Photosensitized free radical polymerization using pyridinium salts

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Summary

The polymerization of methyl methacrylate (MMA), ethyl acrylate (EA), styrene (St) and 2-vinyl pyridine (VP) is initiated upon irradiation at $\lambda > 350$ nm of dichloromethane solutions containing N-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) and anthracene or thioxanthone. Initiation mechanisms involving the formation of ethoxyl radicals during the decomposition of EMP^+ ions via electron transfer are proposed.

Introduction

We have recently proposed[1] N-alkoxy-pyridinium and N-alkoxy-quinolinium salts of the general structure:
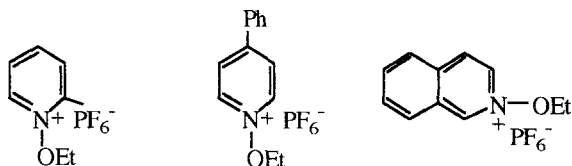
as photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and of vinyl ethers such as n-butyl vinyl ether. It has been suggested that the direct photolysis of N-ethoxy pyridinium ions leads to the formation of pyridinium radical cations and ethoxyl radicals.

$$EMP^+ \xrightarrow{\quad h\nu \quad} (EMP^+)^* \qquad (1)$$

$$(EMP^+)^* \longrightarrow \text{(pyridinium radical cation)} + EtO\cdot \qquad (2)$$
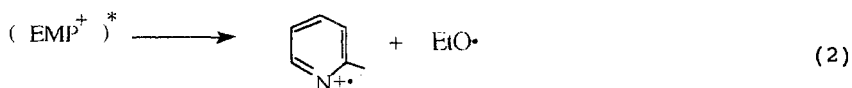
It appears feasible that ethoxyl radicals are capable of initiating the free radical polymerization of appropriate monomers and that, therefore, pyridinium salts might be also used as photoinitiators

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for the free radical polymerization of vinyl compounds. In this connection it is noticeable that free radical initiator systems consisting of amino-substituted 3-ketocoumarins and N methoxy 4 phenyl pyridinium salt or N benzoyloxyphthalimide were reported to act as effective initiators in free radical polymerizations. However, a reaction mechanism was not given[7].

In the present paper we report on the free radical polymerization of various monomers with the aid of initiator systems consisting of EMP$^+$ / anthracene and EMP$^+$ / thioxanthone. Irradiations were performed at λ_{inc}=350-400 nm, where EMP$^+$ and the monomers are transparent but anthracene and thioxanthone absorb strongly.

Experimental

Materials

N-ethoxy-2-methylpyridinium hexafluorophosphate (EMP$^+$PF$_6^-$) was prepared according to the procedure decribed by Reichard[8]. Anthracene (Aldrich) was purified by sublimation. Thioxanthone (Fluka) was recrystallized from n-hexane. Methyl methacrylate (MMA), styrene (St), ethyl acrylate (EA), 2-vinyl pyridine (VP), ethylene glycol dimethacrylate (EGDA) and dichloromethane were purified by conventional drying and distillation procedures.

Photopolymerization

Dichloromethane solutions containing monomers, sensitizers and EMP$^+$PF$_6^-$ were irradiated in Pyrex tubes in an annular-type photoreactor (Applied Photophysics). The nominal wavelength of the lamps used was 350 nm. To prevent light absorption by EMP$^+$PF$_6^-$, light of wavelenghts lower than 350 nm was filtered off with the aid of a n-hexane solution of phenanthrene (10^{-2} mol l^{-1}). Prior to irradiation nitrogen was bubbled through the solutions.
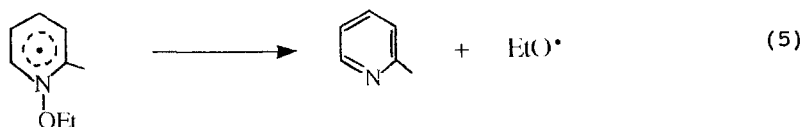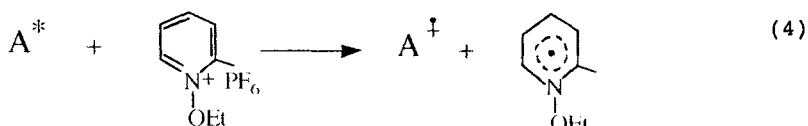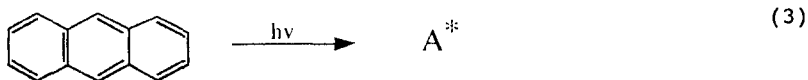
Polymer characterization

Polymers formed during the irradiation were precipitated with methanol and dried in a vacuum oven at room temperature for 24 hours. Molecular weights of polymers were determined by gel permeation chromatography using polystrene standard samples. A Knauer M-64 instrument was employed. Tetrahydrofuran served as eluent. The flow rate was 1 ml min^{-1}.

Result and Discussion

Establishment of the useful role of various photosensitizers in cationic polymerization using pyridinium salts has prompted an examination of the potential usefulness of these systems in free radical polymerization. As can be seen from Table 1 and Figure 1 the polymerization of vinyl monomers is initiated effectively upon irradiation of solutions of monomers in dichloromethane containing EMP$^+$ and anthracene. At the irradiation wavelengths ($\lambda > 350$ nm) EMP$^+$ and monomers are transparent and the initiation of the

polymerization is only caused by light absorbed by anthracene. Notably, the conversion of monomer to polymer is quite low in the absence the pyridinium salt (see Figure 3).

A possible mechanism for the initiation of the free radical polymerization applies to electron transfer between photoexcited sensitizer molecules and pyridinium ions as was evidenced by flash photolysis studies[9].

$$\text{(anthracene)} \xrightarrow{\ hv\ } A^* \tag{3}$$

$$A^* \ + \ \text{(2-methylpyridinium } N^+ \text{ } PF_6 \text{, } OEt) \longrightarrow A^{\dagger} \ + \ \text{(pyridinyl radical, } OEt) \tag{4}$$

$$\text{(pyridinyl radical, } OEt) \longrightarrow \text{(2-methylpyridine)} \ + \ EtO^{\bullet} \tag{5}$$

$$EtO^{\bullet} \ + \ M \longrightarrow \text{polymer} \tag{6}$$

From the results obtained it is concluded that ethoxyl radicals formed according to reaction 5 are capable of initiating the free radical polymerization. This conclusion was substantiated recently by Hizal et al.[10] who used polymeric N-alkoxy pyridinium salts as coinitiator for the photosensitized free radical polymerization. In this case block copolymers are readily formed indicating the initiation capability of polymeric alkoxyl radicals. Figure 2 shows data concerning the photosensitized polymerization of MMA in the presence of EMP[+] at various concentrations of anthracene.The irradiations were carried out at a constant irradiation time of 4h. The curve shows a maximum sensitization effect at an anthracene concentration of 1.6 x 10^{-3} mol 1^{-1}. As the concentration of anthracene is further increased, the conversion drops. This behaviour may be attributed to aggregation of anthracene molecules and resultant self quenching. The dependence of monomer conversion on the EMP[+] concentration was also studied. It turned out that the conversion increases with increasing pyridinium ion concentration (Figure 3).

Apart from anthracene, the sensitization power of thioxanthone was also examined. Triplet excited thioxanthone is known [11] to abstract hydrogen from various compounds. Figure 4 shows two curves

Table 1. Sensitized photopolymerization of various monomers in dichloromethane solution using anthracene (8.02×10^{-3} mol l^{-1}) and $EMP^{+}PF_{6-}$ (4.24×10^{-3} mol l^{-1}) at $\lambda > 350$ nm.

| Monomer	[Monomer] (mol l^{-1})	Conversion[a] (%)	Mn[b]
MMA	5.35	7.47	$6,4 \times 10^4$
EA	5.28	44.33	2.0×10^4
St	4.99	7.02	0.5×10^4
VP	5.31	2.67	-

[a] Conversion after 4 h irradiation
[b] Determined by GPC measurements (polystyrene calibration)
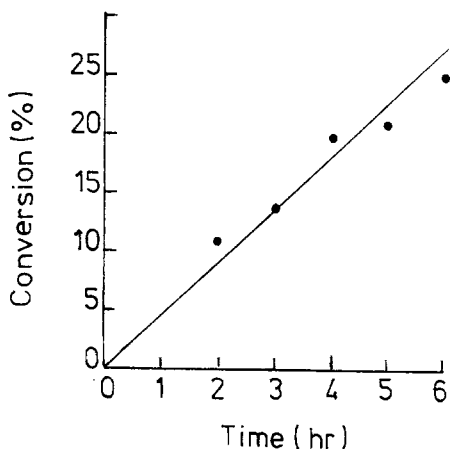
Figure 1. Sensitized photopolymerization of MMA (5.35 mol l^{-1}) in dichloromethane solution containing $EMP^{+}PF_{6-}$ (4.24×10^{-3} mol l^{-1}) and anthracene (1.6×10^{-3} mol l^{-1}), $\lambda > 350$ nm.
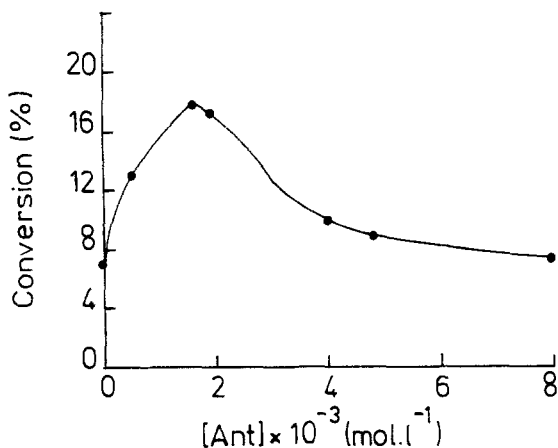
Figure 2. Effect of the anthracene concentration on the sensitized photopolymerization of MMA (5.35 mol l^{-1}) in dichloromethane solution containing EMP$^+$PF$_6^-$ (4.24 x 10^{-3} mol l^{-1}), λ > 350 nm.
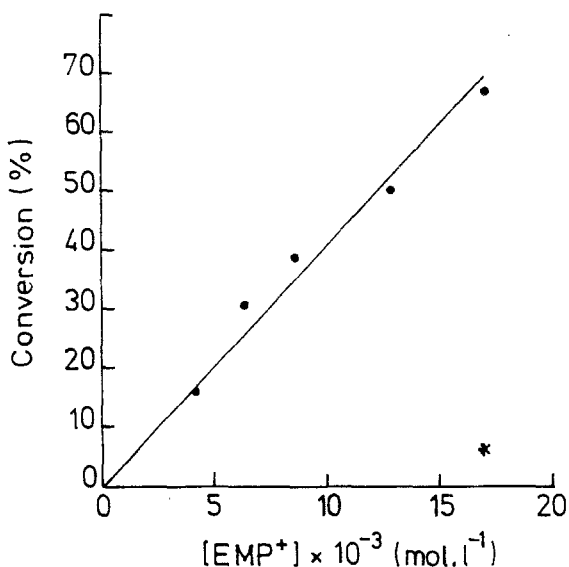

Figure 3. Effect of the EMP$^+$ concentration on the sensitized photopolymerization of MMA (5.35 mol l^{-1})in dichloromethane solution containing anthracene (1.6 x 10^{-3} mol l^{-1}), λ > 350 nm, time: 4h.
*: in the absence of anthracene

for the photosensitized polymerization of MMA in the absence and presence of EMP⁺. There is a considerable enhancement of the rate of polymerization when EMP⁺ is used in the system. Two mechanisms for the generation of ethoxyl radicals are feasible. The first involves electron transfer between the pinacol type radical, formed by hydrogen abstraction by triplet thioxanthone, and EMP⁺. Subsequent decomposition of pyridinyl radicals would then generate ethoxyl radicals.

An alternative mechanism which also must be considered occurs in an identical fashion to that proposed for anthracene sensitization. Electron transfer can occur between photoexited thioxanthone and EMP⁺ resulting in the production of thioxanthone radical cations and pyridinyl radicals which decompose to ethoxyl radicals. Although a distinction between these two alternative mechanisms is not possible at this stage, observation of the polymerization also in the absence of EMP⁺ and laser flash photolysis studies[11] suggest that the mechanism according to reactions (7-10) plays an important role regarding the initiation of free radical polymerizations. By laser flash photolysis studies it was found that polymerizable monomers are rather reactive towards triplet excited thioxanthones. Typically, the rate constant of the reaction of triplet thioxanthone with MMA is 1.5×10^7 l mol s^{-1}. Further investigations concerning the elucidation of the initiation mechanism are in progress.
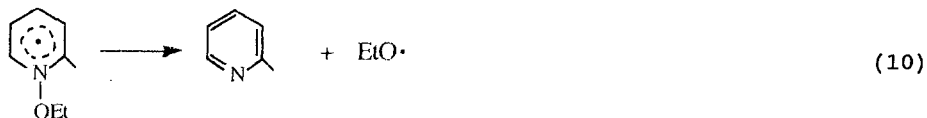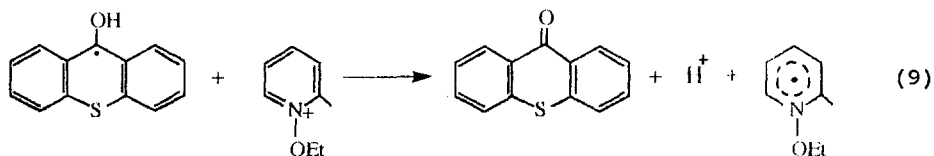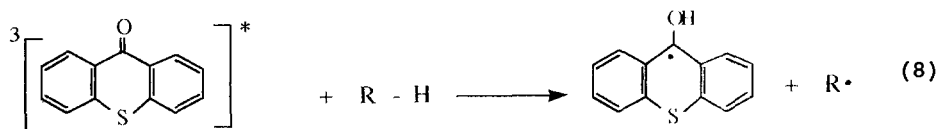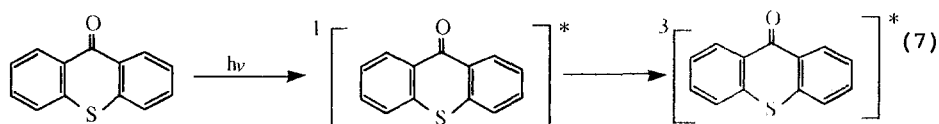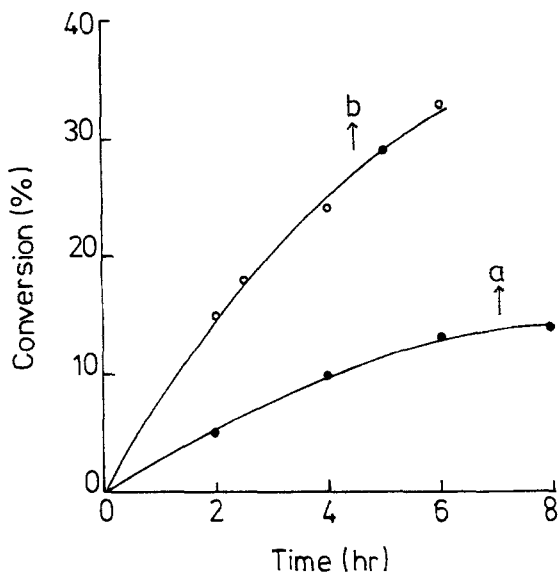
Figure 4. Photopolymerization of MMA (5.35 mol l^{-1}) in dichloromethane solution containing thioxanthone (2.69 x 10^{-3} mol l^{-1}), (a) in the absence of EMP$^+$PF$_6^-$ and (b) in the presence of EMP$^+$PF$_6^-$ (4.24 x 10^{-3} mol l^{-1}), λ > 350 nm.

Table 2. Photoinitiated Gel Formation of Acrylate System[*]

Photoinitiator	Gel Time (min)
Anthracene / EMP$^+$	15
Thioxanthone / EMP$^+$	50
Benzoin methyl ether	8
Benzophenone / Dimethylamino ethanol	18

[*] EGDA / MMA / CH$_2$Cl$_2$ (w/w/w): 50/20/30

As a very simple demonstration of the possible value of photosensitized free radical polymerization by pyridinium salts in u.v curing applications, several experiments were performed using a monomer mixture containing ethylene glycol dimethacrylate. Because of the presence of two methacrylate groups, this monomer ultimately forms intermolecularly crosslinked gels. Here we will consider only the results, listed in Table 2, in which the photosensitizer systems studied in this work are compared with the commercially available photoinitiators benzoin methyl ether and benzophenone / dimethylamino ethanol. It is interesting to note that the anthracene-EMP$^+$ system exhibits intermediate behavior.

Acknowledgement

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