# Photosensitized cationic polymerization of cyclohexene oxide: a mechanistic study concerning the use of pyridinium-type salts

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The photoinitiation of the polymerization of bulk cyclohexene oxide (CHO) containing $N$-ethoxy-2-methyl pyridinium hexafluorophosphate (EMP$^+$PF$_6^-$) and either anthracene or thioxanthone (TX) at $\lambda_{inc} > 340$ nm was studied. Regarding the action of anthracene it is notable that upon u.v. irradiation of a CHO solution of poly(tetrahydrofuran) bearing terminal anthryl groups a block copolymer, poly(tetrahydrofuran-*block*-cyclohexane oxide), is formed. The optical absorption spectrum of the block copolymer does not possess bands characteristic for anthracene. Therefore, the following mechanism is postulated: electron transfer from singlet excited anthracene molecules to EMP$^+$ ions results in the formation of anthracene radical cations that react with ethoxyl radicals stemming from the decomposition of EMP• radicals. 9-Ethoxy-9,10-dihydroanthryl ions generated in this way react with CHO thus initiating its polymerization. Regarding the action of TX it seems that the polymerization of CHO is essentially initiated by protons. The generation of protons has been evidenced. In propylene carbonate solution protons are generated with $\Phi(H^+) = 0.27$ whereas $\Phi(-TX) = 0.028$. The postulated mechanism is based on the reaction of triplets, $^3TX^*$, with both CHO ($k_{RH} = 3 \times 10^4$ l mol$^{-1}$ s$^{-1}$) and EMP$^+$ ions ($k_{ET} = 4 \times 10^7$ l mol$^{-1}$ s$^{-1}$). At low concentration of EMP$^+$PF$_6^-$ ($6.8 \times 10^{-4}$ mol$^{-1}$ l$^{-1}$) $^3TX^*$ molecules react almost exclusively (93%) with CHO and it appears that ketyl radicals thus formed react with EMP$^+$ ions, a process eventually resulting in the formation of protons and the regeneration of TX. At relatively high concentration of EMP$^+$PF$_6^-$ ($6.8 \times 10^{-3}$ mol l$^{-1}$), thioxanthone triplets are largely (47%) deactivated by electron transfer to EMP$^+$ ions. The importance of this reaction with respect to its contribution to the initiation of the polymerization of CHO has not yet been revealed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cationic polymerization; cyclohexene oxide; pyridinium ions)

## INTRODUCTION

$N$-Alkoxy-pyridinium and $N$-alkoxy-quinolinium salts are effective photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide, or of vinyl ethers such as n-butyl vinyl ether[1–4]. The application of these salts is limited to the wavelength range $\lambda \lesssim 350$ nm, since they are transparent at longer wavelengths. To overcome this problem photosensitizers absorbing light at longer wavelengths, e.g. anthracene, perylene, phenothiazine and thioxanthone were employed successfully and flash photolysis studies revealed that pyridinium ions readily undergo electron transfer reactions with several electronically excited photosensitizers (PS) as depicted by reactions (1) and (2)[5]:

$$PS + h\nu \longrightarrow PS^* \tag{1}$$

$$PS^* + EMP^+ \longrightarrow PS^{+\bullet} + EMP\bullet \tag{2}$$
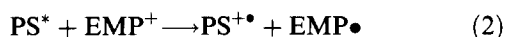
where EMP$^+$ represents the $N$-ethoxy-2-methyl-pyridinium ion.

Since our former investigations did not give an answer to the question of whether radical cations PS$^{+\bullet}$ formed according to reaction (2) react directly with the monomers and, in this way, start their polymerization, or whether another initiation mechanism prevails, the present study with anthracene and thioxanthone was performed. These compounds are considered to represent two families of sensitizers, namely polynuclear aromatic compounds and aromatic carbonyl compounds, respectively.

## EXPERIMENTAL

### Materials

Tetrahydrofuran (THF; E. Merck) was dried over potassium hydroxide and distilled from sodium wire prior to use. Anthracene and 9-anthryl methanol (Aldrich) were recrystallized from ethanol. Thioxanthone (Fluka) was recrystallized from n-hexane,. Cyclohexene oxide (CHO) was distilled from CaH$_2$ under argon. 2,6-Di-*tert*-butyl-4-methylphenol (DBMP; Aldrich) was dried overnight at 50°C. Triflic anhydride, NaH (80% dispersion in mineral oil) and (±) propylene

carbonate were used as received from Aldrich. Dichloromethane (E. Merck) was treated with concentrated $H_2SO_4$ and washed with aqueous $Na_2CO_3$ solution and neat water. After drying with $CaH_2$ it was distilled from $P_2O_5$. Finally, it was stored over activated molecular sieve (Type 4). 2-Methyl pyridinium $N$-oxide and triethyloxonium hexafluorophosphate (Aldrich) were used as received. $N$-Ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) was prepared according to a procedure described previously[1].

### Preparation of sodium 9-anthryl methoxide

Sodium hydride dispersion containing $1.9 \times 10^{-3}$ mol NaH was added to a solution of $1.9 \times 10^{-3}$ mol 9-anthryl methanol in toluene/dioxane mixture (1 : 3, v : v). During mixing hydrogen evolved and a homogeneous solution formed. It was kept under dry nitrogen in a refrigerator until used.

### Synthesis of poly(tetrahydrofuran) having terminal anthryl groups

A three-necked flask equipped with an argon inlet and a rubber septum was connected to a vacuum line that was dried at 130°C and subsequently cooled to room temperature. After 50 ml THF had been distilled into the flask it was filled with argon and disconnected from the vacuum line. Then, the polymerization of the THF was initiated by the addition of $1.9 \times 10^{-4}$ mol triflic anhydride under stirring at 25°C. After a given time the polymerization was terminated by the addition of a solution of sodium 9-anthryl methoxide ($1.9 \times 10^{-3}$ mol in toluene/dioxane mixture (1 : 3, v : v)). The mixture was stirred for 15 min at room temperature and then cooled down to −20°C. At this temperature, the polymer was precipitated by the addition of methanol. Reprecipitation was performed by dissolving the polymer in methanol at room temperature and cooling the solution down to −20°C. This procedure was repeated until the

u.v. spectrum of the polymer did not change any more. As can be seen from *Figure 1* the absorption spectrum of the polymer strongly resembles that of anthryl methanol, indicating that the living propagating poly(tetrahydrofuran) (PTHF) cations were terminated by anthryl methoxide according to the mechanism shown in *Scheme 1*.

### Polymerization of cyclohexene oxide

$EMP^+PF_6^-$ ($6.8 \times 10^{-4}$ mol l$^{-1}$) and sensitizer (anthracene or thioxanthone) at concentrations ranging from $4.7 \times 10^{-5}$ to $4.7 \times 10^{-4}$ mol l$^{-1}$ were dissolved in CHO. Portions (5 ml) of the solution were put into Pyrex tubes (i.d. 1 cm) and saturated with argon. The tubes were sealed and irradiated at $\lambda > 340$ nm in a Rayonet reactor (RPR 100) equipped with a rotating sample holder. Cut-off filters (WH 360, 3 mm) were placed in front of the tubes. The polymer formed during the irradiation was precipitated by the addition of methanol and dried *in vacuo*. In other experiments PTHF bearing terminal anthryl groups was used as a sensitizer: 0.0245 g of this polymer and 0.096 g $EMP^+PF_6^-$ were dissolved in 2 ml dichloromethane. After addition of 3 ml CHO the solution was purged with argon and irradiated at $\lambda = 350$ nm. Subsequently, the polymer was precipitated by the addition of methanol at room temperature. When the supernatant solution was cooled down to −20°C a second polymer fraction (unreacted PTHF) precipitated overnight. Both fractions were dried and characterized by size exclusion chromatography and optical spectroscopy.

### Determination of acid

Protons generated during the irradiation of propylene carbonate solutions containing both TX and $EMP^+PF_6^-$ were detected potentiometrically with the aid of a glass electrode (Ingold, 450-S7).

### Flash photolysis

A ruby laser (Korad, model K1 QS2) operated with a frequency doubler was used to generate 20 ns flashes ($\lambda_{inc} = 347$ nm). Prior to irradiation in rectangular quartz cells the solutions were flushed with argon.

### Characterization of the polymers

Size exclusion chromatography was carried out with a set-up consisting of a Shimadzu pump (model LC6A) and four Ultrastyragel columns (porosity: $10^5$, $10^4$, $10^3$ and $5 \times 10^2$ Å). THF was used as eluent at a flow rate of 1 ml min$^{-1}$. Detection was performed with a Waters differential refractometer (model 410). Molecular weights were estimated with the aid of polystyrene standards.
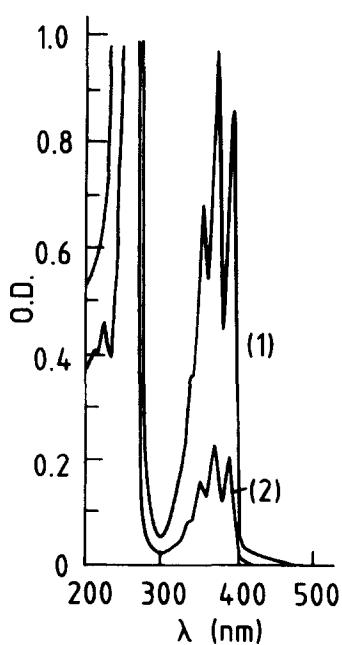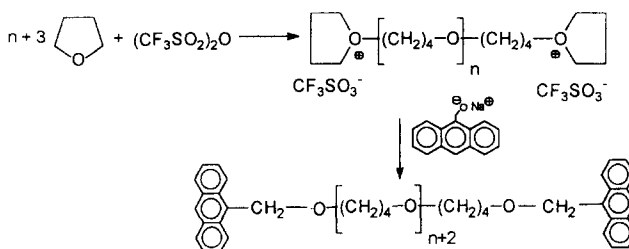


**Figure 1** Optical absorption spectra of dichloromethane solutions of PTHF containing terminal anthryl groups at $c = 0.4$ g l$^{-1}$ (1), and of 9-anthryl methanol at $c = 0.034$ g l$^{-1}$ (2), recorded at room temperature
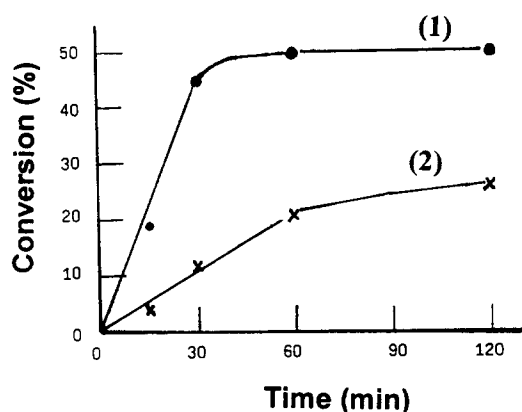


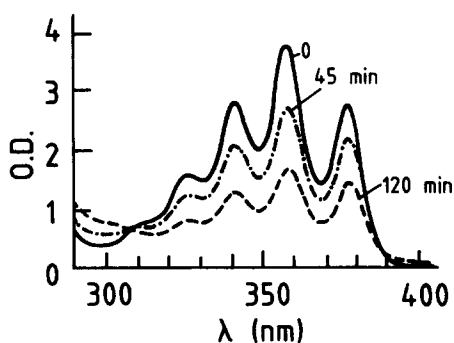**Scheme 1** Formation of poly(tetrahydrofuran) bearing anthryl groups

# RESULTS

## Sensitization by anthracene

*Polymerization experiments.* Cyclohexene oxide containing $EMP^+PF_6^-$ and anthracene is converted into poly(cyclohexene oxide) upon irradiation with u.v. light at $\lambda_{inc} > 340$ nm. Conversion–time profiles obtained with CHO containing anthracene $(4.7 \times 10^{-4}\,mol\,l^{-1})$ and $EMP^+PF_6^-$ at two different concentrations are presented in *Figure 2*. The conversion of CHO increases with increasing irradiation time and approaches a limiting value corresponding to about 27 and 50% at $[EMP^+] = 6.8 \times 10^4\,mol\,l^{-1}$ and $6.8 \times 10^{-3}\,mol\,l^{-1}$, respectively. Actually, anthracene is consumed during the polymerization. This can be seen in *Figure 3* where optical absorption spectra recorded after various irradiation times are presented.

*Synthesis of block copolymers.* When CHO containing PTHF bearing terminal anthryl groups and $EMP^+PF_6^-$ were irradiated for 60 min at $\lambda_{inc} > 340$ nm, a large portion of the anthryl groups was consumed as is inferred from the decrease in the intensity of the characteristic absorption bands which is quite similar to the case of irradiation of neat anthracene described in the previous section. The CHO conversion amounted to about 62%. Notably, upon the addition of methanol, 85% of the polymer precipitated at room temperature and 15% at −20°C. *Figure 4* presents size exclusion

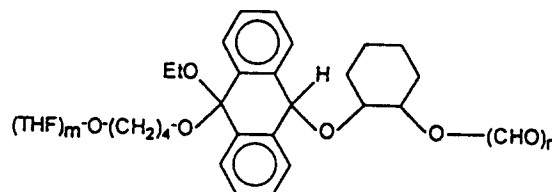chromatograms of the unirradiated anthryl groups bearing PTHF and of the fraction of the product polymer that precipitated at room temperature. The chromatogram of the latter consists of a broad peak with a maximum shifted into the direction of high molar masses indicating the formation of block copolymer. Notably, the polymer does not exhibit the absorption bands of the anthryl groups. Therefore, it is concluded that the block copolymer formed consists of PTHF and PCHO blocks that are connected by groups of the following structure:
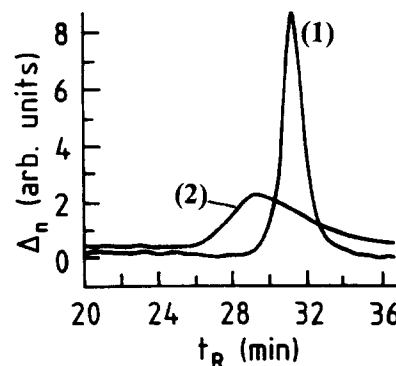


Provided *Scheme 1* is fully applicable to the reaction of growing PTHF chains with sodium anthryl methoxide, all PTHF molecules should possess anthryl groups at both ends and the block copolymer formed should be of the structure A–B–A, where A and B denote CHO and THF blocks, respectively. However, a portion of the PTHF molecules might possess only one anthryl group with the consequent formation of block copolymer molecules of the structure A–B. This might explain the rather broad molar mass distribution indicated by the broad peak in the chromatogram of the product polymer in *Figure 4*.

## Sensitization by thioxanthone

*Flash photolysis.* Irradiation of TX results in the formation of excited triplet states $(^3TX^*)$ which are prone to abstract hydrogen from surrounding molecules thus forming ketyl radicals ($\bullet$ TXH)[6]. In order to measure the rate constant $k_{RH}$ of the reaction of thioxanthone triplets with CHO, given by

$$^3TX^* + CHO \xrightarrow{k_{RH}} \bullet TXH + R\bullet \qquad (3)$$

(where, $R\bullet$: $[CHO(-H)]\bullet$), flash photolysis experiments were carried out in benzene solutions containing TX



**Figure 2** Bulk polymerization of CHO at 30°C and $\lambda > 340$ nm initiated by anthracene/$EMP^+PF_6^-$. Conversion *versus* time of irradiation. $[A] = 4.7 \times 10^{-4}\,mol\,l^{-1}$. $[EMP^+PF_6^-] = 6.8 \times 10^{-3}\,mol\,l^{-1}$ (1) and $6.8 \times 10^{-4}\,mol\,l^{-1}$ (2)



**Figure 3** Optical absorption spectra of a CHO solution containing anthracene $(4.7 \times 10^{-4}\,mol\,l^{-1})$ and $EMP^+PF_6^-$ $(6.8 \times 10^{-4}\,mol\,l^{-1})$ recorded before and after (45 and 120 min) irradiation at $\lambda > 340$ nm



**Figure 4** Size exclusion chromatograms of PTHF containing terminal anthryl groups (1) and of the same polymer after having photoinitiated the reaction with CHO (2), $t_{irr} = 60$ min

$(5 \times 10^{-5} \, \text{mol} \, l^{-1})$ and different amounts of CHO. The decay of the T–T absorption at 630 nm followed first-order kinetics. Plotting of the experimentally measured rate constant $k_1$ *versus* the CHO concentration resulted in a straight line as expected according to:

$$k_1 = k_0 + k_{RH}[\text{CHO}] \qquad (4)$$

From the slope of the straight line $k_{RH} = 3.6 \times 10^4 \, \text{mol}^{-1} \, \text{litre} \, s^{-1}$ is obtained. As has been found previously[5], thioxanthone triplets react with $\text{EMP}^+$ ions with a rate constant $k_{ET} = 4 \times 10^7 \, \text{mol}^{-1} \, \text{litre} \, s^{-1}$. Therefore, the fraction of thioxanthone triplets undergoing hydrogen abstraction from CHO in the presence of $\text{EPM}^+$ is given by the following expression:
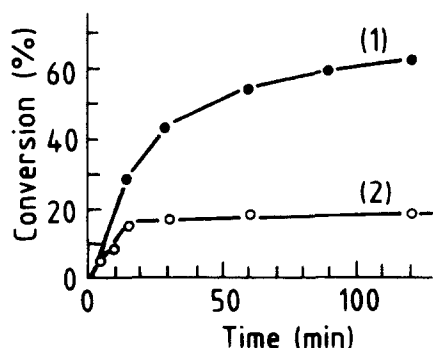
$$w_{RH} = v_{RH} / (v_{RH} + v_{ET})$$

$$= k_{RH}[\text{CHO}] / (k_{RH}[\text{CHO}] + k_{ET}[\text{EMP}^+]) \quad (5)$$

where $v$ denotes the rate of the reaction. Accordingly, one obtains $w_{RH} = 0.93$ at $[\text{EMP}^+] = 6.8 \times 10^{-4} \, \text{mol} \, l^{-1}$ and $w_{RH} = 0.57$ at $[\text{EMP}^+] = 6.8 \times 10^{-3} \, \text{mol} \, l^{-1}$, i.e. at the low $\text{EMP}^+$ concentration hydrogen abstraction is the dominating process and with increasing $\text{EMP}^+$ concentration the importance of the reaction $^3\text{TX}^* + \text{EMP}^+$ is augmented.

## Continuous irradiations

*Polymerization experiments.* Conversion–time profiles regarding the bulk polymerization of CHO containing thioxanthone $(4.7 \times 10^{-4} \, \text{mol} \, l^{-1})$ and $\text{EMP}^+\text{PF}_6^-$ at two different concentrations are presented in *Figure 5*. It can be seen that the conversion of CHO into poly-(cyclohexene oxide) increases with increasing irradiation time and approaches a limiting value corresponding to about 18 and 62% at $[\text{EMP}^+] = 6.8 \times 10^{-4} \, \text{mol} \, l^{-1}$ and $6.8 \times 10^{-3} \, \text{mol} \, l^{-1}$, respectively. Notably, the polymerization of CHO is strongly affected by DBMP, a typical radical scavenger, as can be seen from *Table 1*. DBMP is very likely to react with the free radicals formed by the reaction of thioxanthone triplets with CHO according to reaction (3). Consequently, the results presented in *Table 1* suggest that radicals formed in reaction (3) play an important role in the initiation mechanism.

*Optical absorption measurements.* Thioxanthone decomposed during the polymerization of CHO as is indicated by the decrease in the absorption band at 380 nm. This is shown in *Figure 6* where optical absorption spectra recorded after various irradiation times are presented. A similar behaviour was observed when a propylene carbonate solution containing TX $(5.47 \times 10^{-4} \, \text{mol} \, l^{-1})$ and $\text{EMP}^+\text{PF}_6^-$ $(3.1 \times 10^{-3} \, \text{mol} \, l^{-1})$ was irradiated with monochromatic light $(\lambda_{inc} = 360 \, \text{nm}$, absorbed dose rate $Dr_{abs} = 5.2 \times 10^{-5}$ einstein $l^{-1} \, \text{min}^{-1})$. *Figure 7a* depicts the decrease in the TX concentration as a function of irradiation time. From the slope of the straight line the quantum yield $\Phi(-\text{TX}) = 0.028$ is obtained.

*Acid formation.* Upon irradiation of the propylene carbonate solution, mentioned in the last paragraph, acid $(\text{HPF}_6^-)$ was formed. *Figure 7b* presents a plot of the proton concentration *versus* the irradiation time. From the slope of the straight line the quantum yield $\Phi(\text{H}^+) = 0.27$ is obtained. Interestingly, this value is about 10 times larger than the $\Phi(-\text{TX})$ value. Moreover, it is notable that acid could not be detected in irradiated CHO solutions which indicates a rapid reaction of protons with CHO.

## DISCUSSION

### Polymerization of CHO sensitized by anthryl groups bearing PTHF

The employment of anthryl group bearing PTHF as a photosensitizer for the polymerization of cyclohexene oxide gives rise to the formation of a block copolymer. However, the block copolymer does not contain anthryl

**Table 1** The influence of DBMP on the CHO conversion at $30^{\circ}\text{C}$. $[\text{TX}] = 4.7 \times 10^{-4} \, \text{mol} \, l^{-1}$. $[\text{EMP}^+\text{PF}_6^-] = 6.8 \times 10^{-3} \, \text{mol} \, l^{-1}$

| [DBMP] (mol $l^{-1}$) | Conversion[a] (%) |
|---|---|
| 0 | 54 |
| 0.005 | 39 |
| 0.05 | 5 |
| 0.10 | 3 |

[a] At $t_{irr} = 60 \, \text{min}$



**Figure 5** Bulk polymerization of CHO at $30^{\circ}\text{C}$ and $\lambda > 340 \, \text{nm}$ initiated by thioxanthone/$\text{EMP}^+\text{PF}_6^-$. Conversion *versus* time of irradiation. $[\text{TX}] = 4.7 \times 10^{-4} \, \text{mol} \, l^{-1}$. $[\text{EMP}^+\text{PF}_6^-] = 6.8 \times 10^{-3} \, \text{mol} \, l^{-1}$ (1) and $6.8 \times 10^{-4} \, \text{mol} \, l^{-1}$ (2)
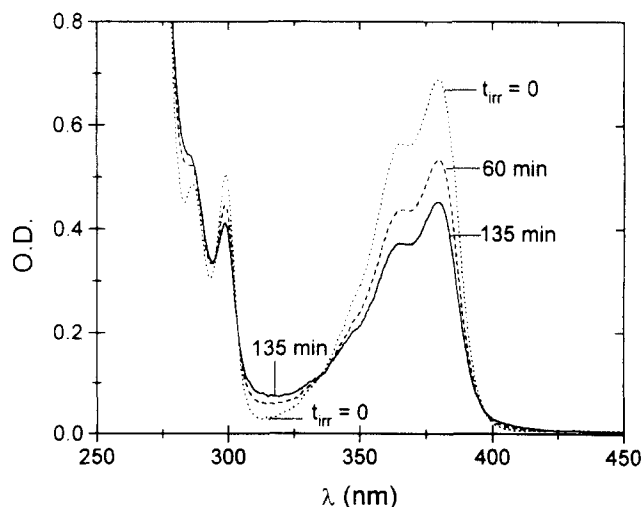


**Figure 6** Optical absorption spectra of a CHO solution containing thioxanthone $(4.7 \times 10^{-4} \, \text{mol} \, l^{-1})$ and $\text{EMP}^+\text{PF}_6^-$ $(6.8 \times 10^{-4} \, \text{mol} \, l^{-1})$ recorded before and after (60 and 135 min) irradiation at $\lambda = 360 \, \text{nm}$ using a xenon lamp in conjunction with a monochromator
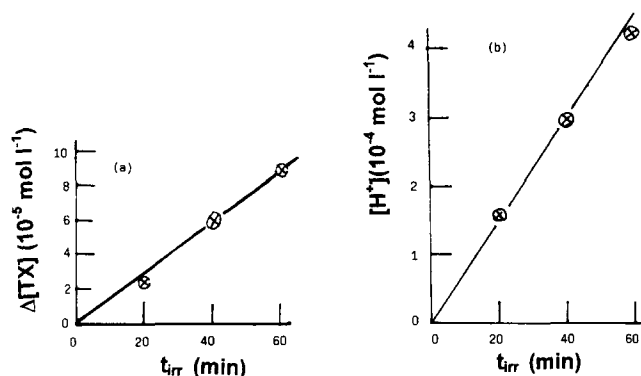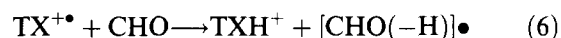
groups. Therefore, it is concluded that anthryl radical cations are not directly involved in the initiation of the polymerization of CHO. It is feasible that anthryl radical cations, instead of reacting with CHO molecules, undergo other reactions that alter the anthracene structure. Very likely they react with ethoxyl radicals formed by the decomposition of *N*-ethoxy pyridinium radicals. The latter are formed when electrons are transferred from excited anthracene molecules to EMP$^+$ ions. A reaction mechanism taking this into account is proposed in *Scheme 2*. Accordingly, cations generated by reaction (c) in *Scheme 2* are supposed to react with CHO in reaction (d). The latter reaction is the



**Figure 7** Irradiation of thioxanthone ($5.47 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$) in argon-saturated propylene carbonate solution containing EMP$^+$PF$_6^-$ ($3.1 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$) at $\lambda = 360\,\mathrm{nm}$ using a xenon lamp in conjunction with a monochromator, $Dr_{\mathrm{abs}} = 5.2 \times 10^{-5}$ einstein $\mathrm{l^{-1}\,min^{-1}}$. (a) Decrease in the TX concentration *versus* irradiation time. (b) Proton concentration *versus* irradiation time

initiation step of the cationic chain reaction leading to the formation of PCHO.
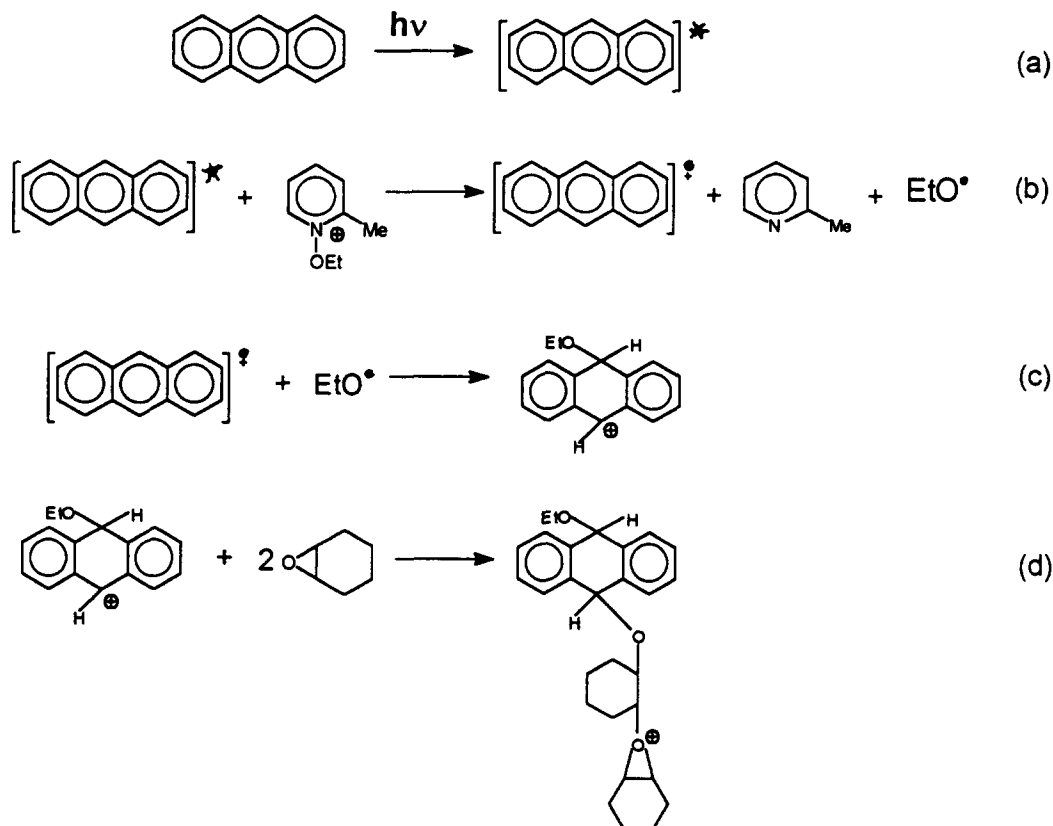
### Polymerization of CHO sensitized by thioxanthone

At the lower onium salt concentration ($6.8 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$) employed in this study, most of the thioxanthone triplets (93%) are deactivated via reaction (3) and also at the higher onium salt concentration ($6.8 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$) a large portion of the TX triplets (53%) reacts with CHO molecules. This implies that free radicals are formed. Moreover, the polymerization of CHO is suppressed by DBMP, a radical scavenger. Therefore, it is concluded that, in its absence, free radicals generated by reaction (3) react with EMP$^+$ ions and, in subsequent reactions, reactive ionic species capable of initiating the polymerization of CHO are formed. The fact that protons are generated with a rather high quantum yield suggests that, to a great extent, these species are protons. A mechanism taking this into account is presented in *Scheme 3*.

According to this mechanism ketyl radicals are oxidized by EMP$^+$ ions which gives rise to the formation of protons and the regeneration of thioxanthone. Evidence for the regeneration of thioxanthone comes from the fact that $\Phi(\mathrm{H^+})$ is about one order of magnitude larger than $\Phi(-\mathrm{TX})$. The consumption of TX is probably due to (not yet identified) addition of thioxanthone radical cations, TX$^{+\bullet}$, to CHO molecules, or to other (not yet detected) side reactions. Principally, the polymerization of CHO could also be initiated by a hydrogen abstraction reaction:

$$\mathrm{TX^{+\bullet} + CHO \longrightarrow TXH^+ + [CHO(-H)]\bullet} \qquad (6)$$
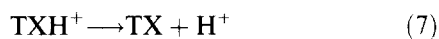


**Scheme 2** The action of anthracene as a photosensitizer for the initiation of the polymerization of CHO in conjunction with EMP$^+$PF$_6^-$
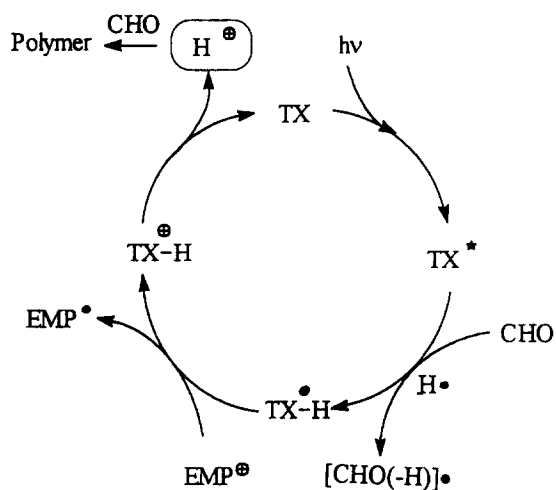
**Scheme 3** The action of thioxanthone as a photosensitizer for the initiation of the polymerization of CHO in conjunction with $EMP^+PF_6^-$

followed by:

$$TXH^+ \longrightarrow TX + H^+ \qquad (7)$$

This mechanism, which also involves the regeneration of TX, should apply when the probability for the formation of $TX^{+\bullet}$ is high, i.e. at high onium salt concentration. However, so far it has not yet been revealed whether it substantially contributes to the initiation of the polymerization of CHO. Since both onium ions and thioxanthone molecules are consumed during the polymerization, it becomes obvious why conversion–time curves bend over towards the abscissa at longer irradiation times.

## ACKNOWLEDGEMENT

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