

Thermally and photochemically induced cationic polymerization using 2-methyl-1-(2-phenyl-2-propenyloxy)-pyridinium salts as initiators

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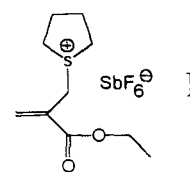
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2-Methyl-1-(2-phenyl-2-propenyloxy)-pyridinium hexafluoroantimonate (**III**) and hexafluorophosphate (**IV**) were synthesized. Their capability to act as initiator or coinitiator for the cationic polymerization of oxiranes and vinyl ethers was examined. Monomers under investigation were cyclohexene oxide (CHO), vinyl cyclohexene dioxide (VCHD), and n-butyl vinyl ether (nBVE). These monomers turned out to be polymerizable in the presence of **III** or **IV** provided free radicals are generated thermally at 80°C or photochemically at $\lambda > 360$ nm with the aid of appropriate radical sources, e.g. 2,2'-azobisisobutyronitrile, phenylazotriphenylmethane (PAT), and dibenzoyl peroxide (thermal radical sources) and benzoin, PAT and trimethylbenzoyl diphenylphosphine oxide (TMDPO) (photochemical radical sources). The polymerization of CHO is also induced in the absence of a free radical source at $\lambda = 300$ nm where **III** absorbs light and also thermally at 80°C, but here at a low rate. The latter process is very likely to be due to self-initiated free radical generation similar to that known for neat styrene. Regarding sources generating electrophilic free radicals the mode of action of **III** concerning the promotion of the cationic polymerization seems to be based on the addition-fragmentation mechanism. Accordingly, a free radical adds to the carbon-carbon double bond and fragmentation of the adduct radical results in the formation of a reactive onium radical cation. Evidence for the oxidation of nucleophilic radicals such as the triphenylmethyl radical by the onium ion was not obtained in this work. In conclusion, a wide range of radical sources can be employed in conjunction with onium salt **III** or **IV** to tune conditions (temperature and wavelength, respectively) for the cationic polymerization of various monomers. © 1997 Elsevier Science Ltd.

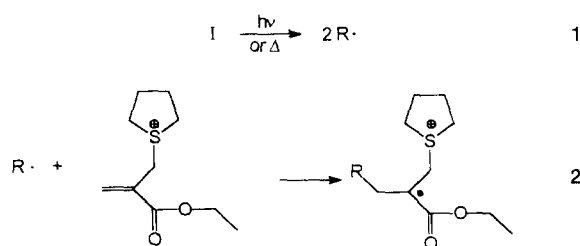
(Keywords: cationic polymerization; addition fragmentation; pyridinium salt initiators)

INTRODUCTION

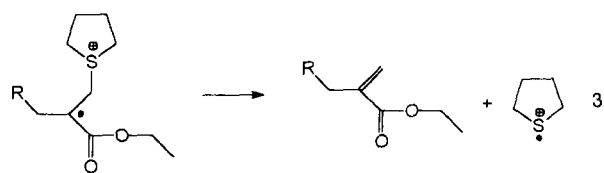
Cationic polymerizations¹ induced by thermally and photochemically latent onium type salts are of interest due to their industrial applications in coating, printing inks and resist technology. Diaryl iodonium^{2,3}, triaryl sulfonium⁴ N-alkoxy pyridinium salts⁵ are known as effective initiators for cationic polymerization of cyclic ethers and alkyl vinyl ethers. Regarding photochemical applications these salts can act directly provided they are light-absorbing. On the other hand, indirect action can become operative via the oxidation of photochemically or thermally generated free radicals by onium ions⁶. As was reported recently⁷ the allyl group containing sulfonium salt **I** can also be used to initiate cationic polymerizations. In this case two initiation mechanisms are feasible depending on the nucleophilicity of the free radical generated thermally or photochemically: (a) the addition-fragmentation mechanism and (b) the electron transfer (radical oxidation) mechanism. In the case of (a) radicals of low nucleophilicity add to the carbon-carbon



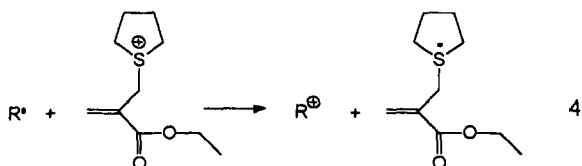
double bond. The subsequent decomposition of the adduct radical yields a reactive cation radical and a substituted ethyl methacrylate, as illustrated below:



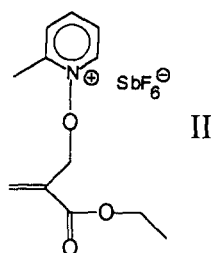
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In the case of (b) highly nucleophilic radicals are oxidized according to reaction (4). The resulting carbocations are capable of initiating cationic polymerizations.



In this connection it is also interesting to note that, recently, the pyridinium salt **II**, 1-(2-ethoxycarbonyl-2-propenyloxy)-2-methyl-pyridinium hexafluoroantimonate, having a structure similar to that of **I**, was found



capable of initiating cationic polymerizations⁸. In continuation of this work the present paper describes the synthesis of two other pyridinium salts, namely 2-methyl-1-(2-phenyl-2-propenyloxy)-pyridinium hexafluoroantimonate, **III**, and the corresponding hexafluorophosphate (**IV**), that possess a styrene instead of a methacrylate moiety. The utilization of **III** and **IV** as initiators or coinitiators for cationic polymerizations in conjunction with photochemically and thermally produced free radicals was examined with the aid of cyclohexene oxide (CHO), vinyl cyclohexene dioxide (VCHD), and n-butyl vinyl ether (nBVE). These compounds represent the only cationically polymerizable monomer families of oxiranes and alkyl vinyl ethers.

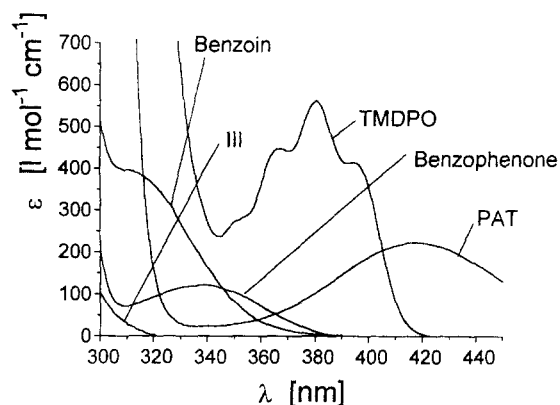
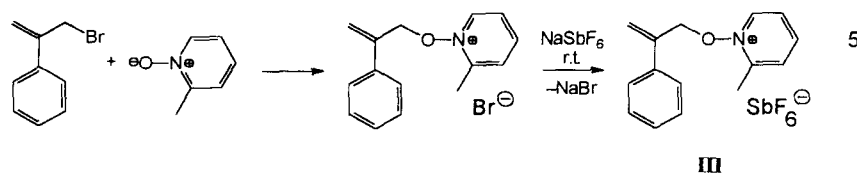
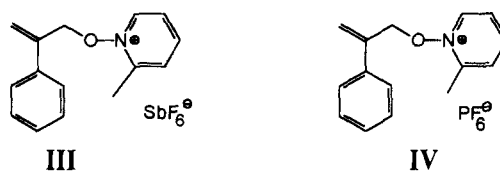


Figure 1 Optical absorption spectra of various compounds used in this work. The spectra were recorded at room temperature with acetonitrile solutions



EXPERIMENTAL

Materials

Cyclohexene oxide (CHO) (Aldrich) and n-butyl vinyl ether (nBVE) (Aldrich) were distilled from CaH_2 *in vacuo*. Vinyl cyclohexene dioxide (VCHD) (mixture of isomers, Fluka) was distilled *in vacuo*. Reagent-grade solvents were used after distillation. 2,2'-Azobisisobutyronitrile (AIBN) (Fluka) and benzoin (**B**) (Merck) were recrystallized from ethanol. Dibenzoyl peroxide (DBP) (Fluka) was recrystallized from diethyl ether. 2,4,6-Trimethylbenzoyl diphenylphosphine oxide (TMDPO) (BASF) was recrystallized from ethanol/diethyl ether. Phenylazotriphenylmethane (PAT) was prepared as described previously⁹. The absorption spectra of these compounds recorded in acetonitrile solution at ambient temperature are presented in Figure 1.

Synthesis of 2-methyl-1-(2-phenyl-2-propenyloxy)-pyridinium hexafluoroantimonate (**III**)

2-Phenyl-2-propenyl bromide (α -(bromomethyl)styrene, b.p. 67°C at 1.5 Torr) was prepared according to the prescription of Pines *et al.*¹⁰ by bromination of α -methylstyrene with N-bromosuccinimide. Subsequently, **III** was synthesized by the reaction of 2-phenyl-2-propenyl bromide with 2-picoline-N-oxide and the subsequent anion exchange, i.e. Br^- vs. SbF_6^- , (reaction (5)):

In detail, the mixture of 35 g (0.124 mol) 2-phenyl-2-propenyl bromide and 13.6 g (0.124 mol) 2-picoline-N-oxide in 30 ml dry acetonitrile was stirred at room temperature for 12 h. The white precipitate formed was filtered off, washed with dry diethyl ether and dried to afford 19.3 g (50%) 2-methyl-1-(2-phenyl-2-propenyl-oxy)-pyridinium bromide. The synthesis was completed by exchanging Br^- by SbF_6^- in the following way: 3 g (9.8 mmol) of the bromide were thoroughly mixed with 3 g (11.6 mmol) NaSbF_6 and water (100 ml) was added slowly. The mixture was stirred for 3 h at room temperature. The white precipitate formed was filtered off, washed with water and dried *in vacuo* at room temperature. Yield: 3.38 g (74%), m.p.: 115.6°C. The structure of **III** was confirmed both by spectroscopic measurements and by elemental analysis. The optical absorption spectrum of **III** recorded in acetonitrile solution possesses a band at $\lambda_{\text{max}} = 270 \text{ nm}$, $\epsilon_{\text{max}} = 5.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$, which is characteristic of pyridinium salts, e.g. 1-ethoxy-2-methyl pyridinium hexafluoroantimonate ($\lambda_{\text{max}} = 266 \text{ nm}$, $\epsilon_{\text{max}} = 5.93 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$). Elemental analysis: Found: C: 38.87; H: 3.43; N: 3.14; O: 3.62. Calculated: C: 38.99; H: 3.49; N: 3.03; O: 3.46. I.r. main bands (cm^{-1}): 3136, 3098, 1618, 1497, 1479, 1384, 925, 787, 714, 658. ^1H n.m.r. (d/acetone- d_6 ; ppm): 9.4–8.1 (Ar-pyridinium), 7.7–7.3 (Ar-phenyl), 6.0–5.6 ($\text{C}=\text{CH}_2$), 2.8, ($-\text{OCH}_2$), 2.1 ($-\text{CH}_3$). The reduction potential of **III** in aqueous 0.1 N HCl solution was determined by polarography: $E_{1/2} = -0.67 \text{ V}$ (SCE).

Attempts to react α (bromomethyl)-styrene with other N-oxides (isoquinolinium- and 4-phenylpyridinium-N-oxide) failed.

Synthesis of 2-methyl-1-(2-phenyl-2-propenyloxy)-pyridinium hexafluorophosphate (**IV**)

50 ml water was added slowly to a mixture of 1.5 g (4.9 mmol) 2-methyl-1-(2-phenyl-2-propenyloxy) pyridinium bromide and 0.9 g (5.3 mmol) NaPF_6 . The mixture was stirred for 3 h at room temperature and the white precipitate formed was filtered off, washed with water and dried *in vacuo* at room temperature. Yield: 1.6 g (88%), m.p.: 124.5°C. Elemental analysis: Found: C: 48.51; H: 4.18; N: 3.80; O: 4.57. Calculated: C: 48.53; H: 4.34; N: 3.77; O: 4.31. I.r. main bands (cm^{-1}): 3141, 3107, 1619, 1497, 1481, 1386, 928, 881, 834, 782, 710, 558.

Polymerizations

Thermal polymerization. Monomer solutions, in pyrex tubes, containing **III** and a radical source, were deaerated by bubbling with argon and immersed for a given time in an oil bath kept at constant temperature (60°C or 80°C). **III** and **IV** are insoluble in nBVE and, therefore, the polymerization was carried out in this case in propylene carbonate (PC) solution. Poly-(n-butyl vinyl ether) is insoluble in PC and, therefore, the polymer separated from the reaction mixture during the polymerization.

Photopolymerization. Monomer solutions, in quartz tubes, containing photoinitiator and **III** or **IV** were bubbled with argon and subsequently irradiated in a Rayonet photoreactor equipped with lamps emitting at nominally 300 nm or 350 nm. In the latter case a 360 nm cut-off filter was employed.

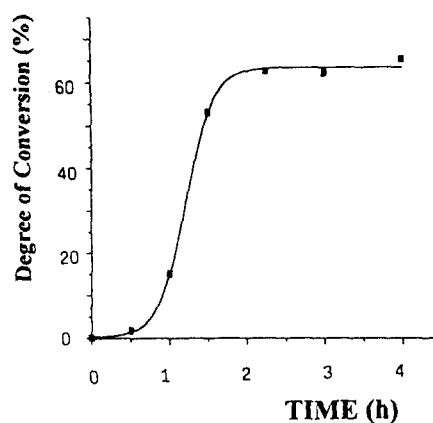


Figure 2 Thermal polymerization of CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) in the absence of a free radical source. $T = 80^\circ\text{C}$. Monomer conversion vs. time

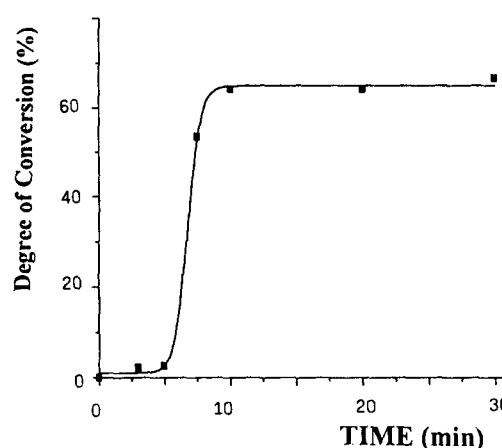


Figure 3 Thermal polymerization of CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) in the presence of a free radical source: DBP ($7.5 \times 10^{-3} \text{ mol l}^{-1}$). $T = 80^\circ\text{C}$. Monomer conversion vs. time

Polymer characterization

Polymers were obtained from the reaction mixture by precipitation with a ten-fold excess of methanol. Size exclusion chromatography (s.e.c.) analyses of the polymers were performed with a setup consisting of a pump and four ultrastyrigel columns of different porosities: 10^5 , 10^4 , 10^3 and 500 Å. THF was used as the eluent (flow rate: 1 ml min^{-1}) and the detection was carried out with the aid of a differential refractometer. The weight average molar mass M_w was calculated with the aid of a calibration curve obtained with polystyrene standards. In certain cases M_w was determined with the aid of the light scattering method using ethyl acetate/n-hexane (23/77, v/v) as solvent, $dn/dc = 0.138 \text{ ml g}^{-1}$. U.v. absorption spectra were recorded with a Shimadzu UV-VIS spectrophotometer (model UV-2101 PC). I.r. spectra were recorded with a Bio-Rad spectrometer (model FTS-7 IR). ^1H n.m.r. measurements were performed in acetone- d_6 solutions using a Bruker 200 MHz instrument.

RESULTS

Thermal polymerization of CHO

Polymerization in the absence of a free radical source. CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) is rather stable

Table 1 Thermal polymerization of bulk CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$)

Temperature (°C)	Radical source (mol l^{-1})	Time (min)	Conversion (%)	M_w^a (g mol^{-1})
60	—	60	0.7	
60	AIBN, 7.5×10^{-3}	60	2.7	
60	PAT, 7.5×10^{-3}	30	79.5	1.0×10^4 (1.5×10^4) ^b
80	—	30	1.8	
80	DBP, 7.5×10^{-3}	10	63.9	3.7×10^3

^a Determined by s.e.c. with the aid of polystyrene standards

^b Determined with aid of the light scattering method

Table 2 Thermal polymerization of bulk VCHD containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$)

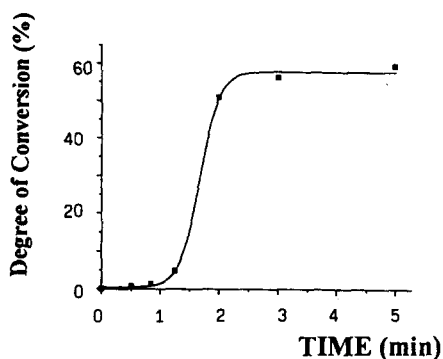
Temperature (°C)	Radical source (mol l^{-1})	Time (min)	Conversion (%)
60	—	150	0.4
60	PAT, 7.5×10^{-3}	15	c. 100 ^a
80	—	120	28.8
80	DBP, 7.5×10^{-3}	25	c. 100 ^a

^a Sample totally gelled

Table 3 Thermal polymerization of nBVE in propylene carbonate solution containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$). $[\text{n-BVE}] = 5.2 \text{ mol l}^{-1}$

Temperature (°C)	Radical source (mol l^{-1})	Time (min)	Conversion (%)	M_w^a (g mol^{-1})
60	—	30	0.0	
60	PAT, 7.5×10^{-3}	30	52.0	1.1×10^4
80	—	30	0.0	
80	DBP, 7.5×10^{-3}	10	35.7	1.0×10^4

^a Determined by s.e.c. with the aid of polystyrene standards


Figure 4 Photopolymerization of CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) in the absence of a free radical source at room temperature. $\lambda_{\text{inc}} = 300 \text{ nm}$. Monomer conversion vs. time of irradiation

at temperatures up to 60°C , but polymerizes at higher temperatures. As can be seen from the conversion–time profile recorded at 80°C (Figure 2) the monomer conversion commences after an induction period of about 30 min and, after passing through a time regime of fast increase, approaches a limiting value of about 65%.

Polymerization in the presence of a free radical source. In the presence of a free radical source (PAT or DBP) the polymerization rate is strongly accelerated and the limiting conversion is achieved within a few minutes. Figure 3 shows a conversion–time profile

recorded at 80°C with CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) and DBP ($7.5 \times 10^{-3} \text{ mol l}^{-1}$). The induction period, observed also in this case, might be indicative of a very reactive impurity that prevents propagation until it is totally consumed. The accelerating effect of compounds decomposing thermally into free radicals is demonstrated by the results compiled in Table 1, where it is seen that, contrary to AIBN, PAT becomes effective already at 60°C because it decomposes significantly already at this temperature.

Thermal polymerization of VCHD

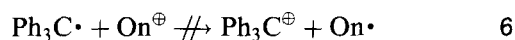
The bifunctional monomer VCHD exhibits a behavior similar to that of CHO. VCHD containing **III** is converted slowly, but significantly, at 80°C and very slowly at 60°C if a free radical source is absent. However, in the presence of PAT or DBP the polymerization is accelerated and proceeds rather fast. Typical results are compiled in Table 2. Because of its bifunctionality the polymerization of VCHD renders an insoluble three-dimensionally crosslinked polymeric product.

Thermal polymerization of nBVE

nBVE, a typical vinyl ether monomer, does not dissolve **III**. Therefore, polymerizability tests were performed with the aid of propylene carbonate solutions containing **III** and 5.2 mol l^{-1} nBVE. Table 3 presents typical results. In the absence of a free radical source nBVE containing **III** is not converted at all at 60°C or 80°C . Again, the addition of PAT and or DBP causes monomer conversion resulting in a polymer of $M_w \approx 10^4 \text{ g mol}^{-1}$.

Reaction of PAT with cations of III

Upon heating a solution containing PAT ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) and **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) for 60 min at 60°C the optical absorption spectrum changed: Notably, the new spectrum does not contain new bands around 420 nm and 450 nm, where characteristic absorption bands of trityl cations are located, but a new band with a maximum at about 370 nm. This implies that PAT undergoes thermolysis. But the trityl radicals generated in this way do not react with cations of **III** according to reaction (6):



Photopolymerization of CHO

Polymerization in the absence of a free radical source. Irradiation of CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at $\lambda_{\text{inc}} = 300 \text{ nm}$ (where **III** absorbs light) results in rapid polymerization. As can be seen from Figure 4 the conversion–time profile is S-shaped: a pronounced increase in monomer conversion sets in after an induction period (about 1 min) and the limiting conversion of about 58% is reached in less than 3 min after the irradiation was started. Obviously, **III** is an effective photoinitiator for the polymerization of CHO and in this respect resembles N-ethoxy pyridinium salts that have been investigated earlier⁵.

Polymerization in the presence of a free radical source. No polymer is formed when CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) is irradiated at $\lambda_{\text{inc}} > 360 \text{ nm}$, where **III** is transparent. However, the polymerization of CHO is induced upon the addition of a compound acting as a

free radical source, i.e. decomposing into free radicals upon irradiation at $\lambda_{\text{inc}} > 360 \text{ nm}$. Benzoin is such a compound. It decomposes spontaneously into benzoyl and hydroxybenzyl radicals after absorption of a photon:

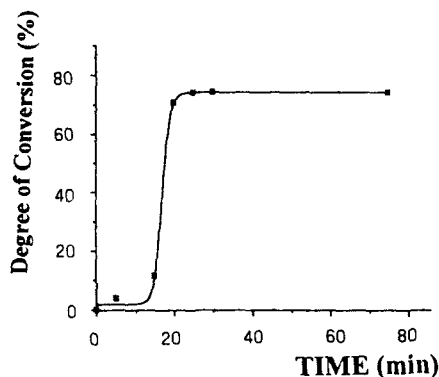
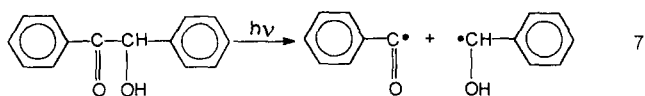


Figure 5 Photopolymerization of CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) in the presence of a free radical source: benzoin ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at room temperature. $\lambda_{\text{inc}} > 360 \text{ nm}$. Monomer conversion vs. time of irradiation

Table 4 Photopolymerization of bulk CHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at ambient temperature. $\lambda_{\text{inc}} > 360 \text{ nm}$

Radical source ^a	Time (min)	Conversion (%)	M_w^b (g mol ⁻¹)	M_w^c (g mol ⁻¹)
None	90	0		
PAT	90	53.7	8.0×10^3	1.4×10^4
TMDPO	90	18.4	5.3×10^3	
Benzoin	30	74.3	4.3×10^3	
Benzophenone	30	78.8	8.4×10^3	

^a Concentration: $7.5 \times 10^{-3} \text{ mol l}^{-1}$

^b Determined by s.e.c. with the aid of polystyrene standards

^c Determined with the aid of the light scattering method

Table 5 Photopolymerization of VCHD containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at ambient temperature. $\lambda_{\text{inc}} > 360 \text{ nm}$

[Benzoin] (mol l ⁻¹)	Time (min)	Conversion (%)
0	60	0
7.5×10^{-3}	15	c. 100 ^a

^a Sample totally gelled

Table 6 Photopolymerization of nBVE (5.2 mol l^{-1}) in propylene carbonate solution containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at ambient temperature. $\lambda_{\text{inc}} > 360 \text{ nm}$

[Benzoin] (mol l ⁻¹)	Time (min)	Conversion (%)	M_w^a (g mol ⁻¹)
0	180	0	—
7.5×10^{-3}	70	35.8	1.1×10^4

^a Determined by s.e.c. with the aid of polystyrene standards

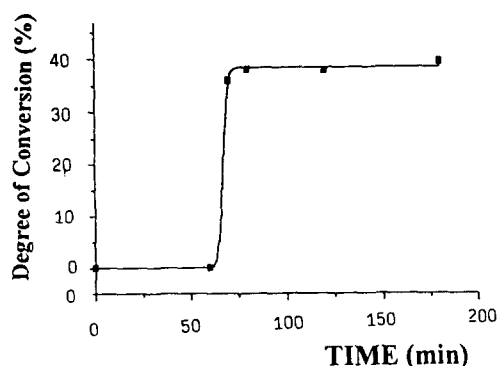


Figure 6 Photopolymerization of nBVE (5.2 mol l^{-1}) in propylene carbonate solution containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) in the presence of a free radical source: benzoin ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at room temperature. $\lambda_{\text{inc}} > 360 \text{ nm}$. Monomer conversion vs. time of irradiation

According to the time-conversion profile shown in *Figure 5* the polymerization sets in after an induction period of about 16 min after the start of the irradiation and the limiting conversion of about 74% (somewhat higher than in the experiment described in the previous section) is reached about 3 min later. Other compounds known to be fragmented into free radicals by u.v. light, i.e. PAT and TMDPO were also examined. They are also appropriate to act as initiators for the polymerization of CHO in conjunction with **III** (see *Table 4*). Notably, PAT and TMDP are less effective than benzoin under the chosen conditions. This might be due to differences in light absorption, quantum yield and reactivity of the free radicals towards **III**. Notably, benzophenone that does not decompose spontaneously after light absorption, is also capable of inducing the polymerization of CHO in conjunction with **III**. Formation of free radicals via hydrogen abstraction from the monomer is the most likely mode of action in this case, whereas, for energetic reasons, energy or electron transfer from electronically excited benzophenone to the onium ion are quite improbable processes.

Photopolymerization of VCHO

No polymer was formed upon irradiation of VCHO containing **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at $\lambda_{\text{inc}} > 360 \text{ nm}$. However, when benzoin was added ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) VCHO polymerized and total gelation was achieved after 15 min (see *Table 5*).

Photopolymerization of nBVE

No polymer was generated upon irradiation of a propylene carbonate solution containing nBVE (5.2 mol l^{-1}) and **III** ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) at $\lambda_{\text{inc}} > 360 \text{ nm}$. However, poly(n-butyl vinyl ether) of average molar mass 1.1×10^4 was formed upon irradiation of a propylene carbonate solution containing apart from nBVE and **III** also benzoin ($7.5 \times 10^{-3} \text{ mol l}^{-1}$). Typical results are presented in *Table 6* and *Figure 6*.

On the reactivity of **III** and **IV**

Results obtained from experiments performed with monomer systems containing CHO and either **III** or **IV** are shown in *Table 7*. Obviously, the phosphate **IV** is less effective an initiator or coinitiator than the antimonate **III**. This holds both for the photopolymerization induced at $\lambda_{\text{inc}} = 300 \text{ nm}$ (direct effect) or at $\lambda_{\text{inc}} > 360 \text{ nm}$ (indirect effect) and for the thermal polymerization.

Table 7 The initiator efficiency of the onium salts **III** and **IV** in the thermally and photochemically induced polymerization of bulk CHO

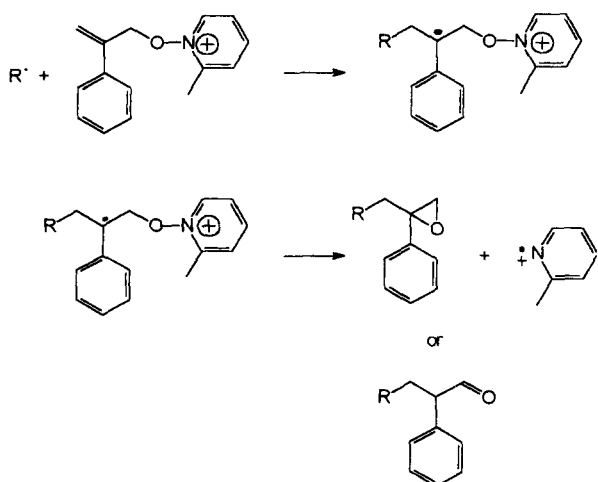
Onium salt	Conditions	Radical source (mol ⁻¹)	Time (min)	Conversion (%)
III	λ = 300 nm	None	3	56.2
IV	λ = 300 nm	None	3	16.8
III	λ > 360 nm	Benzoin 7.5 × 10 ⁻³	20	72.9
IV	λ > 360 nm	Benzoin 7.5 × 10 ⁻³	20	11.7
III	T = 60°C	PAT 7.5 × 10 ⁻³	30	79.5
IV	T = 60°C	PAT 7.5 × 10 ⁻³	30	6.6
III	T = 80°C	BP 7.5 × 10 ⁻³	7	47.8
IV	T = 80°C	BP 7.5 × 10 ⁻³	7	2.2

DISCUSSION

Thermal polymerization in the presence of a free radical source

The results reported in this paper demonstrate that the thermal initiation of the cationic polymerization of CHO, VCHD and nBVE is accelerated or promoted provided onium salt **III** or **IV** and, in addition, a compound decomposing into free radicals upon heating are present. As discussed in the Introduction, with respect to the salts **I** and **II**, two mechanisms for the initiation of the polymerization are also feasible: (a) the addition-fragmentation mechanism and (b) the electron transfer mechanism. In the present case it is unlikely that mechanism (b) contributes essentially to the initiation. In the case of the thermolysis of PAT in the presence of **III** the formation of trityl cations was not detected and, therefore, the possibility of a reaction of trityl radicals with cations of **III** is to be discarded. Moreover, free radicals generated from AIBN and DBP, i.e. (CH₃)₂(CN)C•, PhCOO• and Ph• are non-nucleophilic and, therefore, unreactive towards cations of **III**.

Therefore, it appears that the initiation is predominantly based on the addition-fragmentation mechanism. Accordingly, radicals generated by the thermolysis of the initiator are supposed to add to the allylic double bond of **III** or **IV**, respectively. The subsequent

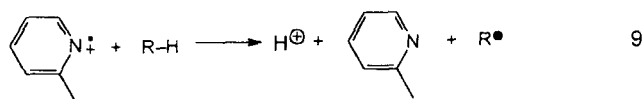

Scheme 1 Addition of free radical R• to the cation of **III** or **IV** and spontaneous decomposition of the adduct radical

spontaneous decomposition of the adduct radical yields pyridinium radical cations as illustrated by *Scheme 1*.

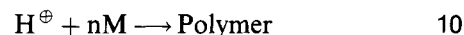
The pyridinium radical cation may directly initiate the cationic polymerization of monomer M:



Alternatively, protons can be formed when the radical cation abstracts hydrogen from the solvent or the monomer:



Protons generated in this way may then initiate the polymerization of M:

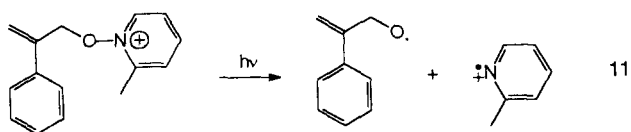


Thermal polymerization in the absence of a free radical source

Obviously, the polymerization of CHO, though at a very low rate, is induced by heating CHO containing **III** in the absence of an additional radical forming compound to 60°C or 80°C. In discussing the mechanism of this process it can be anticipated that the initiation is not due to the breakage of the N–O bond, because of its high thermal stability. By contrast, the styrene moiety in the onium salts under investigation is likely to undergo a purely thermal radical generating process and the radicals formed in this way undergo cation generating reactions by mechanisms (a) and/or (b). The mechanism of the radical generating process (and the identity of the radicals) might be quite similar to that discussed for the thermal self-initiated polymerization of styrene. Notably, aspects of thermal self-initiated polymerization have been reviewed recently in the book of Moad and Solomon¹² and should not be an object of this paper. In this connection it is noticeable that purely thermal homopolymerization has also been unequivocally demonstrated for methyl methacrylate (MMA)¹² and it is interesting to point out that onium salt **II** which contains the MMA moiety can also initiate the polymerization of CHO at elevated temperatures in the absence of a radical source⁸.

Photopolymerization in the absence of a free radical source

Onium salt **III** is quite effective an initiator of the cationic polymerization of CHO upon irradiation at 300 nm where it is light-absorbing. The initiation is assumed to proceed by direct action of light, i.e. pyridinium radical cations are generated via homolytic scission of the N–O bond as proposed and evidenced for simple N-alkoxy-pyridinium salts⁵.

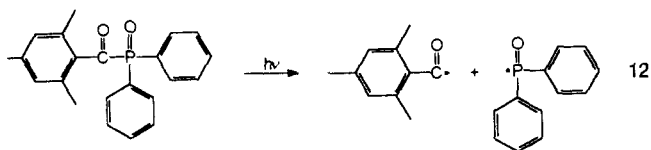


Further steps of the initiation mechanism involve reactions (8) and/or (9) (*vide ante*).

Photopolymerization in the presence of a free radical source

Regarding the photoinitiation at wavelengths where the onium salts are transparent, i.e. at $\lambda > 360$ nm light-absorbing free radical sources are afforded. Principally, both mechanisms (a) and (b) can be considered applicable for the reaction of free radicals with the cation of **III** and **IV**.

However, in certain cases quite electrophilic radicals are formed and electron transfer from the radical to the onium ion is extremely unlikely. This applies, for instance, to electrophilic radicals of the benzoyl and the phosphinoyl type, respectively, generated by the photolysis of TMDPO¹³.



Neither of these radicals reacts with Ph_2I^+ ions or onium ions having a redox potential lower (more negative) than that of Ph_2I^+ ions ($E_{1/2} = -0.2$ V, SCE)¹⁴. Notably, $E_{1/2} = -0.67$ V, SCE, was found for the cation of **III** in this work. In conclusion, regarding electrophilic radicals the observed initiation of cationic polymerization is very likely to be based on the addition-fragmentation mechanism.

CONCLUSION

From the results presented above it is concluded that the initiation of the cationic polymerization of CHO, VCHD and nBVE with the aid of initiator systems consisting of **III** or **IV** and a radical source producing electrophilic radicals is possible. In this case the generation of reactive cations occurs via the addition-fragmentation mechanism. It can, therefore, also be concluded that a wide range of thermal and photochemical free radical sources can be employed to tune the conditions (temperature and wavelength, respectively) for the cationic polymerization of various monomers.

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