Photosensitized cationic polymerization using *N*-ethoxy-2-methylpyridinium hexafluorophosphate

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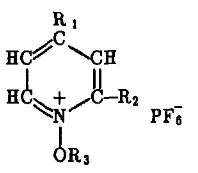
The cationic polymerization of cyclohexene oxide is initiated at room temperature upon irradiation at $\lambda_{inc} > 350$ nm of CH_2Cl_2 solutions containing *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) and one of the following compounds: thioxanthone, anthracene, perylene or phenothiazine. Poly(cyclohexene oxide) of molar mass exceeding 10^5 is produced. In the absence of $EMP^+PF_6^-$, which is transparent at $\lambda_{inc} > 350$ nm, these sensitizers are ineffective. Acetophenone and benzophenone do not act as sensitizers. An initiation mechanism involving electron transfer from the excited sensitizers to EMP^+ ions is proposed. In flash photolysis experiments, electron transfer was evidenced by the formation of radical cations in the cases of anthracene, perylene or phenothiazine.

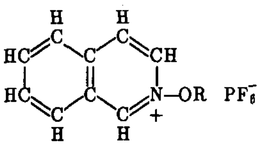
(Keywords: photoinitiated cationic polymerization; pyridinium salts; photosensitization; cyclohexene oxide)

INTRODUCTION

It has been shown recently[1] that certain *N*-alkoxypyridinium and *N*-alkoxyquinolinium salts of the general structure:



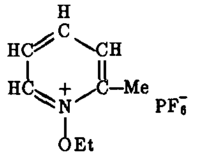
(I)



(II)

are capable of acting as photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and vinyl ethers such as n-butyl vinyl ether.

For practical applications, these compounds should absorb light appreciably at wavelengths longer than 350 nm. Since this requirement is not fulfilled for certain easily available pyridinium salts, it was tried to find out whether sensitization with the aid of appropriate compounds absorbing light at longer wavelengths can help to extend their photosensitivity to wavelengths $\lambda > 350$ nm. For this purpose the sensitization of the conversion of *N*-ethoxy-2-methylpyridinium ions (EMP^+)



(EMP^+)

by thioxanthone, anthracene, perylene and phenothiazine was studied. These compounds strongly absorb light between 350 and 400 nm, as can be seen from *Figure 1*. The polymerization of cyclohexene oxide (CHO) served as a probe reaction for the conversion of EMP^+ ions into species capable of initiating cationic polymerizations. CHO polymerizes only via a cationic mechanism.

EXPERIMENTAL

Materials

1,2-Epoxycyclohexane (cyclohexene oxide, CHO; Aldrich) was distilled from CaH_2; b.p. 38°C at 53 mbar. Dichloromethane (Aldrich) was treated with conc. H_2SO_4, and washed with aqueous Na_2CO_3 solution (5%)

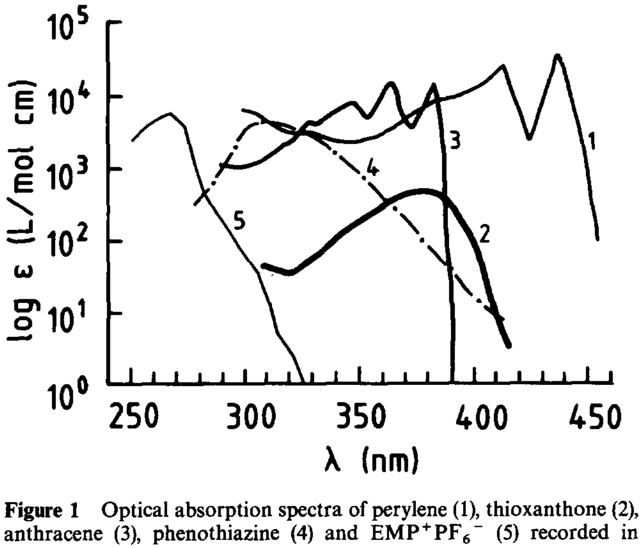


Figure 1 Optical absorption spectra of perylene (1), thioxanthone (2), anthracene (3), phenothiazine (4) and $EMP^+PF_6^-$ (5) recorded in CH_2Cl_2 solution at room temperature

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and water. Subsequently, it was dried with $CaCl_2$ and refluxed and distilled from CaH_2. *N*-Ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) was prepared according to the procedure described by Reichardt[2]. Benzophenone (BP; E. Merck) was recrystallized from n-heptane. Acetophenone was purified by distillation. Perylene and phenothiazine (Aldrich) were recrystallized from toluene. Thioxanthone (Fluka) was recrystallized from n-hexane.

Polymerizations

Dichloromethane solutions containing CHO (5.8 mol l^{-1}), $EMP^+PF_6^-$ ($6.8 \times 10^{-3} \text{ mol l}^{-1}$) and sensitizer (5 to $7 \times 10^{-3} \text{ mol l}^{-1}$) were irradiated in glass tubes (Pyrex) in a Rayonet merry-go-round photoreactor. The nominal wavelength of the lamps used was 350 nm. To prevent absorption by $EMP^+PF_6^-$, light of wavelength lower than 350 nm was filtered off with the aid of an n-hexane solution of phenanthrene ($10^{-2} \text{ mol l}^{-1}$). Prior to irradiation, argon was bubbled through the solutions.

Polymer characterization

Polymer formed during irradiation was precipitated with methanol and dried after several reprecipitations. Weight-average molar masses M_w were determined by light scattering measurements with a low-angle light scattering photometer (Chromatix KMX-6, $\lambda_{obs} = 632$ nm). Ethyl acetate/n-hexane (23:77, v/v) served as a solvent ($dn/dc = 0.138 \text{ ml g}^{-1}$). An LKB spectrophotometer (Ultraspec 4050) was used to record u.v.-vis. absorption spectra.

Table 1 Sensitized photopolymerization of CHO (5.8 mol l^{-1}) in CH_2Cl_2 solution containing $EMP^+PF_6^-$ ($6.8 \times 10^{-3} \text{ mol l}^{-1}$) at $\lambda_{inc} > 350$ nm

Sensitizer	Sensitizer concentration (mol l^{-1})	Conversion[a] (% w/w)	M_w^b
Benzophenone	5×10^{-3}	<0.1	
Acetophenone	7×10^{-3}	<0.1	
Thioxanthone	5×10^{-3}	23	1.2×10^5
Anthracene	5×10^{-3}	61.5	1.3×10^5
Perylene	5×10^{-3}	59.1	1.4×10^5
Phenothiazine	5×10^{-3}	29.1	1.2×10^5

[a] Conversion after 30 min irradiation

[b] Weight-average molar mass determined by the light scattering method

Flash photolysis

A ruby laser (Korad, model K1QS2) operated with a frequency doubler was used to generate 20 ns flashes ($\lambda_{inc} = 347$ nm). The irradiation of solutions was performed in a rectangular quartz cell, which was connected to a flow system. The solutions were purged with argon prior to irradiation.

RESULTS

Polymerizations

When a solution of CHO in methylene chloride (CH_2Cl_2) containing $EMP^+PF_6^-$ was irradiated with u.v. light ($\lambda > 350$ nm), polymerization did not take place in accordance with the fact that EMP^+ is transparent in this wavelength range. CHO polymerized, however, when in addition to $EMP^+PF_6^-$ the solutions contained either thioxanthone, anthracene, perylene or phenothiazine. Typical results are presented in *Table 1*. It is to be pointed out that all sensitizers were ineffective in initiating cationic polymerizations in the absence of the onium salt. Notably, acetophenone and benzophenone did not act as sensitizers.

Reactions of EMP^+ ions with excited sensitizer molecules

Flash photolysis experiments were performed to characterize the nature of the reactive excited state of the sensitizer and to find out whether the mechanism of the interaction between EMP^+ ions and excited sensitizer molecules is based on energy transfer or electron transfer.

Experiments with anthracene. In CH_2Cl_2 solutions containing both anthracene and $EMP^+PF_6^-$, the absorption band of the radical cation of anthracene ($\lambda_{max} \simeq 720$ nm (refs. 3, 4)) was formed during the flash (see *Figure 2a*). Notably, the intensity of the triplet–triplet (T–T) absorption band ($\lambda_{max} \simeq 435$ nm), which was also formed during the flash, decreased with increasing EMP^+ concentration but its decay rate was not affected by EMP^+ ions ($k \ll 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$). From these results the following conclusions are drawn: (a) Electrons

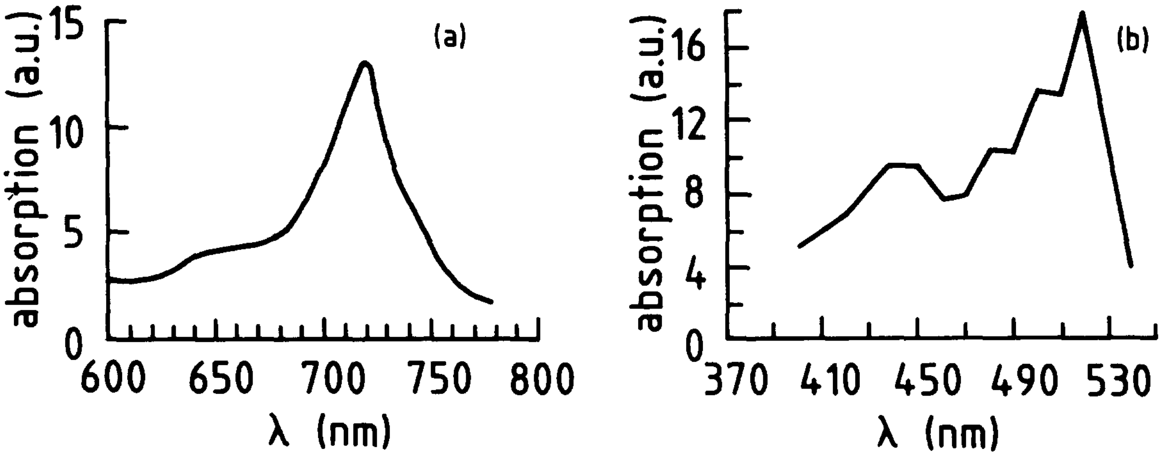


Figure 2 Transient optical absorption spectra recorded at the end of the flash (20 ns, $\lambda = 347$ nm) at room temperature in Ar-saturated solutions: (a) anthracene ($4.5 \times 10^{-5} \text{ mol l}^{-1}$) and $EMP^+PF_6^-$ ($4.7 \times 10^{-2} \text{ mol l}^{-1}$) in dichloromethane; (b) phenothiazine ($2.0 \times 10^{-4} \text{ mol l}^{-1}$) and $EMP^+PF_6^-$ ($5.8 \times 10^{-3} \text{ mol l}^{-1}$) in acetonitrile

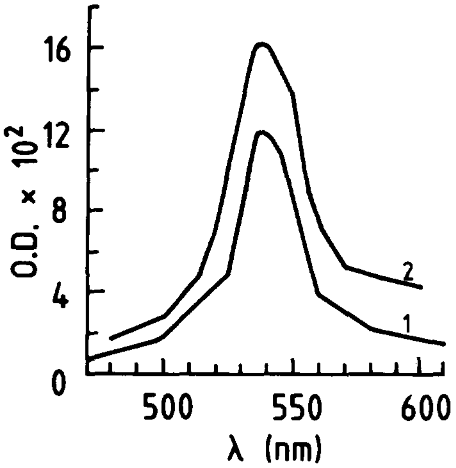


Figure 3 Transient optical absorption spectra recorded at the end of the flash (20 ns, $\lambda = 347$ nm) at room temperature in Ar-saturated CH_2Cl_2 solution of perylene (1.0×10^{-4} mol l^{-1}) in the absence (1) and the presence (2) of $EMP^+PF_6^-$ (3.6×10^{-2} mol l^{-1})

are transferred from excited singlets to EMP^+ ions. The rate constant of the electron-transfer process is high: $k \simeq 5 \times 10^9$ l mol^{-1} s^{-1}. (b) Anthracene triplets are unreactive towards EMP^+ ions.

Experiments with phenothiazine. In CH_3CN solutions containing both phenothiazine and $EMP^+PF_6^-$, the absorption band of the radical cation of phenothiazine ($\lambda_{max} \simeq 520$ nm (refs. 5–7)) was formed during the flash (see *Figure 2b*). In this case electrons are transferred from excited triplets to EMP^+ ions at a very high rate ($k = 8 \times 10^9$ l mol^{-1} s^{-1}). This was concluded from the simultaneous decay of the T–T absorption at 465 nm and the increase in the absorption of the radical cation at 520 nm.

Experiments with perylene. Upon irradiation of perylene in CH_2Cl_2 solution at the very high light intensity that prevails under the conditions applied in our flash photolysis experiments, radical cations are formed even in the absence of $EMP^+PF_6^-$. This can be seen from *Figure 3* where the absorption band around 535 nm formed during the flash is shown. This band corresponds to that of perylene radical cations reported in the literature[3,8,9]. In this case radical cation formation is due to a biphotonic effect[10]. In the presence of $EMP^+PF_6^-$ the intensity of the band around 535 nm is significantly increased, indicating that excited perylene molecules transfer electrons to EMP^+ ions. Reportedly[10], the triplet quantum yield is low and the fluorescence quantum yield is high ($\phi_{fl} = 0.98$). Consequently, based on the fact that EMP^+ ions effectively quench the fluorescence of perylene, it is concluded that excited perylene singlets react with EMP^+ ions.

Experiments with thioxanthone. Flash photolysis of thioxanthone in CH_2Cl_2 solution resulted in the formation of the T–T absorption spectrum ($\lambda_{max} \simeq 640$ nm) in accordance with the known fact that intersystem crossing is very effective in this case. The intensity of the T–T absorption was not affected by $EMP^+PF_6^-$ but the triplet decay rate was accelerated, indicating that thioxanthone triplets react with EMP^+ ions. A value $k_2 = 4 \times 10^7$ l mol^{-1} s^{-1} was obtained with the aid of a pseudo-first-order data treatment. Notably, the formation of a transient absorption due to radical cations was not observed in this case, although a transient absorption band with a maximum at about 430 nm assigned to the radical cation was detected upon reacting triplets of thioxanthone derivatives with diphenyliodonium ions[11].

Reactions of anthracene radical cations with monomers

In a CH_2Cl_2 solution containing anthracene (4.4×10^{-5} mol l^{-1}) and $EMP^+PF_6^-$ (1.1×10^{-2} mol l^{-1}), anthracene radical cations decay in a first-order process ($k_1 = 2 \times 10^4$ s^{-1}). Upon addition of n-butyl vinyl ether the decay constant increased linearly with the concentration of the additive. Pseudo-first-order data treatment yielded the rate constant of the reaction of anthracene radical cations with n-butyl vinyl ether: $k_2 = 9 \times 10^4$ l mol^{-1} s^{-1}. Analogous experiments with cyclohexene oxide revealed a much lower rate constant: $k_2 < 10^4$ l mol^{-1} s^{-1}.

DISCUSSION

Principally, the sensitizing action of the compounds used in this work can be based on either (i) energy transfer from the electronically excited sensitizer (PS*) to the onium ion followed by decomposition or reaction of the excited onium ion (On^+) according to the equation:

$$PS* + On^+ \rightarrow PS + (On^+)* \qquad (1)$$

or (ii) electron transfer resulting in the formation of the radical cation of the sensitizer according to the equation:

$$PS* + On^+ \rightarrow PS^{+\bullet} + On^{\bullet} \qquad (2)$$

As far as energy transfer is concerned, singlet–singlet routes can be excluded, because the singlet energies of all sensitizers studied in this work are lower than that of EMP^+. Regarding triplet–triplet energy transfer, conclusions cannot be drawn because the triplet energy of EMP^+ is unknown.

According to the Rehm–Weller equation[12], electron transfer from sensitizer to pyridinium ion is feasible if the change in free energy is negative:

$$\Delta G = f_c(E^{ox}_{1/2} - E^{red}_{1/2}) - E(PS*) \qquad (3)$$

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

The ΔG values listed in *Table 2* suggest that electron transfer from triplet or singlet excited states of the sensitizers to EMP^+ ions is favourable in the cases of thioxanthone, anthracene, perylene and phenothiazine.

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

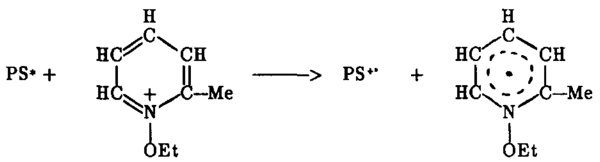
Sensitizer	E(PS) (kJ mol^{-1})	$E^{ox}_{1/2}$ (V)	ΔG^a (kJ mol^{-1})	Photosensitization
Benzophenone	290 (E_t)	2.7[13]	+39.8	–
Acetophenone	308 (E_t)	2.9[13]	+41.2	–
Thioxanthone	277 (E_t)	1.7[14]	−44.2	+
Anthracene	319 (E_s)	1.1[15]	−144.4	+
Perylene	277 (E_s)	0.9[15]	−121.8	+
Phenothiazine	239 (E_t)	0.6[15]	−112.9	+

[a] Calculated with the aid of equation (3) with $E^{red}_{1/2} = -0.7$ V for EMP^+ ions

The flash photolysis studies performed in this work show that, in the cases of anthracene and perylene, sensitizer molecules in excited singlet states effectively react with EMP^+ ions by electron transfer. In the cases of phenothiazine and thioxanthone, triplets were found to react with EMP^+ ions. However, by absorption spectroscopy, electron transfer only was evidenced in the case of perylene. In this connection it is interesting to note that, in the electronically excited state, the sensitizers studied in this work have been reported to transfer electrons to sulfonium and iodonium ions of the structures R_2I^+ and R_3S^+ (at least one R being an aromatic group)[11,16,17]. Since the reduction potential of EMP^+ (-0.7 V) lies in between those of diphenyliodonium (-0.2 V) and triphenylsulfonium ions (-1.06 V)[18], the readiness of EMP^+ ions to act as electron acceptors appears to be indicated.

A mechanism based on electron transfer concerning the reaction of PS* with EMP^+ is described by the reactions:

$$PS + h\nu \rightarrow PS* \qquad (4)$$



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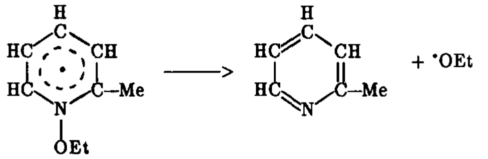

(6)

Hence, various mechanisms for the initiation of cationic polymerizations are feasible. (a) Cation radicals $PS^{+\bullet}$ react directly with the monomer M:

$$PS^{+\bullet} + M \rightarrow {}^{\bullet}PS\text{–}M^+ \xrightarrow{nM} {}^{\bullet}PS\text{–}(M)_nM^+ \qquad (7)$$

(b) Cation radicals $PS^{+\bullet}$ abstract hydrogen from the solvent or the monomer and the resulting intermediate dissociates:

$$PS^{+\bullet} + RH \rightarrow H\text{–}PS^+ + R^{\bullet} \qquad (8)$$

$$H\text{–}PS^+ \rightarrow PS + H^+ \qquad (9)$$

Protons generated in this way add to the monomer, thus forming species capable of initiating the cationic polymerization of M:

$$H^+ + M \rightarrow H\text{–}M^+ \xrightarrow{nM} H\text{–}(M)_nM^+ \qquad (10)$$

The rather low reactivity of anthracene radical cations towards n-butyl vinyl ether and cyclohexene oxide found in this work suggests that mechanisms according to equation (7) do not play an important role regarding the initiation of cationic polymerizations. Further investigations concerning the elucidation of the initiation process are in progress.

CONCLUSIONS

In this work it has been shown that the conversion of *N*-ethoxy-2-methylpyridinium ions (EMP^+) can be photosensitized by thioxanthone, anthracene, perylene and phenothiazine, which absorb strongly between 350 and 400 nm. This was evidenced by means of the polymerization of cyclohexene oxide (CHO). Since CHO polymerizes only cationically it is concluded that the interaction of electronically excited sensitizer molecules with EMP^+ ions results in the formation of ionic species capable of reacting with CHO molecules.

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REFERENCES

1 Yağci, Y., Kornowski, A. and Schnabel, W. *J. Polym. Sci., Polym. Chem. Edn.* 1992, **30**, 1987; Yağci, Y., Kornowski, A., Massone, K. and Schnabel, W., Patent DE-P-4103906, February 1991
2 Reichardt, C. *Chem. Ber.* 1966, **99**, 1769
3 Shida, T. 'Electronic Absorption Spectra of Radical Ions', Elsevier, Amsterdam, 1988
4 Grellmann, K. H., Watkins, A. R. and Weller, A. *J. Phys. Chem.* 1972, **76**, 469 and 3132
5 Shine, H. J. and Mach, E. E. *J. Org. Chem.* 1965, **30**, 2130
6 Iwaoka, T., Kokubun, H. and Koizumi, M. *Bull. Chem. Soc. Japan* 1971, **44**, 341 and 3466
7 Hanson, P. and Norman, R. O. C. *J. Chem. Soc., Perkin Trans. II* 1973, 264
8 Mataga, N., Asahi, T., Kanda, Y., Okada, T. and Kakitani, T. *Chem. Phys.* 1988, **127**, 249
9 Lewitzka, F. and Löhmannsröben, H.-G. *Z. Phys. Chem. NF* 1990, **169**, 203
10 Konuk, R., Cornelisse, J. and McGlynn, S. P. *J. Chem. Phys.* 1985, **82**, 3929
11 Manivannan, G. and Fouassier, J. P. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 1113
12 Rehm, D. and Weller, A. *Ber. Bunsenges. Phys. Chem.* 1969, **73**, 834
13 Miller, L. L., Nordbohm, G. D. and Mayeda, E. A. *J. Org. Chem.* 1972, **37**, 916
14 Kissinger, P. T., Holt, P. T. and Reilley, C. N. *J. Electroanal. Chem.* 1971, **33**, 1
15 Siegerman, H. in 'Techniques of Electroorganic Synthesis' (Ed. N. L. Weinberg) Part II, Vol. V of 'Techniques of Chemistry' (Ed. A. Weissberger), Wiley, New York, 1975
16 Crivello, J. V. and Lee, J. L. *Macromolecules* 1981, **14**, 1141
17 Pappas, S. P., Gatechair, L. and Jilek, J. H. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 77
18 Böttcher, A., Hasebe, K., Hizal, G., Yağci, Y., Stellberg, P. and Schnabel, W. *Polymer* 1991, **32**, 2289