Polymeric pyridinium salts as photoinitiators for cationic polymerization

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Polymeric pyridinium salts were synthesized and used as photoinitiators for the cationic polymerization of cyclic ethers and vinyl ethers. A possible application of these salts as positive photoresists is also demonstrated.

(Keywords: cationic polymerization; photoinitiator; pyridinium salt)

Introduction

We have recently described the use of *N*-alkoxy pyridinium and *N*-alkoxy quinolinium salts with non-nucleophilic anions as photoinitiators for cationic polymerization. Upon irradiation, these photoinitiators yield pyridinium radical cations and protons, and they are therefore capable of initiating the polymerization of cyclic ethers, such as cyclohexene oxide, and alkyl vinyl ethers, such as n-butyl vinyl ether[1,2]. The use of these pyridinium salts in combination with photosensitizers[3] and free radical sources[1,4–6] to induce cationic polymerization has also been reported.

It seemed that polymeric pyridinium salts would be of considerable interest as photoinitiators for several reasons. Such polymeric initiators would be expected to have low toxicity and low migration[7]. Their photoproducts would exhibit similar advantages since initiator fragments would be attached to the backbone of a polymer chain. In addition, they would be easily isolated and purified by conventional polymer isolation techniques.

In the present paper, we describe the synthesis of polymeric pyridinium salts and their use as cationic photoinitiators.

Experimental

Materials. Styrene (St), 2-vinyl pyridine (VP), cyclohexene oxide (CHO), *N*-butyl vinyl ether (BVE), *N*-vinyl carbazole (NVC), dichloromethane and acetonitrile were purified by conventional drying and distillation procedures. 2,2′-Azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from ethanol. *m*-Chloroperbenzoic acid and triethyloxonium hexafluorophosphate were used as received.

*Preparation of poly(styrene-*co*-2-vinyl pyridine).* Bulk styrene and 2-vinyl pyridine, at different ratios, and 2.9×10^{-2} mol l^{-1} of AIBN were degassed in Pyrex tubes by purging with nitrogen. For polymerization, the tubes were immersed in a constant temperature bath at 60°C. At the end of a given time the reaction mixtures were poured into a ten-fold excess of heptane. The precipitated polymers were filtered off and dried.

Preparation of polymeric pyridinium salts. The copolymers obtained as described above were oxidized by using 0.01 mol equivalence of *m*-chloroperbenzoic acid according to the pyridine content of polymers. Subsequently, the *N*-oxide polymers were treated with triethyloxonium hexafluorophosphate (1/1 mol ratio).

Photopolymerization. Appropriate solutions of monomers, containing a given amount of polymeric pyridinium salt, were placed in Pyrex tubes. The mixtures were degassed prior to irradiation in an annular-type photoreactor (Applied Photophysics). At the end of a given reaction time, the polymers were obtained from the reaction mixture by precipitation with methanol. In the case of heterogeneous polymerization, insoluble polymeric initiator was separated from the reaction mixture by filtration prior to precipitation.

Analysis. Molecular weights of polymers were determined by gel permeation chromatography using polystyrene standard samples. A Knauer M64 instrument, with a differential refractometer and a u.v. (254 nm) detector, was employed and tetrahydrofuran was the eluent. The flow rate was 1 ml min^{-1}. U.v.–vis. spectra were recorded with a Perkin–Elmer UV Lambda 2 spectrometer.

Table 1 Preparation of copolymers of 2-vinyl pyridine (VP)–styrene (St) with various compositions[a]

Monomer feed (mol%)		Conversion (%)	Polymer composition[b] (mol%)		Abbreviation
VP	St		VP[c]	St	
20	80	23	31 (32.5)	69	PSV-1
40	60	39	64 (54)	36	PSV-2
60	40	23	81 (60)	19	PSV-3
80	20	25	92 (64.4)	8	PSV-4
100	0	22	100 (75.8)	0	PSV-5

[a] Polymerization was conducted in bulk with AIBN as a radical initiator. [AIBN] = 2.9×10^{-2} mol l^{-1}, time 2 h, temperature 60°C
[b] Composition of the polymers was determined by ^{1}H n.m.r.
[c] Numbers in parentheses indicate the content of pyridinium ion groups in the polymers after treating with $Et_3O^+PF_6^-$, as determined by u.v. measurements

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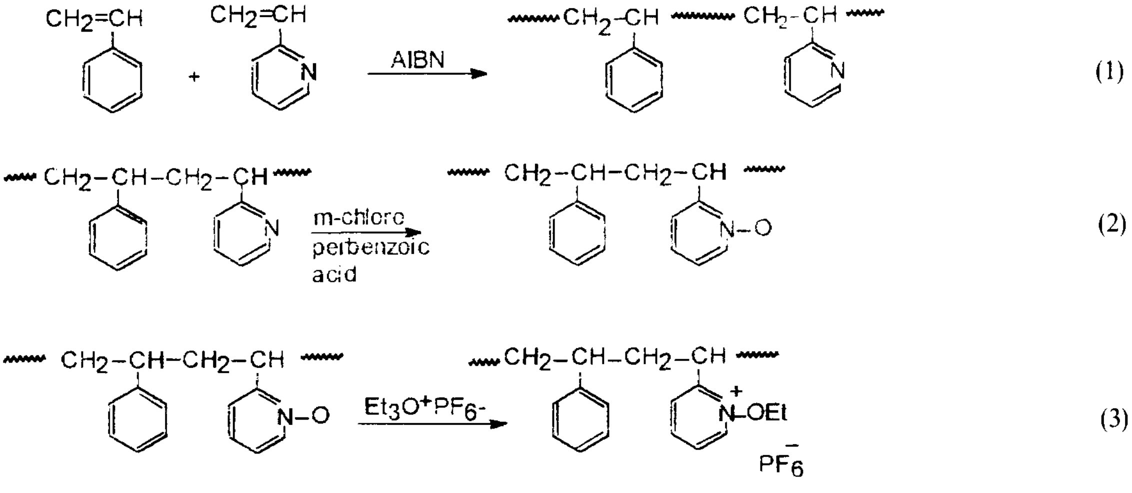
Results and discussion

Polymeric pyridinium salts were synthesized by employing the usual synthetic route described for low molar mass analogues[8] (*Scheme 1*).

Copolymers of styrene and 2-vinyl pyridine at various compositions (*Table 1*) were converted to *N*-oxide derivatives by treating with *m*-chloroperbenzoic acid. Subsequent alkylation with triethyloxonium hexafluorophosphate ($Et_3O^+PF_6^-$) gave the desired polymer bonded pyridinium salt photoinitiator. The pyridinium ion content in the polymers, as calculated by u.v. measurements, is also shown in *Table 1*. The alkylation degree tends to decrease with increase in vinyl pyridine content in the copolymer, presumably resulting from steric hindrance, electrostatic and polarity effects[9].

It was found that the polymeric photoinitiators are



Scheme 1

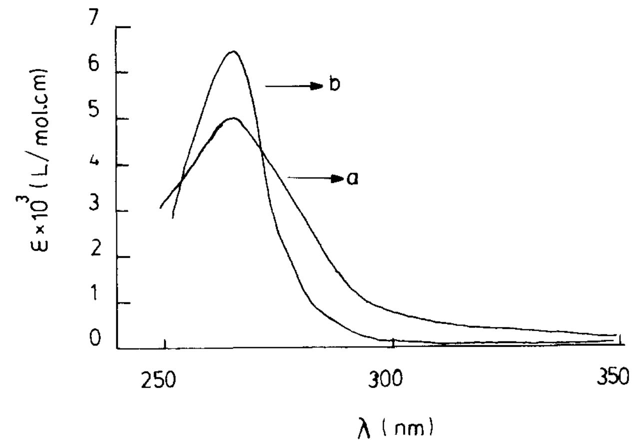


Figure 1 Optical absorption spectra of (a) polymeric pyridinium salt (PSV^+) and (b) *N*-ethoxy-2-methylpyridinium hexafluorophosphate (EMP^+) in acetonitrile

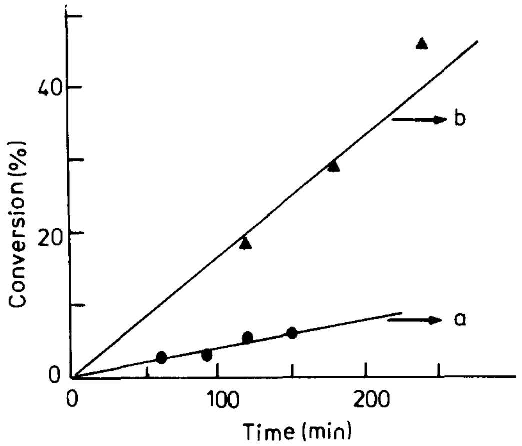


Figure 2 Photopolymerization of cyclohexene oxide using polymeric pyridinium salt: (a) PSV^+-5 in bulk and (b) PSV^+-1 in dichloromethane; [CHO] = 4.94 mol l^{-1}, [PSV^+-1] = 5 g l^{-1}

Table 2 Photopolymerization of various monomers using polymeric pyridinium salts (PSV^+) as initiator

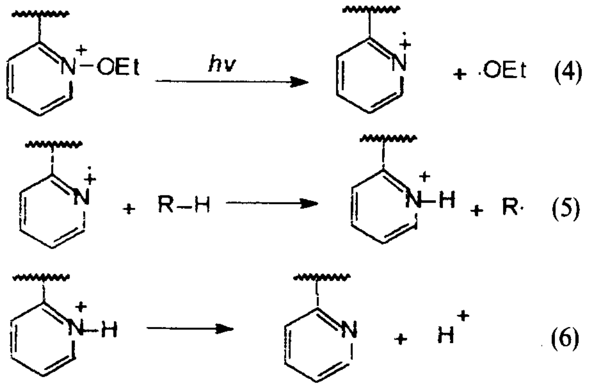
Monomer	[Monomer] (mol l^{-1})	Code[a]	[PSV^+] (g l^{-1})	Time of irradiation (min)	Conversion (%)	$M_n^e \times 10^3$
BVE[b]	2.58	PSV^+-5	3.33	15	55.63	–
CHO[c]	4.94	PSV^+-1	5.00	120	18.28	–
CHO[d]	9.88	PSV^+-5	10.0	120	5.00	5.2
	9.88	PSV^+-4	10.0	120	3.44	–
NVC[c]	6.21	PSV^+-1	5.00	5	49.25	20.6

[a] For convenience the same notation was used, + indicates salt structure
[b] In acetonitrile
[c] In dichloromethane
[d] In bulk; the initiator is insoluble in monomer so the concentration indicates only the amount of initiator in the monomer
[e] Determined by gel permeation chromatography

insoluble in both monomers and non-polar solvents, such as dichloromethane, when the level of pyridinium salt incorporation exceeded 20%; this may be attributed to ionic interaction between polymer chains. All polymers, however, are soluble in polar solvents such as acetonitrile.

Figure 1 shows optical absorption spectra of a polymeric pyridinium salt (PSV$^+$-5) and of *N*-ethoxy-2-methylpyridinium hexafluorophosphate (EMP$^+$). It can be seen that the spectrum of the polymeric pyridinium salt contains an absorption band located at 265 nm, which is also characteristic of the monomeric pyridinium salt, EMP$^+$.

The capability of polymeric pyridinium salts to initiate cationic polymerization was examined with several monomers. Typical results are shown in *Table 2*. All monomers polymerize readily when irradiated at room temperature in the presence of the salts, regardless of the level of pyridinium ion incorporation. It is notable that poly(*N*-ethoxy-2-vinylpyridinium hexafluorophosphate) initiates the polymerization of cyclohexene oxide (CHO) in bulk. In this case the initiator is not soluble in the monomer, and initiating species from hydrogen abstraction of pyridinium radical cations are free of initial polymer chains. A possible mechanism, analogous to monomeric pyridinium salts, for the initiation of cationic polymerization applies to the generation of protons upon photolysis, as illustrated below:



$$H^+ + M \longrightarrow \text{polymer} \qquad (7)$$

In *Figure 2* the conversion of CHO into polycyclohexene oxide is plotted *versus* time. As can be seen, the polymerization started without an induction period and increased almost linearly with time. As a very simple demonstration of the possible value of polymeric pyridinium salts in positive photoresist technology, a film of polymeric pyridinium salt was subjected to u.v. irradiation. Because the pyridinium groups in the irradiated film are converted into non-polar pyridinium groups according to equations (4)–(7), the film becomes soluble in a non-polar solvent such as dichloromethane. Thus, image reversal may be achieved by proper choice of the developer owing to the great difference in the solubility of the exposed and unexposed portions.

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