Initiation of cationic polymerization via oxidation of free radicals using pyridinium salts

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Pyridinium ions of appropriate reduction potential $E_{1/2}^{\rm red}$ are capable of oxidizing carbon-centred free radicals to carbocations that can initiate the polymerization of various compounds. 1-Ethoxy-2-methyl pyridinium ions of $E_{1/2}^{\rm red} = -0.7$ V were found to react with free radicals generated by (a) photolysis or (b) thermolysis of various compounds. Radical generation was achieved in case (a) with benzoinmethylether, diphenyl-2,4,6-trimethylbenzoylphosphine oxide or benzophenone/tetrahydrofuran (BP/THF) and in case (b) with phenylazotriphenylmethane, BP/THF, benzoylperoxide/THF or 2,2-azobisisobutyronitrile/THF. The following monomers were polymerized: 1,2-epoxycyclohexane (cyclohexene oxide) and n-butylvinyl ether.

(Keywords: pyridinium salts; photoinitiated cationic polymerization; oxidation of radicals)

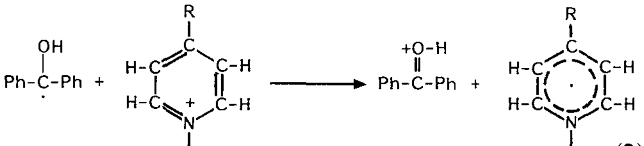
INTRODUCTION

An elegant method of generating carbocations capable of initiating the cationic polymerization of compounds such as epoxides, cyclic ethers and alkyl vinyl ethers is based on electron transfer from free radicals to onium salts according to the reaction[1–3]

$$R^{\cdot} + On^{+} \rightarrow R^{+} + On^{\cdot} \qquad (1)$$

Electron-rich free radicals capable of undergoing reaction (1) can be conveniently generated by photolysis or thermolysis of appropriate compounds. Among the onium salts that have been used successfully to initiate cationic polymerizations are diazonium salts, e.g. *p*-chlorophenyldiazonium hexafluorophosphate, $Cl–C_6H_4–N_2^+PF_6^-$, and iodonium salts, e.g. diphenyliodonium hexafluorophosphate, $Ph_2I^+PF_6^-$. Notably, reduction potentials of appropriate onium salts must be relatively low.

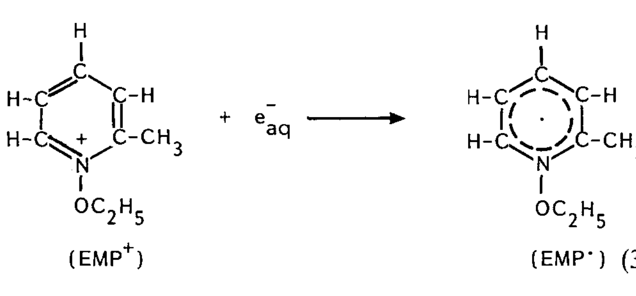
This paper deals with the possibility of applying pyridinium salts as agents for the oxidation of carbon-centred free radicals according to reaction (1). The role of iminium cations as electron acceptors was treated recently by Mariano[4] in a review article. This author also discussed the possibility of pyridinium ions being reduced by diphenylhydroxymethyl radicals which can be generated, for example, by reaction of benzophenone triplet with a hydrogen donor:



(2)

In the present work the 1-ethoxy-2-methylpyridinium ion (EMP$^+$) was examined with respect to its oxidizing power towards carbon-centred free radicals. It will be shown below that carbocations formed with the aid of EMP$^+$ are capable of initiating the polymerization of cyclohexene oxide and n-butylvinylether.

In previous work the reduction of EMP$^+$ by hydrated electrons or formate radical anions was investigated[5]:



(3)

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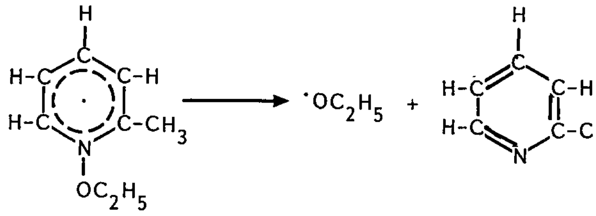
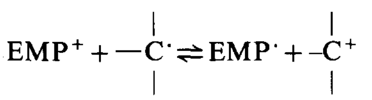
It turned out that the pyridinyl radical formed in this case was very short-lived. Its decomposition according to the following reaction appeared to be very probable:



(4)

On this basis, EMP^+ was expected to be appropriate for the generation of carbocations via reaction with carbon-centred free radicals, because the occurrence of back reactions in the following process can be excluded:



$$EMP^+ + \text{—}\overset{|}{\underset{|}{C}}{}^{\cdot} \rightleftharpoons EMP^{\cdot} + \text{—}\overset{|}{\underset{|}{C}}{}^{+} \qquad (5)$$

In connection with this paper we refer to the work of Uno and Endo[6], who reported on the thermal polymerization of 1-phenyl-4-ethyl-2,6,7-trioxabicyclo-2,2,2-octane. The initiator used was *p*-chlorobenzyl-*p*-cyanopyridinium hexafluoroantimonate, which was supposed to form benzyl cations upon thermally reacting with the monomer.

EXPERIMENTAL

Materials

Monomers and solvents. Tetrahydrofuran (THF), from Aldrich, was stored over NaOH for 24 h, filtered and distilled from CaH_2. Subsequently, it was refluxed with Na under nitrogen and distilled. 1,2-Epoxycyclohexane (cyclohexene oxide, CHO), from Aldrich, was distilled from CaH_2 (b.p. 38°C at 53 mbar = 5.3 kPa). n-Butylvinyl ether, from EGA, was washed with aqueous NaOH solution (10%) and water. After drying with $CaCl_2$ and Na_2SO_4 it was distilled from CaH_2 at 94°C. Dichloromethane, from Aldrich, was treated with concentrated H_2SO_4, washed with Na_2CO_3 solution (5%) and water. Subsequently, it was dried with $CaCl_2$ and refluxed and distilled from P_2O_5.

Initiators. 1-Ethoxy-2-methylpyridiniumhexafluorophosphate ($EMP^+PF_6^-$) was prepared according to a procedure described by Reichardt[7]. Benzoinmethylether (BME), from Aldrich, was recrystallized from ether/petrol ether. Benzophenone (BP), from E. Merck, was recrystallized from n-heptane. Diphenyl-2,4,6-trimethylbenzoylphosphine oxide (TMDPO) and dimethoxy-2,6-dimethoxybenzoyl phosphine oxide (DMPME), both from BASF, were recrystallized from diethylether. Benzoylperoxide (BPO), from Fluka, was recrystallized from diethylether. 2,2-Azobisisobutyronitrile (AIBN), from Fluka, was recrystallized from ethanol. Phenylazotriphenylmethane (PAT) was prepared according to a procedure described by Otsu and Tazaki[8]. It was recrystallized from dichloromethane/ethanol.

Polymerization

Photopolymerization. Solutions of monomer, pyridinium salt and initiator were prepared separately. Appropriate amounts of the solutions were transferred to a rectangular quartz tube. The mixture was bubbled with argon before irradiation with a xenon lamp equipped with a monochromator.

Thermal polymerization. Solutions of monomer, pyridinium salt and initiator were mixed in Pyrex tubes (20 × 1.5 cm) that were closed with a Teflon stopcock after bubbling with argon. For reaction, the tubes were immersed for a given time into an oil bath which was kept at 70°C.

Characterization of polymers. The polymers, i.e. poly(cyclohexene oxide), PCHO, and poly(n-butylvinyl ether), PBVE, were obtained from the reaction mixture by precipitation with methanol. In the case of PBVE the polymer was separated by filtration at −70°C. The weight average molecular weight was determined by light scattering measurements ($\lambda_{obs} = 632$ nm) using a low angle light scattering photometer (KMX-6, Chromatix). Ethylacetate/n-hexane (23:77, v/v, $dn/dc = 0.138$ ml g^{-1}) and methylethylketone ($dn/dc = 0.077$ ml g^{-1}) served as solvents for PCHO and PVBE, respectively.

RESULTS

Reactions of radicals generated by photolysis

Figure 1 shows optical absorption spectra of $EMP^+PF_6^-$ and benzoinmethylether (BME). Since the pyridinium

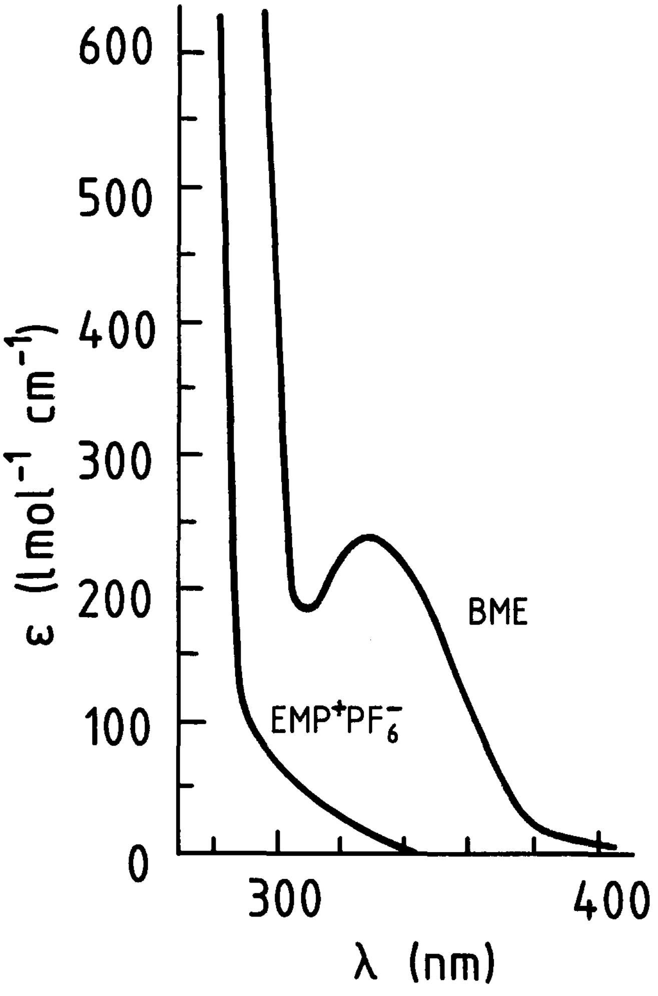


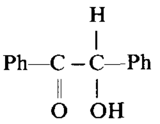
Figure 1 Optical absorption spectra recorded in dichloromethane at room temperature for $EMP^+PF_6^-$ and BME

Table 1 Photopolymerization of cyclohexene oxide in Ar-saturated dichloromethane solution containing 1-ethoxy-2-methylpyridinium hexafluorophosphate (5×10^{-3} mol l^{-1}) and a free radical initiator (irradiation time: 4 h)

Free radical source				
Initiator	Concentration (mol l^{-1})	λ_{inc} (m)	Conversion (%)	M_w[a]
BME[b]	6×10^{-3}	345	72.2	≈25 000
DMPME[c]	5×10^{-3}	348	4.5	
BP/THF[d]	5×10^{-3}	340	52	
TMPDO/THF[e]	5×10^{-3}	379	10	

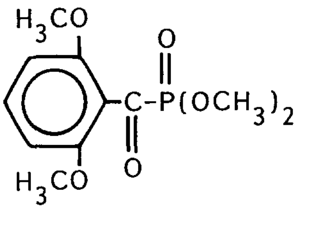
[a] Weight average molecular weight, determined by light scattering measurements

[b] BME: benzoinmethylether,

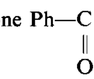


$$\mathrm{Ph{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{{-}Ph}$$

[c] DMPME: dimethoxy-2,6-dimethoxybenzoyl phosphine oxide



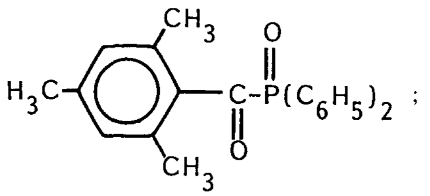
[d] BP: benzophenone



$$\mathrm{Ph{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}Ph}$$

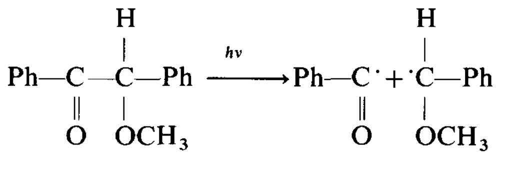
; [THF] = 6×10^{-3} mol l^{-1}

[e] TMDPO: diphenyl-2,4,6-trimethylbenzoylphosphine oxide



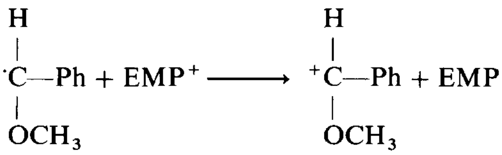
[THF] = 6×10^{-3} mol l^{-1}

salt does not absorb at $\lambda > 340$ nm all irradiations were performed at $\lambda_{inc} \geq 340$ nm. As can be seen from *Table 1* cyclohexene oxide (CHO) was polymerized quite effectively with BME as free radical source. Upon absorption of ultraviolet (u.v.) light this compound is photolysed according to the reaction:



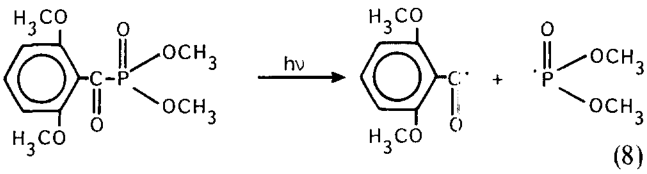
$$\mathrm{Ph{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{OCH_3}}{|}}{\mathrm{C}}}\mathrm{{-}Ph} \xrightarrow{h\nu} \mathrm{Ph{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}{}^{\cdot} + {}^{\cdot}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{OCH_3}}{|}}{\mathrm{C}}}\mathrm{{-}Ph} \quad (6)$$

It is assumed that in the system under consideration the methoxyphenylmethyl radical acts as a powerful reducing agent:

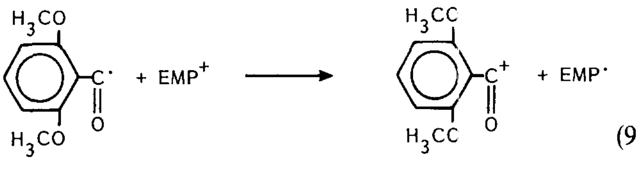


$${}^{\cdot}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{OCH_3}}{|}}{\mathrm{C}}}\mathrm{{-}Ph} + \mathrm{EMP^{+}} \longrightarrow {}^{+}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{OCH_3}}{|}}{\mathrm{C}}}\mathrm{{-}Ph} + \mathrm{EMP^{\cdot}} \quad (7)$$

As shown in *Figure 2* the polymerization started after a certain induction time and then increased almost linearly with time. The induction time is probably due to the presence of an impurity which reacted with the carbocations generated in the initial stage. Also, in the presence of dimethoxy-2,6-dimethoxybenzoylphosphine oxide (DMPME) cyclohexene oxide polymerized upon irradiation. It is assumed that 2,6-dimethoxybenzoyl radicals, formed by photolysis of DMPME according to reaction (8), are capable of reducing EMP^+:



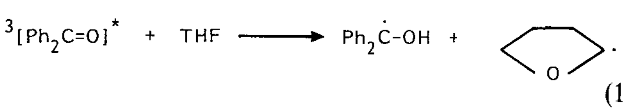
(8)



(9)

Benzophenone (BP) and diphenyl-2,4,6-trimethylbenzoyl phosphine oxide (TMDPO) acted as a free radical source for the reduction of EMP^+ if irradiated in the presence of tetrahydrofuran (THF). Typical results concerning the polymerization of CHO initiated by these systems are also presented in *Table 1*. Initiation of the cationic polymerization, in the case of BP, is envisaged on the basis of the following reaction sequence:

$$\mathrm{Ph_2C{=}O} + h\nu \longrightarrow {}^{1}[\mathrm{Ph_2C{=}O}]^{*} \longrightarrow {}^{3}[\mathrm{Ph_2C{=}O}]^{*} \quad (10)$$



(11)

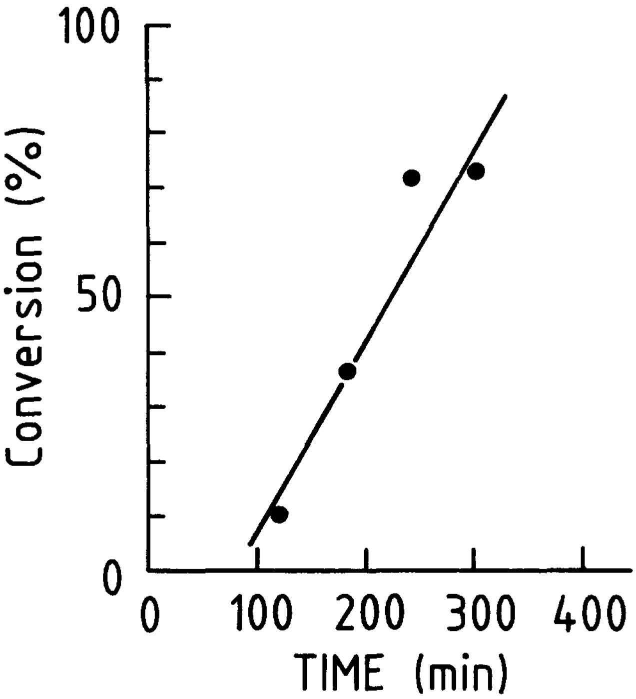
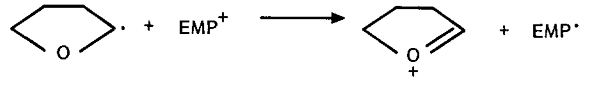


Figure 2 Photopolymerization of cyclohexene oxide in Ar-saturated dichloromethane solution at room temperature: [CHO] = 5.76 mol l^{-1}; [BME] = 5×10^{-3} mol l^{-1}; [$EMP^+PF_6^-$] = 5×10^{-3} mol l^{-1}; λ_{inc} = 345 nm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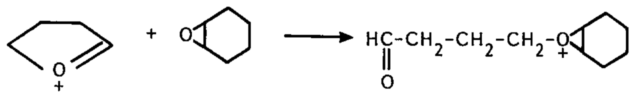

(13)

In principle, a reaction of cyclohexene oxide with benzophenone triplets analogous to reaction (11) is possible. However, CHO is much less reactive towards BP triplets than THF. In the present work, this was inferred from the fact that polymer was not formed when a CHO solution containing $EMP^+PF_6^-$ and BP but no THF was irradiated with u.v. light.

Reactions of radicals generated by thermolysis

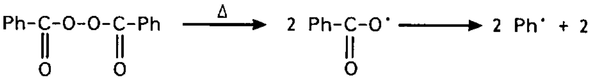
Polymerization of cyclohexene oxide (CHO). Upon thermal decomposition of two azo compounds and one peroxide in dichloromethane solutions containing CHO ($5.76\ mol\ l^{-1}$) and EMP^+ ($5 \times 10^{-3}\ mol\ l^{-1}$) a significant CHO conversion to polymer was observed only in the case of phenylazotriphenylmethane (PAT), as can be seen from *Table 2*. The thermolysis of PAT yields phenyl and triphenylmethyl radicals according to

$$Ph{-}N{=}N{-}C(Ph)_3 \xrightarrow{\Delta} Ph^{\cdot} + N_2 + {}^{\cdot}C(Ph)_3 \quad (14)$$

The triphenylmethyl radical is probably oxidized by EMP^+:

$$Ph_3C^{\cdot} + EMP^+ \longrightarrow Ph_3C^+ + EMP^{\cdot} \quad (15)$$

The ensuing carbocation is capable of initiating the polymerization of CHO. Radicals originating from the thermolysis of benzoylperoxide (BPO) and 2,2-azoisobutyronitrile (AIBN) are unreactive towards EMP^+. As can be seen also from *Table 2*, quite high polymer yields were obtained with solutions containing a small amount of tetrahydrofuran in addition to BPO or AIBN. This result is explained on the basis of the following mechanism: free radicals formed by thermolysis according to reactions (14) or (16) abstract hydrogens from THF as depicted by reaction (17):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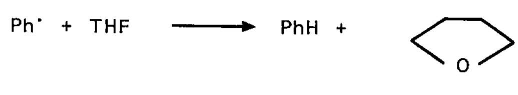

(17)

THF radicals formed this way can react according to reaction (12).

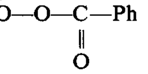
Table 2 Polymerization of cyclohexene oxide (CHO) in dichloromethane solution initiated by thermal decomposition (at 70°C) of free radical initiators in the presence of 1-ethoxy-2-methyl-pyridinium hexafluorophosphate ($5 \times 10^{-3}\ mol\ l^{-1}$) (reaction time: 4 h; [CHO] = $5.76\ mol\ l^{-1}$)

Free radical source				
Initiator	Concentration ($mol\ l^{-1}$)	[THF] ($mol\ l^{-1}$)	Conversion (%)	M_w[a]
PAT[b]	5×10^{-3}	-	14.6	
BPO[c]	5×10^{-3}	-	<1	
BPO	5×10^{-3}	5×10^{-3}	6.8	≈20000
AIBN[d]	5×10^{-3}		<1	
AIBN	5×10^{-3}	5×10^{-3}	11.8	

[a] Weight average molecular weight, determined by light scattering measurements

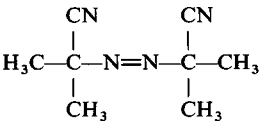
[b] Phenylazotriphenylmethane, $Ph{-}N{=}N{-}C(Ph)_3$

[c] Benzoylperoxide,



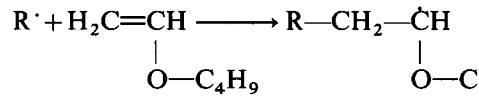
$Ph{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}O{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}Ph$

[d] 2,2-Azoisobutyronitrile,



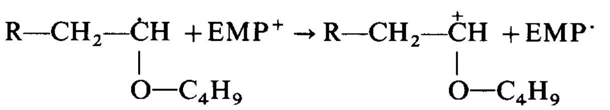
$H_3C{-}\overset{\displaystyle CN}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}N{=}N{-}\overset{\displaystyle CN}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3$

Polymerization of n-butylvinylether (nBVE). nBVE polymerizes only by a cationic mechanism. However, it undergoes an addition reaction quite readily with many free radicals:



$$R^{\cdot} + H_2C{=}\underset{\displaystyle O{-}C_4H_9}{\underset{|}{CH}} \longrightarrow R{-}CH_2{-}\underset{\displaystyle O{-}C_4H_9}{\underset{|}{\dot{C}H}} \quad (18)$$

nBVE was polymerized to quite high yields when heated to 70°C in the presence of $EMP^+PF_6^-$ and AIBN, BPO or PAT. This can be seen from *Figure 3* where the monomer conversion is plotted *versus* the reaction time. The weight average molecular weight of the polymers was ≈14 000. These results are explained in terms of free radicals generated according to reaction (18) being capable of reacting with EMP^+:



$$R{-}CH_2{-}\underset{\displaystyle O{-}C_4H_9}{\underset{|}{\dot{C}H}} + EMP^+ \rightarrow R{-}CH_2{-}\underset{\displaystyle O{-}C_4H_9}{\underset{|}{\overset{+}{C}H}} + EMP^{\cdot} \quad (19)$$

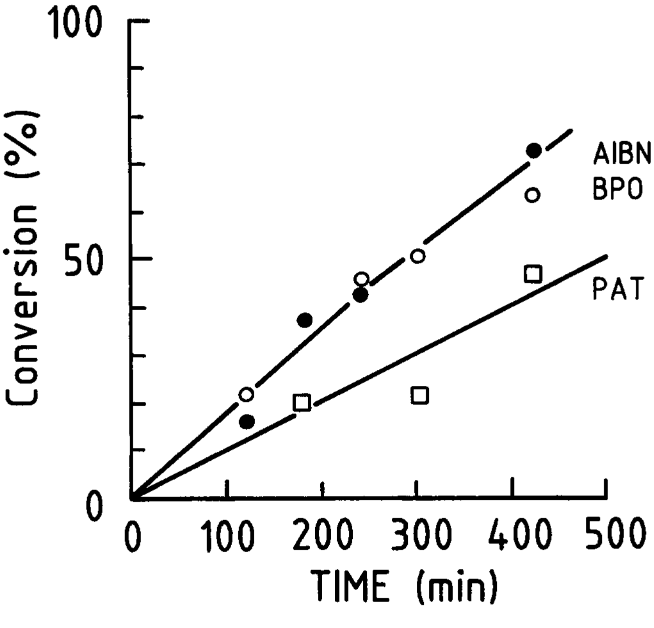
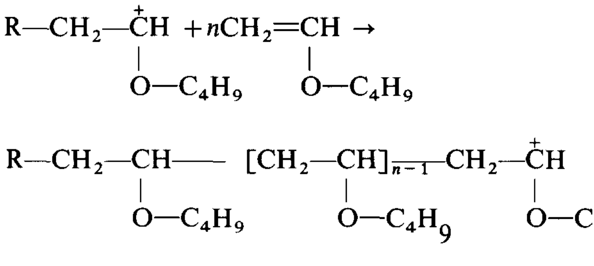


Figure 3 Thermal polymerization of n-butylvinyl ether in Ar-saturated dichloromethane solution at 70°C initiated by AIBN, PAT or BPO: [initiator] = $5 \times 10^{-3}\ mol\ l^{-1}$; [$EMP^+PF_6^-$] = $5 \times 10^{-3}\ mol\ l^{-1}$; [BVE] = $7.7\ mol\ l^{-1}$

Carbocations formed in this way initiate the polymerization of nBVE:



$$R-CH_2-\underset{O-C_4H_9}{\overset{+}{C}H} + nCH_2=\underset{O-C_4H_9}{CH} \rightarrow$$

$$R-CH_2-\underset{O-C_4H_9}{CH}-[CH_2-\underset{O-C_4H_9}{CH}]_{n-1}-CH_2-\underset{O-C_4H_9}{\overset{+}{C}H} \qquad (20)$$

CONCLUSIONS

From the results described above it is inferred that several free radicals can reduce EMP^+ ions. In principle, electron transfer from radical to onium ion is feasible if the free energy ΔG is negative. ΔG is given by the following equation[9]:

$$\Delta G = E^{ox}_{1/2}(R^{\cdot}) - E^{red}_{1/2}(On^+) \qquad (21)$$

Here, $E^{ox}_{1/2}(R^{\cdot})$ and $E^{red}_{1/2}(On^+)$ denote the half wave oxidation and reduction potentials of the free radical and of the onium ion, respectively. Unfortunately, $E^{ox}_{1/2}(R^{\cdot})$ is not known for most radicals and also has not yet been measured for the radicals encountered in this work. Therefore, ΔG cannot be estimated. On the other hand, values of $E^{red}_{1/2}(On^+)$ are known for various onium salts. $E^{red}_{1/2}(EMP^+) = -0.7$ V was determined in this work.

As can be seen from *Table 3* this value lies between the reduction potential of Ph_2I^+ (-0.2 V) and that of Ph_3S^+ (-1.06 V). In all cases studied so far Ph_3S^+ was found to be less reactive than Ph_2I^+ regarding its reactivity with respect to a given radical[10]. In this connection it is interesting to note that EMP^+ exhibits intermediate behaviour, as would be expected on the basis of its reduction potential. Moreover, EMP^+ seems to be favoured as oxidizing agent for radicals over other substituted pyridinium ions possessing more negative reduction potentials such as 1-methylpyridinium or 1-methoxy-4-phenylpyridinium ions (see *Table 3*).

Table 3 Reduction potentials of onium salts

Onium ion	$E^{red}_{1/2}$ (V) *versus* SCE[c]	Reference
$4\text{-}Cl-C_6H_4-N_2^+$	0.35	11
Ph_2I^+	−0.2	12
EMP^+	−0.7	This work
Ph_3S^+	−1.06	13
MPY[a]	−1.476	This work
MPPY[b]	−1.580	This work

[a] MPY: 1-methylpyridinium ion

[b] MPPY: 1-methoxy-4-phenylpyridinium ion

[c] Standard calomel electrode

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