not necessarily require thermal energy to achieve full cure.
4. Substrate basicity may inhibit cure. Free radical curing is generally independent of the substrate, once free radicals have been formed.
5. Residual acid may be present in cationic cured films, whilst free radical cured films may contain trapped free radicals.

Cationic polymerizations are usually initiated by electrophilic compounds such as Brønsted or Lewis acids, carbocations, and trialkyloxonium salts [28].

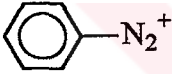
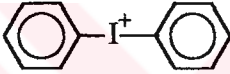
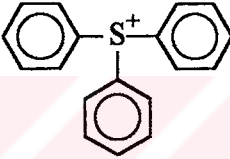
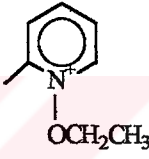
The most widely used cationic photoinitiators are onium salts and organometallic complexes. Other possible but slowly acting structures include [29] alkyl iodides,

inorganic salts and complexes, alkane sulfonic acid salts, unsaturated nitrosamines, and so on.

Onium Salts

Onium salts depicted in Table 2.1 represent a large class of compounds that can be used as cationic photoinitiators of polymerization. These salts consist of a cationic moiety where a positively charged central atom is linked to several alkyl or aromatic groups and an anion. Their history, synthesis, and properties have been reviewed in some excellent papers [25, 30]. These salts are known as stable, nonhydroscopic, and efficient photoinitiators, acting as latent sources of cation radicals and Brønsted acids upon light exposure.

Table 2.1. Onium salts for cationic polymerization

			
Aryldiazonium salt	Iodonium salt	Sulphonium salt	N-alkoxy pyridinium salt

The efficiency of onium salts as photoinitiators of epoxide polymerization reactions is not seriously affected by structural modifications of the onium salts. A change in the anion, on the other hand, has a considerable effect on the rate of polymerization, which is mostly explained in terms of the nucleophilicity of the anion. The anion has hardly any effect on the decomposition rate of the photoinitiator, but play an important role during the development of the polymerization reaction, where the degree of separation in the propagating ion pair is dependent on both of the size and the electron density of the anion: the larger the size, the lower the nucleophilicity is and the higher the propagation rate of the polymerization becomes [31].

Generally, molecular weights and percentage conversions increase in the order $\text{BF}_4^- < \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$ for photoinitiated cationic polymerizations with both ionium [32,33] and metal salts [29]. What type of photoinitiators is applicable to generate cations depends on the chemical constitution of the system used. Regarding onium

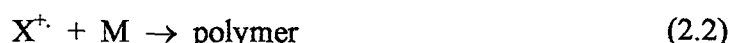
salts, which are the most prominent photoinitiators, direct and indirect acting systems can be applied [34].

2.1.1 Direct Photolysis

Onium salts depicted Table 2.1 generate initiating species upon photolysis at appropriate wavelengths. In general, radical cations were found to be the primary species and play key role for the initiation.



Two different mechanisms were proposed. Radical cations are highly reactive towards monomers and can directly initiate the polymerization.

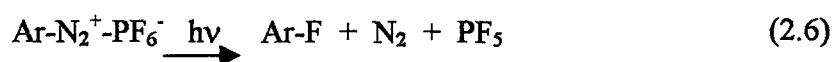


Alternatively, protons generated by hydrogen abstraction of radical cations can add to monomers.



2.1.1.1 Diazonium Salts

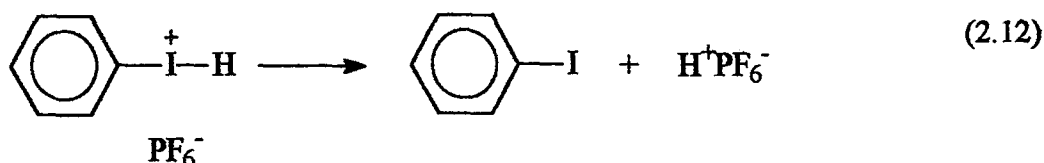
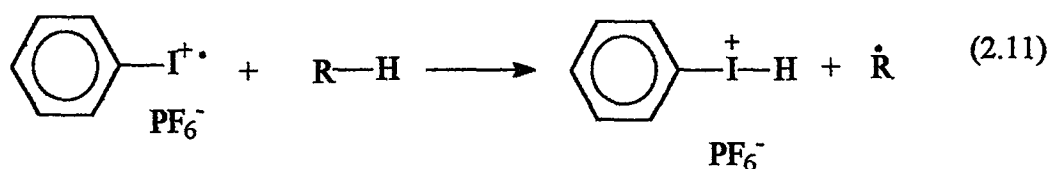
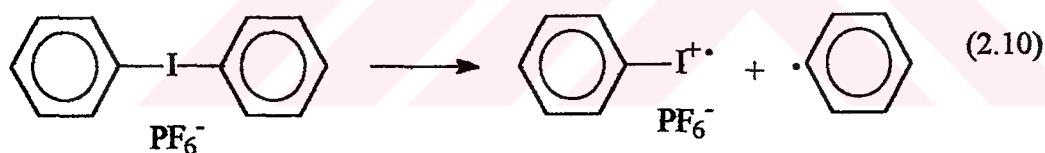
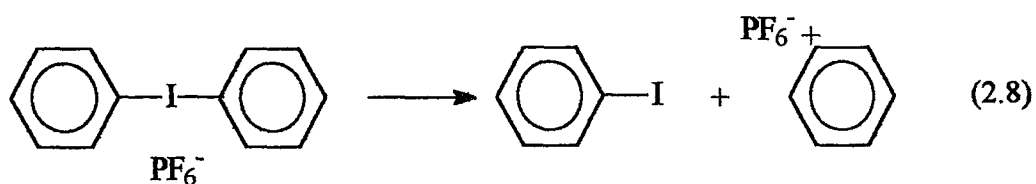
Aryldiazonium salts were the first onium salts to be used as cationic initiators [35]. Upon irradiation, these salts with complex metal halide anions undergo a fragmentation reaction analogous to the thermally activated Schiemann reaction to produce a halogenated aromatic compound and Lewis acid. The latter may be initiate the polymerization directly or react with weakly acid protic species, such as water or alcohol, to yield a strong protic acid.



The absorption of aryldiazonium salts can be varied, by changing the substitution pattern on the aromatic moiety, throughout the UV to the near visible spectral range [36]. Their use for the polymerization is limited by severe drawbacks: poor pot stability in the presence of monomers, poor thermal and photochemical stability, and the release of nitrogen that causes bubbles and pinholes in the coatings.

2.1.1.2 Diaryliodonium Salts

Diaryliodonium salts have received the most attention as cationic photoinitiators, because they are the easiest to prepare and are the most stable. The spectral sensitivity of diaryliodonium salt is relatively poor in the near-UV wavelength region. Upon irradiation, diaryliodonium salts undergo both homolytic and heterolytic cleavages of the carbon-hydrogen bond. The heterolytic pathway generates a phenyl cation and iodobenzene, whilst a phenyl radical and an iodobenzene radical cation are formed by homolytic cleavage [37]. Both mechanisms involve the interaction with a hydrogen donating solvent or monomer yielding Brønsted acid which initiates the polymerization.

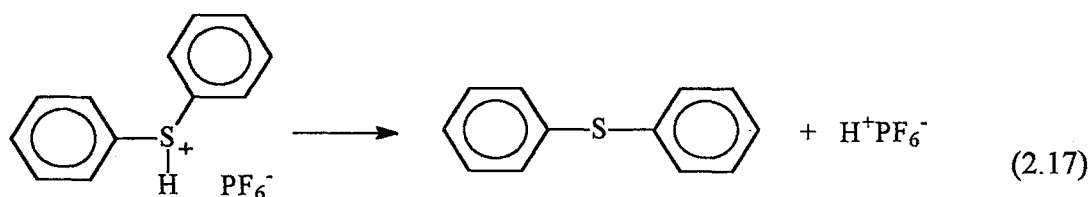
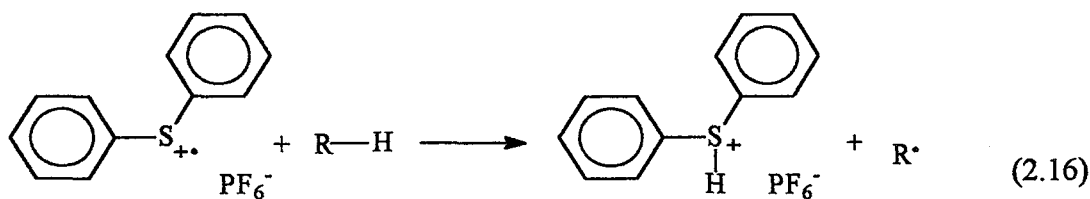
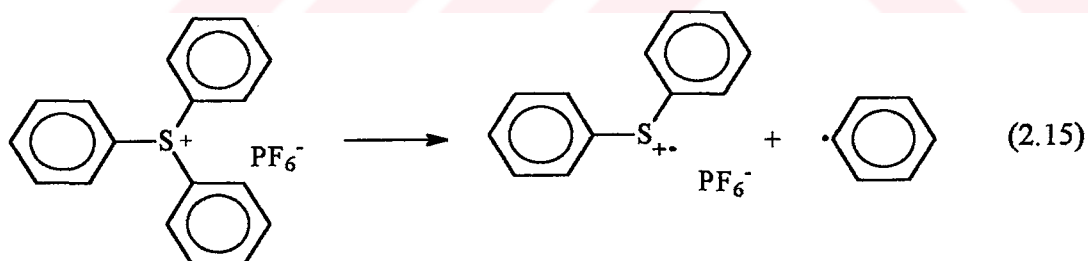
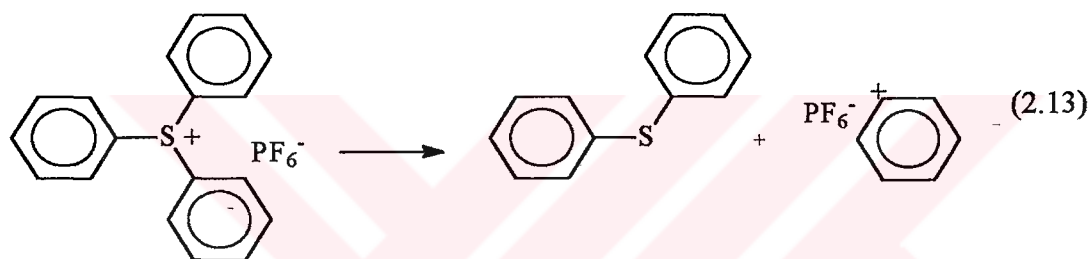


Brønsted acid formed by these reactions is supposed to be the primary initiating species in the photopolymerization reactions. However, the iodobenzene radical cation, formed by homolytic cleavage of iodonium salts, was found to be highly reactive with various nucleophiles, including monomers like cyclohexene oxide and butyl vinyl ethers [38-40].

2.1.1.3 Sulphonium Salts:

Trialkylsulphonium salts spontaneously initiates the cationic polymerization of reactive monomers, like trioxane [41]. Triarylsulphonium salts on the other hand, show little tendency to thermally initiate cationic polymerization. The difference in thermal reactivity of the two types of sulphonium salts is related to their ability to delocalise the positive charge on sulfur.

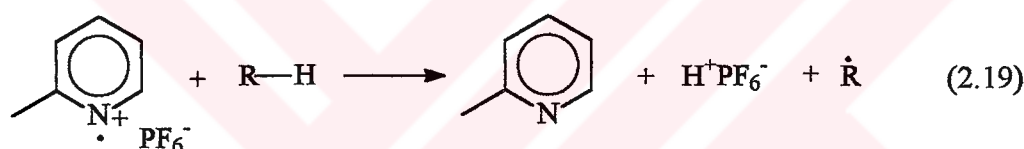
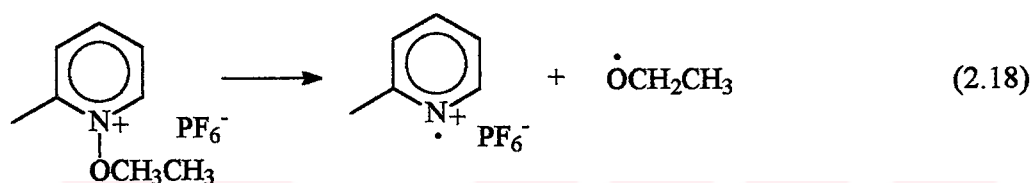
Regarding the photolysis mechanism of triarylsulphonium salts, both heterolytic equations (2.13) and (2.14) and homolytic equations (2.15) and (2.17) bond rupture of one sulfur-carbon bond is evidenced. The heterolytic bond cleavage starting from the excited singlet state is the preferred reaction pathway in direct irradiation [42] and a strong electrophilic Brønsted acid is produced to initiate the cationic polymerization.



2.1.1.4 N-Alkoxy Pyridinium Salts

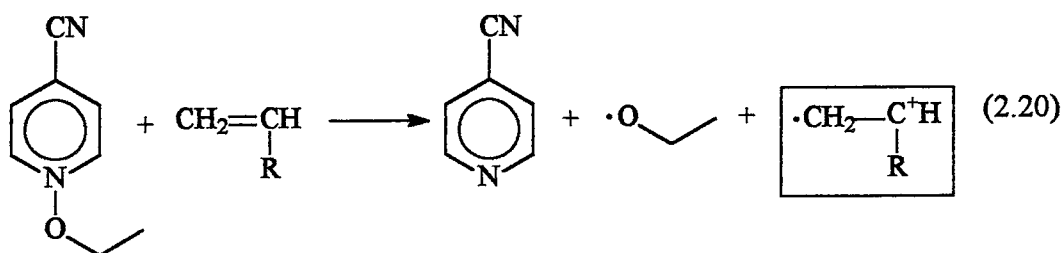
A reaction of pyridine N-oxides with a triethoxonium salt in methylene chloride results in N-alkoxy pyridinium salts [43]. Quinolinium salts are obtained from N-oxides [44]. Since the triethyl oxonium salt is available with non-nucleophilic counter anions, an anion exchange is not necessary in both cases.

As depicted in equations (2.18) and (2.19) for *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$), a pyridinium type radical cation and an alkoxy radical are formed as a result of the initiator's nitrogen-oxygen bond rupture. According to the laser flash photolysis detection, reactivity of the radical cation towards various nucleophilic monomers was found to be very high [45].



In the presence of hydrogen donors (monomer, solvent), Brønsted acid is produced and it initiates polymerization as the radical cation.

In a recent study, Zhu and Schnabel [46] have reported dark polymerization with EMP^+ , *N*-ethoxy-4-cyanopyridinium (EPP^+) and *N*-ethoxyisoquinolinium (EIQ^+) salts. The EMP^+ does not initiate the polymerization reaction in dark while the others polymerize isobutylvinylether and *N*-vinylcarbazol without any irradiation. In contrast, no dark polymerization of cyclohexene oxide was observed for either of the three salts. The mechanism proposed for explaining the dark polymerization involves an electron transfer from monomer to the onium salt. The initiation may be generated by monomer based cation.



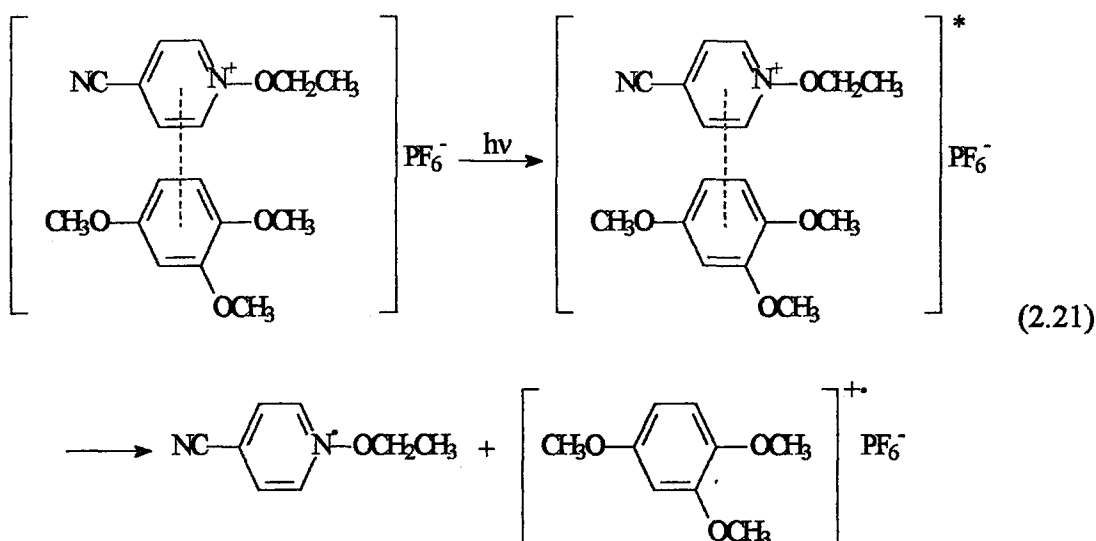
2.1.2 Indirect Acting System

Onium salts used in cationic photopolymerization mainly absorb the wavelengths of light between 225 and 350 nm [25,43,47,48]. Since this requirement is not fulfilled for certain easily available onium salts several systems were developed to extend the applicability of the onium salt photoinitiators. One possible pathway in tackling this dilemma is the chemical attachment of chromophoric groups to the onium salt making it absorb at higher wavelengths. Besides, additives are present which participate in the reaction sequence to yield reactive species capable of initiating the cationic polymerization. At the wavelength chosen for the polymerization, the onium salt initiator is virtually transparent. Incident light is almost entirely absorbed by the additive. Thus, provided the systems obtained do initiate cationic polymerizations. The initiation can be explained through one of the following mechanisms:

- i) Ground State Charge-Transfer Complexes
- ii) Photosensitization via Exciplexes
- iii) Sensitization by Free Radical Initiators
- iv) Sensitization by Classical Energy Transfer

2.1.2.1 Ground State Charge-Transfer Complexes

Pyridinium salts are able to form ground state CT complexes with electron-rich donors such as methyl- and methoxy-substituted benzene [49]. Especially, these complexes absorb at relatively 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. The following mechanism for the initiation of the cationic polymerization has been suggested:



The proton scavenger 2,6-di-*tert*-butylpyridine did not noticeably influence the polymerization. For that reason, the initiation by Brønsted acid 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. However, the photoinitiation of vinyl ethers and *N*-vinyl carbazol can not be generated by this complexes. The latter monomers are already polymerized in a dark reaction upon addition of these complexes.

2.1.2.2 Photosensitization via Exciplex:

Many aromatic hydrocarbons are able to sensitize the decomposition of onium salts via electron transfer in an excited complex referred to as exciplex. 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 Brønsted 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 [50]. For this type of cationic initiation, the following general scheme holds:



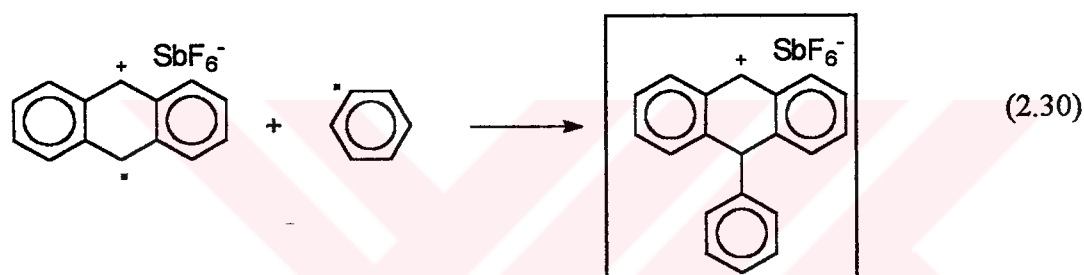
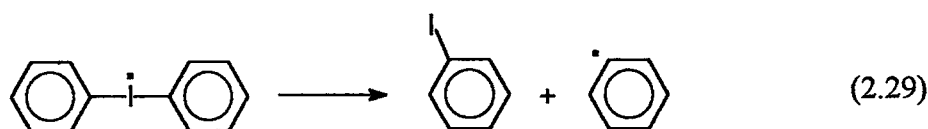
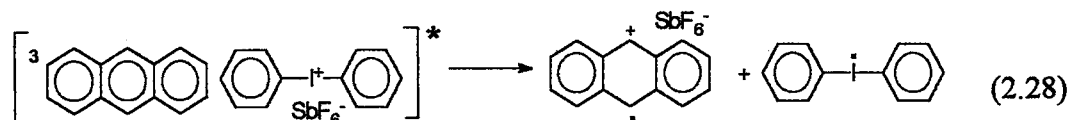
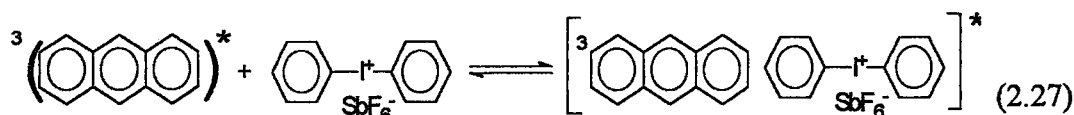
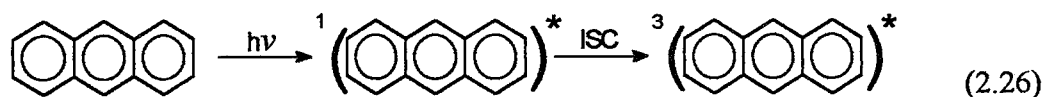
The electron transfer is energetically allowed, if ΔG calculated by (2.25) (extended Rehm-Weller equation) is negative. Since the oxidation potentials of sensitizers, $E_{1/2}^{ox}(S)$, can be easily determined in contrast to that of radicals, the calculation of ΔG is applied in order to predict whether an oxidation would take place.

$$\Delta G = F [E_{1/2}^{ox}(S) - E_{1/2}^{red}(On^+)] - E(S^*) \quad (2.25)$$

F... Faraday constant

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

In a number of papers [51-53], the sensitization of onium salts (especially diphenyliodonium and triphenylsulphonium salts) by anthracene has been investigated in detail. Formation of exciplex is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. These reactions are illustrated below. Diphenyliodonium salt is the example.



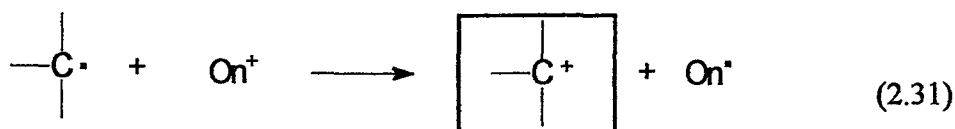
The sensitized decomposition of onium salts via exciplex formation was used in a number of applications. For example, vinyl ether monomers have been synthesized in the liquid crystalline state [54]. Another example, not involving cationic polymerization but employing the oxidation of aromatic compounds by onium salts in the exciplex are novel negative tone photoresists. Vinyl aromatic polymers with electron donating substituents are oxidized by onium salts to their radical cations. These sites can react with each other (releasing protons) thus leading to a fast crosslinking [55,56]. Both the absorption of light by the onium salts and the absorption by an additional photosensitizer (anthracene) is feasible.

2.1.2.3 Sensitization By Free Radical Initiators

Two types of free radical induced initiation are currently available: oxidation of radicals and addition-fragmentation reactions.

i) Oxidation of Radicals

Onium salts are able to initiate a cationic polymerization by themselves. Instead, they may be used to oxidize free radicals according to reaction (2.31) thus generating reactive cations. This process is usually termed as the free radical promoted cationic polymerization.



This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of sensitized cationic polymerization [22,57]. Free radicals may be produced not only by photochemically but also 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.

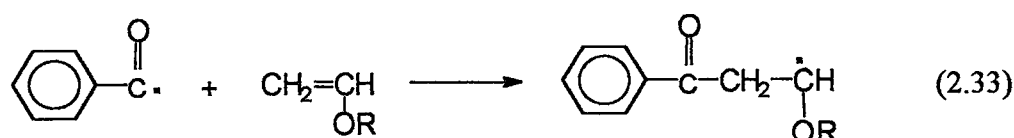
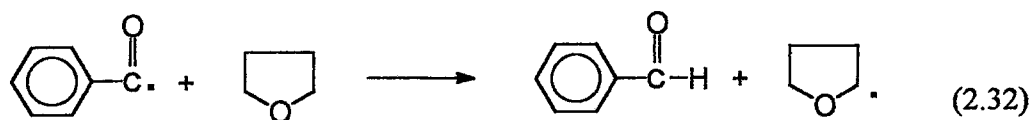
Generally, photoinitiators used in promoted cationic polymerization are benzoin derivatives, acylphosphine oxide, acetophenone. Table 2.2 shows free radical photoinitiator and onium salt combinations generally used in free radical promoted cationic polymerization.

Table 2.2. Initiating system for free radical promoted cationic polymerization

Free Radical Source	Onium Salts
Benzoin derivatives	Iodonium /pyridinium salts
Benzophenone	Iodonium /pyridinium salts
Acylphosphine oxides	Iodonium /pyridinium salts
Dye-amine	Iodonium salt
Vinyl halides	Sulphonium /pyridinium salts
<i>o</i> -Phtaldehyde	Pyridinium salt
Azo compounds	Iodonium /pyridinium salts
Polysilanes	Iodonium /pyridinium salts

The photolysis of benzoin salts results in the generation of strong electron donor radicals. In addition to direct generation of electron donating radicals, non-

nucleophilic radicals, like $\text{PhC}\cdot\text{O}$, $(\text{R}_1\text{R}_2)\text{P}\cdot\text{O}$ and $\text{Ph}\cdot$ formed upon photolysis of the photolabile compound may react with monomer molecules producing electron donating radicals, as described on the example of PhCO in reactions (2.32) and (2.33).



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 $E_{1/2}^{\text{red}}(\text{On}^+)$.

The efficiency of onium salts in this mode of polymerization rises in the order of trialkyl sulfonium salts < alkoxy pyridinium salts < diaryliodonium salts < aryldiazonium salts. Although aryldiazonium salts are the most suitable for the oxidation of radicals, their practical application is hampered by the lack of thermal stability. Diphenyliodonium salts have also a relatively 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 [20,58-60]. In contrast, triphenylsulfonium 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 sulfonium salts [61,62].

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 whether a radical can be oxidized by a given onium salt or not.

$$\Delta G = F [E_{\text{ox}}^{1/2}(\text{R}\cdot) - E_{\text{red}}^{1/2}(\text{On}^+)] \quad (2.34)$$

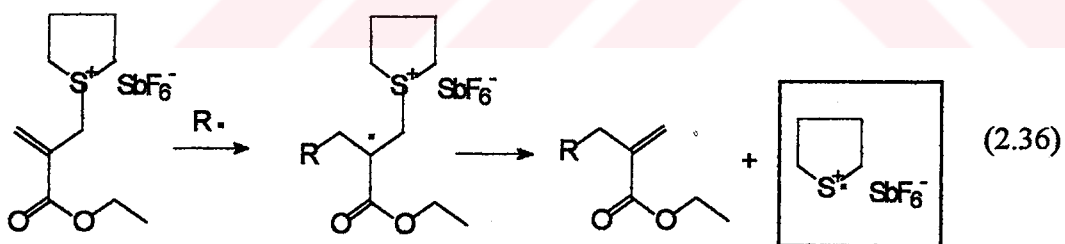
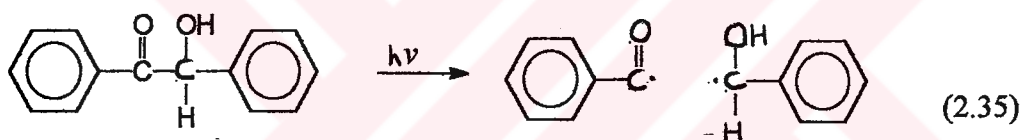
F: Faraday constant

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

ii) Addition Fragmentation Reactions

In recent investigations [63,64], the use of addition fragmentation reactions for photoinduced cationic polymerization has been subjected. Being not based on easily oxidizable radicals, addition fragmentation reactions are indeed a very versatile method to adjust the spectral response of the polymerization mixture with the aid of free radical photoinitiators. The allylic salts have so far been applied for addition fragmentation type initiations.

The mechanism of the addition fragmentation type initiation is depicted on the example of ethyl- α -(tetrahydrothiophenium methyl) acrylate hexafluoroantimonate, $\text{ETM}^+\text{SbF}_6^-$ and benzoin.



The photogeneration of free radicals is the first step. The radicals add to the double bond of the allylonium salt thus producing a radical in β position to the hetero atom of the onium salt cation. Consequently, the molecule undergoes fragmentation yielding initiating cations. The proposed mechanism was evidenced by analysis of the photolysis products.

2.1.2.4 Sensitization by Classical Energy Transfer:

In this mechanism, the electronic excitation of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state is involved. Energy transfer may be generated from the sensitizer (S^*) to the onium salt (I) by either resonance excitation or exchange energy transfer. Depending upon the two components involved the energy transfer may proceed either in the excited singlet or in the triplet state.



As a result of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I^*) are formed. It has been shown that photosensitized decomposition of onium salt follows different route from that observed for direct photolysis of the onium salts [65-67]. This can be attributed to the different spin multiplicities involved in the corresponding decompositions. In contrast, electrons are excited primary to the singlet state through direct irradiation of the onium salt.

The energy transfer sensitization is not a technically useful process since a sufficient energy transfer requires the excitation energy of the sensitizer $E^*(S)$ to be at least as large as the excitation energy of the photoinitiator $E^*(I)$.

Photosensitizers, such as acetophenone or naphthalene are generally used for the sensitization of most onium salts. However, most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt. Therefore in many cases this reaction does not proceed via energy transfer.

3. EXPERIMENTAL PART

3.1 Materials and Chemicals

3.1.1 Monomer

5,5-Dimethyl-1,3-dioxane-2-thione

5,5-dimethyl-1,3-dioxane-2-thione (DDT) was prepared as described previously [68].

3.1.2 Solvents

Dichloromethane (CH₂Cl₂) (Lab-scan)

Dichloromethane (CH₂Cl₂) was used as solvent in polymerization, dilution of polymer solutions and in UV measurements. It was first extracted with sulfuric 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.

Hexane (Technical)

Hexane (technical grade) was used in precipitation processes of polymers.

3.1.3 Initiators

2,2-Dimethoxy-2-phenyl acetophenone (DMPA)

2,2-Dimethoxy-2-phenyl acetophenone (DMPA) was a product of Ciba Specialty Chemicals.

3.1.4 Onium Salts

Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) (Fluka)

Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) was a product of Fluka and used directly.

N-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$)

N-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$) was prepared as described previously [44].

Triphenylsulfonium hexafluoroarsenate ($\text{Ph}_3\text{S}^+\text{AsF}_6^-$) (Johnson Matthey Alfa)

Triphenylsulfonium hexafluoroarsenate ($\text{Ph}_3\text{S}^+\text{AsF}_6^-$) was a product of Johnson Matthey Alfa Products and used directly.

3.1.5 Other Chemicals

Perylene (Aldrich)

Perylene was a product of Aldrich and recrystallized from toluene.

Anthracene (Merck)

Anthracene was a product of Merck and was purified by sublimation.

3.2 Equipment

3.2.1 Photoreactor

Photopolymerizations were performed with Rayonet merry-go-round photoreactor equipped with 16 lamps emitting nominally at 300 and 350 nm.

3.2.2 UV Spectrophotometer

UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer.

3.2.3 Nuclear Magnetic Resonance Spectrometer (NMR)

¹H-NMR analysis were recorded on a Bruker 250 MHz NMR Spectrospin.

3.2.4 Infrared Spectrophotometer (IR)

IR spectra were recorded on a Jasco FT/IR-3 infrared spectrophotometer.

3.2.5 Gel Permeation Chromatography (GPC)

GPC analyses were performed with a setup consisting of a Waters pump and four Waters styragel HR 5E (2000-4 - 106 g/mol), HR4 (5000-60 000 g/mol), HR3 (500-30 000 g/mol), and HR2 (500-20 000 g/mol) columns with THF at a flow rate of 1mL/min, and the detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation of *N*-Ethoxy-2-methylpyridinium hexafluorophosphate, (EMP⁺PF₆⁻)

The mixture of 3.87 mL (48 mmol) of ethyl iodide (C₂H₅I) and 2.1826 g (20 mmol) 2-picolin-*N*-oxide was mixed in an erlenmeyer flask and waited for 24 hours at room temperature. After 24 hours, hexane was added to the mixture to crystallize. Some white precipitation occurred. Precipitated material was filtered and dried. Saturated solution of potassium hexafluorophosphate (KPF₆) was prepared by using 4.5 g of KPF₆, and it was added to previous dry precipitate. This mixture was stirred for one hour, and then the newly formed precipitation was filtered and dried. Dry precipitate was washed with chloroform, recrystallized in methanol and dried at vacuum.

3.4 Preparation of 5,5-Dimethyl-1,3-dioxane-2-thione

A mixture of 2,2-dimethylpropane-1,3-diol with equivalent amount of thiophosgene in the presence of 2 equiv of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one in chloroform was mixed for 12 h at 50°C.

3.5 Photopolymerization

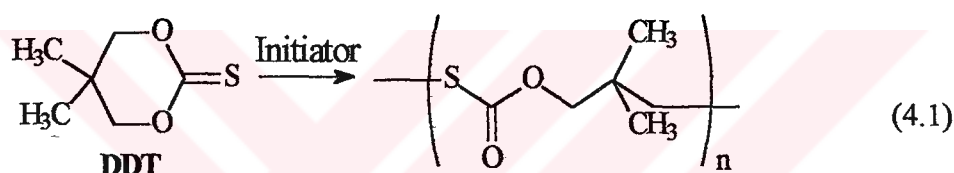
Typical procedure. First, a solution of Ph₂I⁺PF₆⁻ (0.0365 g, 0.005 mmol) and DDT (0.0027 g, 0.25 mmol) in 0.25 ml CH₂Cl₂ was contained in quartz tube (i.d.= 9 mm) and filled with dry nitrogen prior to irradiation from Rayonet merry-go-round photoreactor equipped with 16 lamps emitting nominally at λ = 300 nm. At the end of irradiation for two and half hours, polymers were precipitated in 10-fold excess hexane and dried in vacuum. All the other polymerization using different onium salts and additives (free radical source or sensitizer) were performed under identical conditions except that the pyrex tubes and the lamps emitting nominally at λ = 350 nm were used in free radical promoted and sensitized polymerizations. Conversions for all samples were determined gravimetrically.

3.6 Analysis

GPC analyses of the polymers were performed at room temperature with a setup consisting of a pump (Waters 600E) and four Waters ultrastryragel columns: HR 5E, HR4, HR3, and HR2. THF was used as the eluent (flow rate 1 mL min⁻¹), and the detection was carried out with the aid of a Waters 410 differential refractometer. The number-average molecular weights were determined using Polymer Laboratories polystyrene standards. ¹H-NMR spectra were recorded on a Bruker 250 instrument with CDCl₃ as a solvent and tertamethylsilane (TMS) as the internal standard. UV-vis spectra were taken on an Ati Unicam spectrophotometer. IR spectra were recorded on a Jasco FT/IR-3 spectrometer on a NaBr disc.

4. RESULTS and DISCUSSION

Cyclic carbonates [69-73] are interesting class of monomers that undergo cationic and anionic ring-opening polymerization. Their polymerization accompanies with volume expansion due to the difference in strength of intermolecular interaction between monomers and polymers [74]. Recently, six membered cyclic thiocarbonates such as 5,5-dimethyl-1,3-dioxane-2-thione have been introduced as the structurally related monomers to yield the corresponding polymonothiocarbonates by controlled cationic polymerization [68] (4.1).



Initiator : Et_3OBF_4 , TfOMe , TfOH , BF_3OEt_2

Kricheldorf et. al. [75] previously reported that cationic ring opening polymerization of the unsubstituted monomer, 1,3-dioxane-2-thione, also affords a polymonothiocarbonate. However, the polymers obtained in the latter case were insoluble in common organic solvents. Therefore, the polymerization mechanism and the polymer structure were not evaluated.

There is growing interest in photoinitiated cationic polymerization of many industrially important monomers due to their wide range commercial applications[26,76]. Many cationic photoinitiators are known and their photochemistry [77] has been studied in detail. Onium type photoinitiators such as iodonium [78], sulfonium [79] and alkoxy pyridinium [43] salts occupy an important place among them because of their thermal stability, solubility in most of 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 [80-84].

This study describes photoinitiated cationic ring-opening polymerization of a six-membered monothiocarbonate, 5,5-dimethyl-1,3-dioxane-2-thione (DDT) by using onium salts. Both direct and indirect photoactivation of onium salts are studied.

The cationic polymerization of the monothiocarbonate, DDT, was carried out with diphenyliodonium, triphenyl sulphonium and N-ethoxy-2-methyl pyridinium salts as photoinitiators in CH₂Cl₂ under dry nitrogen atmosphere as summarized in Table 4.1.

Table 4.1. Photoinitiated polymerization^a of 5,5-dimethyl-1,3-dioxane-2-thione (DDT) by using onium salts in CH₂Cl₂ at room temperature.

Run	Onium Salt	Conversion (%)	M_n^c	M_w / M_n^c
1	Ph ₂ I ⁺	82.5	16900	1.68
2 ^b	Ph ₂ I ⁺	79.6	12500	1.65
3	Ph ₃ S ⁺	92.6	15000	1.67
4	EMP ⁺	~1	-	-

^a[DDT] = 1 mol L⁻¹; [Onium Salt] = 2 x 10⁻² mol L⁻¹; λ=300 nm, Irradiation time = 2.5 h.

^bPolymerization was carried out in the presence of air.

^cDetermined by GPC using polystyrene standards.

Both iodonium and sulphonium salts are quite effective as photoinitiators upon irradiation at λ = 300 nm where they absorb the light [85]. Higher reactivity of the sulphonium salts may be attributed to the compatibility of the salt with the monomer since both possess sulfur atom in their structure. The polymerization times are much shorter than those performed with conventional cationic initiators such as triethyl oxonium salts and triflic initiators. Expectedly, oxygen has no inhibitory effect on the polymerization, and similar yield and molecular weight were obtained in the presence of air under identical experimental conditions. Moreover, the photoinitiated polymerizations were conducted at room temperature. This is an obvious advantage

over the thermal polymerization performed moderately elevated temperatures. However, the molecular weight distributions of the polymers obtained by photochemical means are broader and in the range of 1.7 (see Tables 4.1 and Table 4.2). This is expected since in photopolymerization initiating species are generated continuously; growing polymer chains with large differences in chain lengths are present at the same time [86]. Therefore, polymers usually have broad molecular weight distributions. Upon photolysis, onium salt type initiators, undergo irreversible photofragmentation to produce cation radicals and eventually Brønsted acids capable of initiating cationic polymerization as presented on the example of diphenyliodonium salt [87].

The structure of the monomer (DDT) and polymers were examined by $^1\text{H-NMR}$ as in Figure 4.1 and Figure 4.2 respectively. The spectrum of the polymer exhibited three singlet at 0,98, 2,91 and 3,99 ppm, which were assignable to the methyl group and the α - and γ -methylenes with respect to the thiocarbonate sulfur atom.

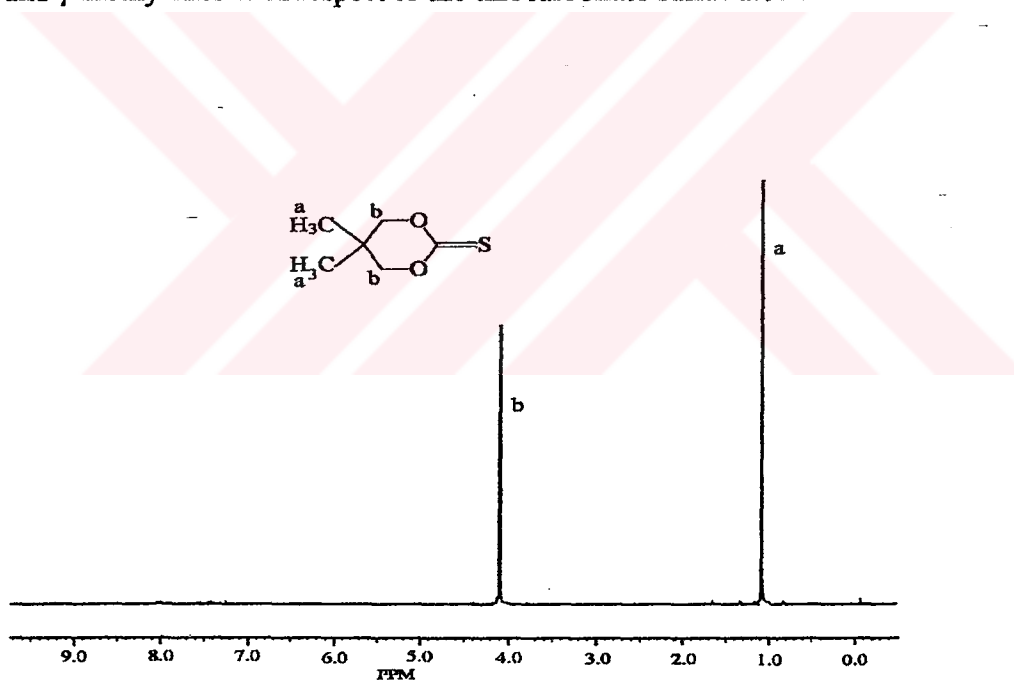


Figure 4.1: ^1H NMR spectrum of 5,5-dimethyl-1,3-dioxane-2-thione (DDT)

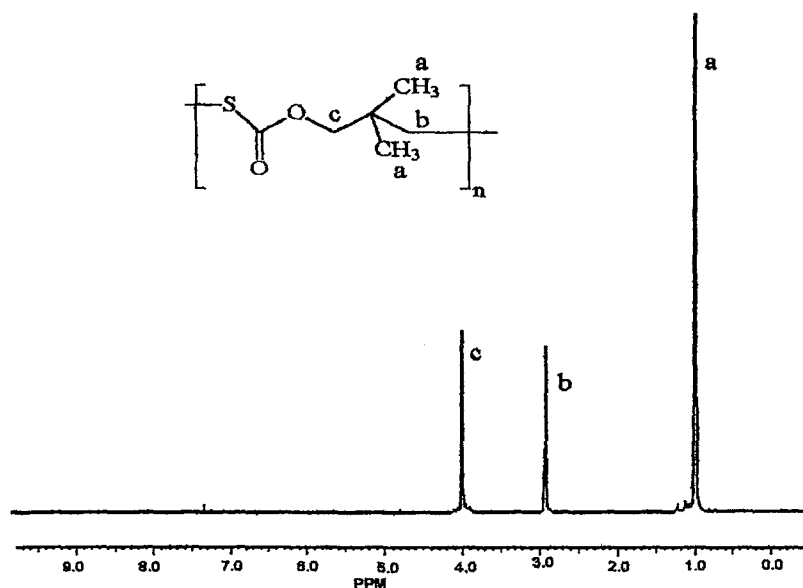
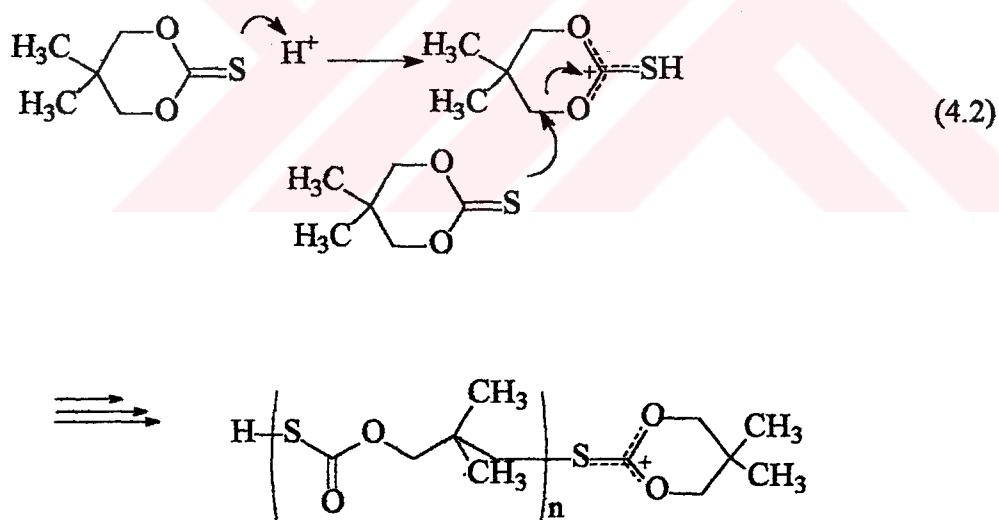


Figure 4.2. ^1H NMR spectrum of the polymer obtained by photoinitiated ring-opening polymerization (Table 4.1, Run 1).

These results indicate that the photoinitiated ring opening polymerization was accompanied with isomerization of the thiocarbonyl group into the carbonyl group (4.2).



This observation was further supported by a carbonyl absorption peak at 1712 cm^{-1} in the IR spectrum of the polymer and absence of carbonyl absorption peak in the IR spectrum of the monomer DDT (Figure 4.3).

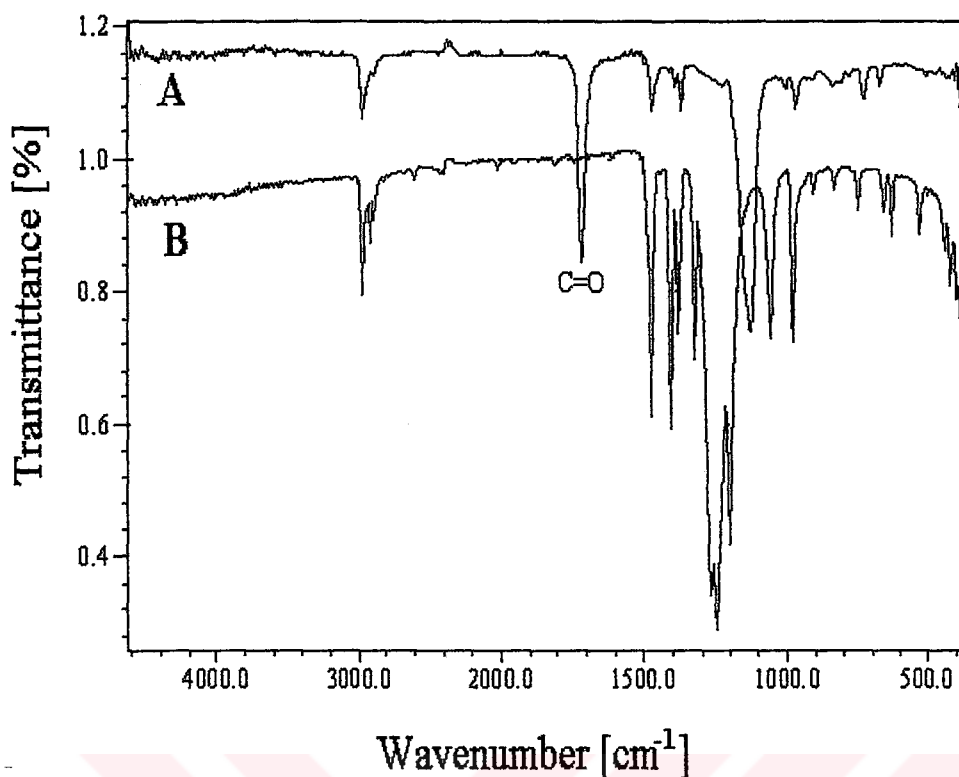


Figure 4.3. FT-IR spectra of the polymer (A) obtained by photoinitiated ring-opening polymerization (Table 4.1, Run 1) and 5,5-dimethyl-1,3-dioxane-2-thione (B).

In this connection, it should be pointed out that thermal polymerization using conventional cationic initiators [68] yielded polymers with the same structures. The M_n s of the polymers increased as the feed ratio of $[1] / [\text{Ph}_2\text{I}^+]$ increased (Figure 4.4). However, in all cases the molecular weight distributions were rather broad than those obtained by conventional thermal cationic initiators [68] ($M_w / M_n = 1.63\text{-}2.34$) (see Table 4.2).

Table 4.2. Photoinitiated cationic ring-opening polymerization^a of 5,5-dimethyl-1,3-dioxane-2-thione (DDT) by using $\text{Ph}_2\text{I}^+ \text{PF}_6^-$ in CH_2Cl_2 at room temperature.

Run	$[\text{DDT}]/[\text{Ph}_2\text{I}^+]$	Conversion (%)	M_n^b	M_w / M_n^b
1	10	58	6400	2.34
2	20	86	10200	1.68
3	30	79	12700	1.77
4	40	85	15000	1.77
5	50	82	16900	1.68
6	60	77	17800	1.63

^a $[\text{DDT}] = 1 \text{ mol L}^{-1}$; $\lambda = 300 \text{ nm}$; Irradiation time = 2,5 h.

^bDetermined by GPC using polystyrene standards.

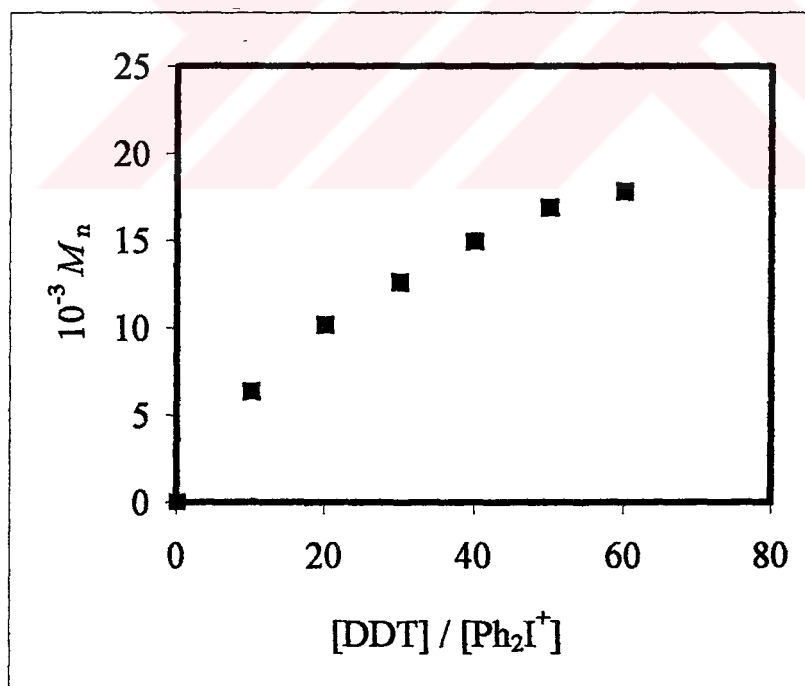
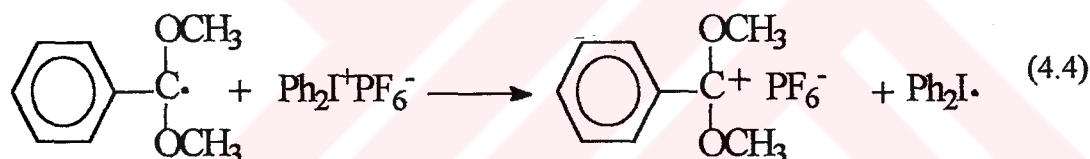
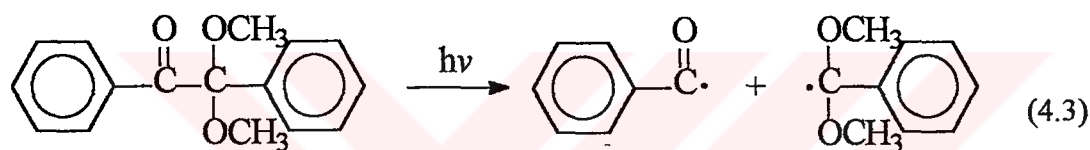


Figure 4.4. The relationship between M_n and the ratio of $[\text{DDT}] / [\text{Ph}_2\text{I}^+]$. Conditions: monomer, 0,25 mmol; solvent, 0,25 mL of CH_2Cl_2 , under exposure of 300 nm wavelength for 2.5 h.

As stated in the introduction section, photodecomposition of onium salts can be induced with the aid of many light sensitive compounds[88]. Among them the use of free radical initiators is fairly flexible way and allows to extend the spectral sensitivity of the cationic initiating system to the absorbency of the free radical initiators. Suitable radical sources with wide range absorption characteristics are available and successfully employed in free radical promoted cationic polymerization. The crucial requirement in such systems is that photochemically generated radicals should be electron donating in order to facilitate successful oxidation to the initiating cations. For our purpose, we have deliberately selected 2,2-dimethoxy-2-phenylacetophenone as the free radical source since it undergoes α -cleavage with high quantum efficiency [89] and produces strong electron donating dimethoxy benzyl radicals which are readily oxidizable to the corresponding cations [90], (4.3) and (4.4).



The efficiency of onium salts as oxidizing agents is related to their electron affinity [44]. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{\text{red}}^{1/2}(\text{On}^+)$. As can be seen from Table 4.3, the iodonium salt is the most powerful oxidation agent which contributes to the higher conversion of monothiocarbonate. Triphenylsulphonium salt does not participate in such electron transfer process due to unfavorable redox potential. In this case cationic polymerization does not proceed. The intermediate behaviour of the pyridinium salt is also related to its redox potential.

Table 4.3. Free radical promoted cationic polymerization^a of 5,5-dimethyl-1,3-dioxane-2-thione (DDT) by using 2, 2-dimethoxy-2-phenyl acetophenone (DMPA) in the presence of onium salts in CH₂Cl₂ at room temperature.

Run	Onium Salts ^b	$E_{\text{red}}^{1/2}$ (V SCE)	Conversion (%)	M_n^b	M_w / M_n^b
1	Ph ₂ I ⁺	-0.2 [91]	60.8	11600	1.16
2	EMP ⁺	-0.7 [92]	42.7	10500	1.31
3	Ph ₃ S ⁺	-1.2 [93]	-	-	-

^a[DDT] = 1 mol L⁻¹; [Onium Salt] = 2 x 10⁻² mol L⁻¹; [DMPA] = 2 x 10⁻² mol L⁻¹
 λ =350 nm, Irradiation time = 2.5 h

^bDetermined by GPC using polystyrene standards.

Photosensitization with the aid of various sensitizers absorbing light at longer wavelengths, i.e., $\lambda > 350$ nm can also help to extend the applicability of onium salts as photoinitiator [94]. For this purpose, the reactions of diphenyliodonium ions with excited states of perylene and anthracene were examined. In the ground state, these compounds absorb the light between 350 and 400 nm. Long wavelength irradiation, i.e., $\lambda = 350$ nm is employed which permits the selection of absorption by the photosensitizer, but not by the iodonium salt. Typical results are presented in Table 4. 4. It should be pointed out that both sensitizers are ineffective for initiating cationic polymerizations in the absence of the iodonium salt. Notably, both compounds act as sensitizers.

Table 4.4. Photosensitized polymerization^a of 5,5-dimethyl-1,3-dioxane-2-thione (DDT) by using onium salts in CH₂Cl₂ at room temperature.

Run	Photosensitizer	Conversion (%)	M_n^c	M_w / M_n^c
1	Perylene	87.6	10800	1.25
2	Anthracene	71.8	13600	1.29

^a[DDT] = 1 mol L⁻¹; [Onium Salt] = 2 x 10⁻² mol L⁻¹; [Sensitizer] = 2 x 10⁻² mol L⁻¹
λ=350 nm, Irradiation time = 2.5 h

^bDetermined by GPC using polystyrene

It was shown that sensitizer radical cations react directly with monomers and initiate the polymerization [83]. In all cases, polymers with the isomerized structures were formed regardless of the initiation method employed.

5. CONCLUSIONS

In conclusion, photoinitiated cationic polymerization of a monothiocarbonate has been demonstrated.

Onium salt type photoinitiators activates the photopolymerization of the monothiocarbonate. Both direct and indirect activation methods utilizing either free radical sources or photosensitizers are efficient in the photoinitiation process. Structural investigations reveals that polymerization is accompanied with isomerization as it is observed with the conventional cationic initiators. Moreover, the polydispersity of the polymers obtained by photochemical means is broader than those obtained by thermal polymerization due to the characteristics of the polymerization mode.

This study further provokes the possibility of the use of thiocarbonate monomers possessing different structural units including polymeric chains in a photoinduced polymers. This way, polythiocarbonate with different properties may be obtained. Further studies in this line are now in progress.

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AUTOBIOGRAPHY

Nihan YÖNET was born in Istanbul in 1980. After graduating from 50. Year Insa High School, she was admitted to Fatih University, Department of Chemistry having a merit scholarship in 1997. She was graduated as a chemist in 2002. She worked as an assistant in the student laboratories of general chemistry and inorganic chemistry courses during 2001-2002 academic year at Fatih University.

She was registered as M.S. student to the Polymer Science and Technology Program of the Institute of Science and Technology of Istanbul Technical University in 2002.

She is the co-author of the following scientific paper, which was published in an international journal:

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Monothiocarbonates,

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