

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

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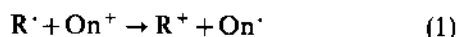
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Pyridinium ions of appropriate reduction potential $E_{1/2}^{\text{red}}$ are capable of oxidizing carbon-centred free radicals to carbocations that can initiate the polymerization of various compounds. 1-Ethoxy-2-methyl pyridinium ions of $E_{1/2}^{\text{red}} = -0.7$ 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

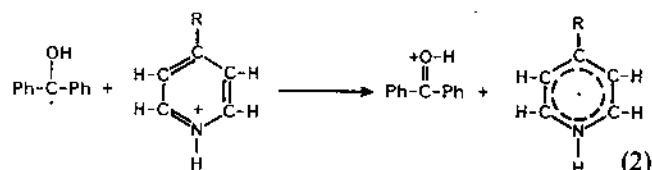
An elegant method of generating carbocations capable of initiating the cationic polymerization of compounds such as epoxides, cyclic ethers and alkyl vinyl ethers is based on electron transfer from free radicals to onium salts according to the reaction¹⁻³



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, $\text{Cl}-\text{C}_6\text{H}_4-\text{N}_2^+ \text{PF}_6^-$, and iodonium salts, e.g. diphenyliodonium hexafluorophosphate, $\text{Ph}_2\text{I}^+ \text{PF}_6^-$. Notably, reduction potentials of appropriate onium salts must be relatively low.

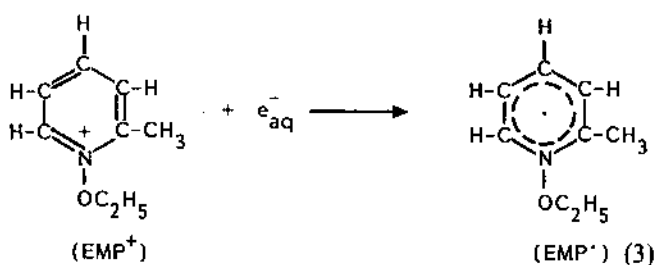
This paper deals with the possibility of applying pyridinium salts as agents for the oxidation of carbon-centred free radicals according to reaction (1). The role of iminium cations as electron acceptors was treated recently by Mariano⁴ in a review article. This author also discussed the possibility of pyridinium ions being reduced by diphenylhydroxymethyl radicals which can be gen-

erated, for example, by reaction of benzophenone triplet with a hydrogen donor:



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 investigated⁵:



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