

Cationic Polymerization of Cyclohexene Oxide Using Polymeric Photosensitizer in the Presence of Pyridinium Salt

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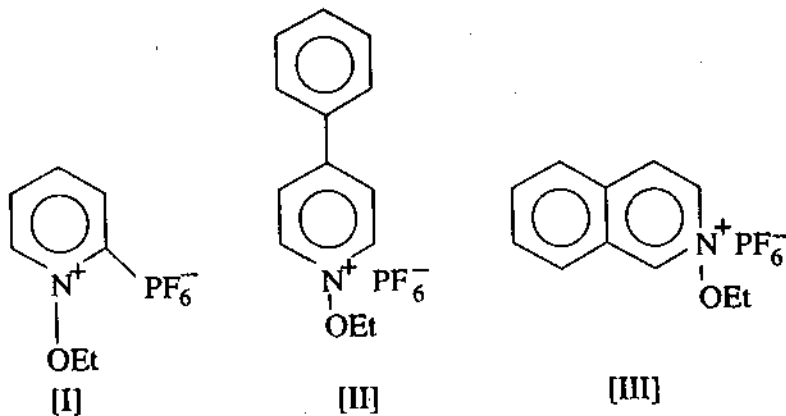
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Polymers with side-chain chromophoric anthracene groups were prepared by free radical copolymerization of 9-vinyl anthracene (VA) with styrene (St). These prepolymers in conjunction with N-ethoxy 2-methylpyridinium hexafluorophosphate ($\text{EMP}^+ \text{PF}_6^-$) were used to initiate cationic polymerization of cyclohexene oxide (CHO). Upon irradiation at $\lambda > 340$ nm, photoexcited anthracene groups undergo internal electron transfer with the pyridinium salt to give initiating anthracene radical cations. Evidence for the proposed mechanism was obtained by extraction and spectral and GPC measurements.

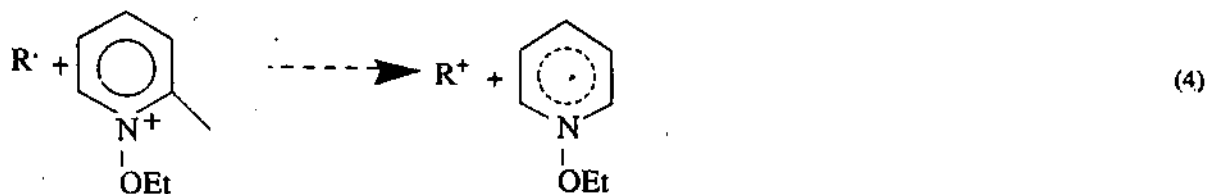
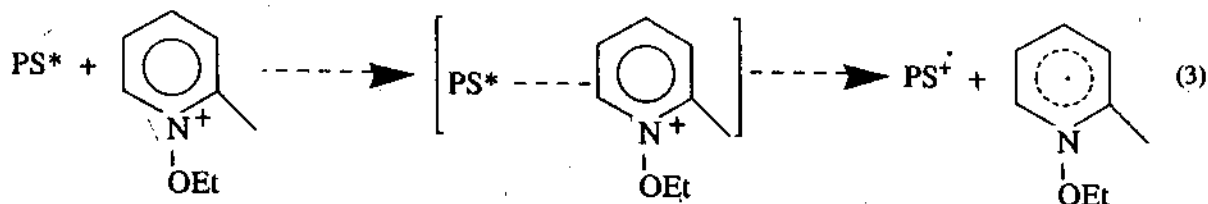
Introduction

Pyridinium salts (I) with non-nucleophilic counter anions have recently been developed as a new class of photoinitiators for cationic polymerization. This class of photoinitiators includes N-alkoxy derivatives of pyridinium (II) and quinolinium salts (III) by which spectral response may be extended into the 300-400 nm region where commercial light sources emit¹.

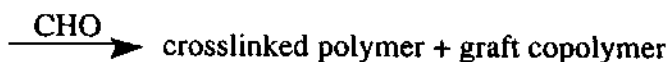
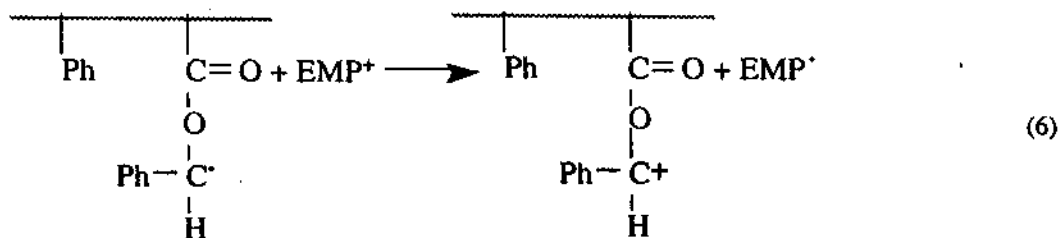
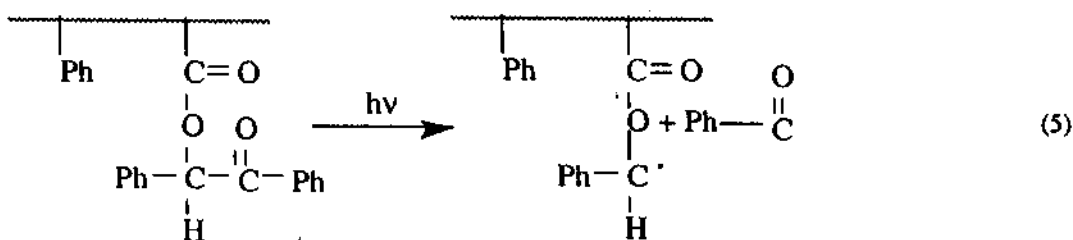


Absorptivity of pyridinium salts is enhanced in this region also by the use of photosensitizers² or photoinitiators producing electron donating radicals upon irradiation³. In these cases, the decomposition of pyridinium

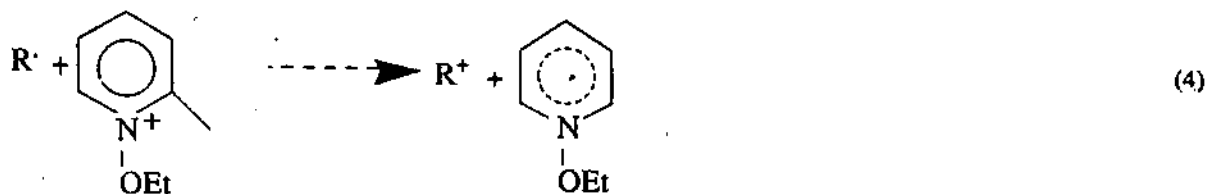
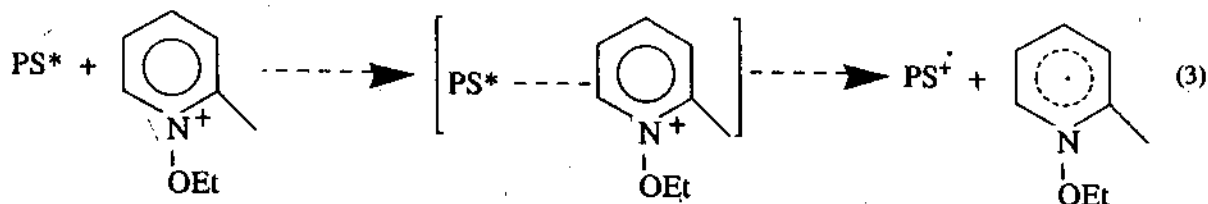
salts leading to the generation of reactive cations pertains to the electron transfer from photoexcited sensitizer (PS*) or electron donor radicals to pyridinium ions.



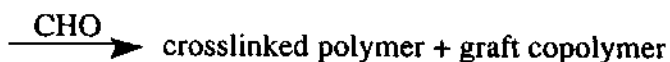
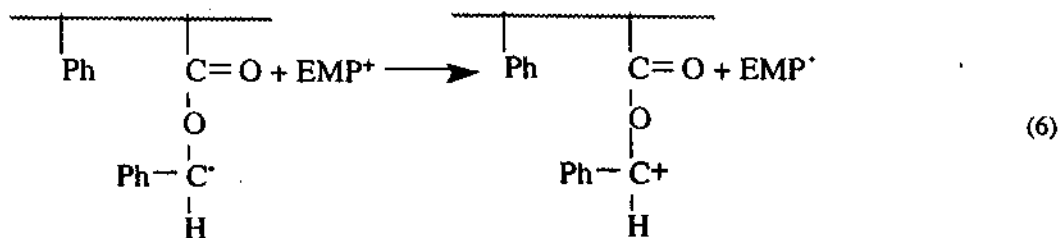
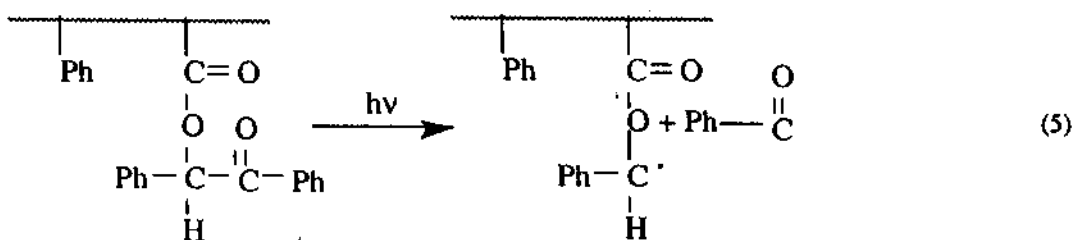
Photosensitizers applied in this process include polynuclear-aromatic hydrocarbons such as anthracene and perylene, thiazine derivatives such as phenothiazine and ketones such as thioxanthone. Recent laser flash photolysis studies² revealed that the photosensitization is based on an electron transfer mechanism. In this study, the formation of photosensitizer radical cations were observed. More recently, we have achieved⁴ promoted cationic polymerization of cyclohexene oxide (CHO) by means of side-chain photopolymers. The photolysis of poly (benzoin acrylate) at appropriate wavelengths leads to polymer-bound free radicals which can be oxidised by pyridinium ions. The resulting cations are capable of readily initiating polymerization of CHO as shown below.



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In this article experiments concerning photosensitization of pyridinium salt by polymers having anthracene side-chain chromophores to induce polymerization of CHO are described.

Experimental

Materials

Styrene (St), cyclohexene oxide (CHO) and 9-vinyl anthracene (VA) (commercial products) were purified by conventional drying, distillation and crystallization procedures. N-Ethoxy-2-methyl pyridinium hexafluorophosphate ($\text{EMP}^+ \text{PF}_6^-$) was prepared by the method described by Reichard⁵.

Preparation of polymers with anthracene side groups

Polymerization of VA and its copolymerization with St were performed in melt using dicumylperoxide (DCP) as initiator. Monomers containing 3% DCP in Pyrex tubes were degassed in a vacuum system. The mixtures were kept at 100° C. After 4 days, the reaction mixtures were poured into excess methanol and slight yellowish powdery polymers were obtained. They were reprecipitated from methylene chloride to methanol several times before using in photopolymerization experiments.

Photosensitized cationic polymerization

Prior to irradiation on a Annular Photoreactor (Applied Photophysics) emitting light nominally at 350 nm, solutions containing CHO, $\text{EMP}^+ \text{PF}_6^-$ and polymeric anthracene sensitizer in methylene chloride were degassed in the usual manner. A phenanthrene solution (10^{-2} mol/l) in n-hexane was used as a filter solution throughout the work to prevent direct absorption by $\text{EMP}^+ \text{PF}_6^-$. After a given time, polymers were obtained from the reaction mixture by precipitation in methanol. Homopoly (cyclohexene oxide) was extracted with n-hexane.

Analysis

GPC chromatograms were obtained by using a Knauer M-64 instrument and THF as eluent at a flow rate of 1 ml/min. Infrared spectra were recorded on a Jasco FT/IR 5300 spectrometer. Ultraviolet spectra were recorded on a Perkin Elmer-Lambda 2 UV-Vis spectrophotometer.

Results and Discussion

Polymerization of VA and its copolymerization with St were accomplished by free radical initiation in melt. The polymerization conditions and results are summarized in Table 1. The compositions of the copolymers was determined by measuring their specific extinction coefficients in methylene chloride solutions at 261 nm. polymerization of VA is rather slow due the stabilization of propagating macroradical by formation of unreactive dibenzylic radicals⁶⁻⁸. However, all the polymers have sufficient absorption at the irradiated wavelengths Figure 1. because of the incorporation of VA groups. Since the pyridinium salt does not absorb at $\lambda > 340 \text{ nm}$, all irradiations were performed at $\lambda_{inc} > 340 \text{ nm}$. CHO was polymerized quite effectively with polymers possessing anthracene side groups. Upon absorption of ultraviolet (u.v) light anthracene groups are excited according to reaction

Table 1. Copolymerization^a of 9-vinyl anthracene (VA) with styrene

Code	VA (mol)	St (m)	VA in polymer (mol %)
PVAS 1	20	80	11
PVAS 2	50	50	30
PVAS 3	80	20	59
PVA	100	0	100

^a Melt polymerization at 100° C, [DCP]= 3 %, time:4 days

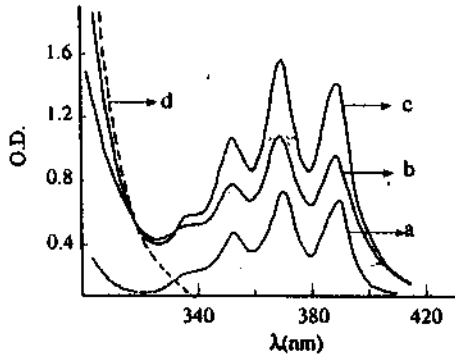
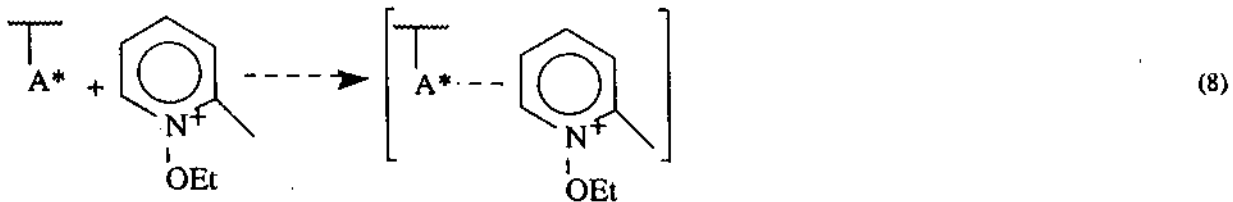
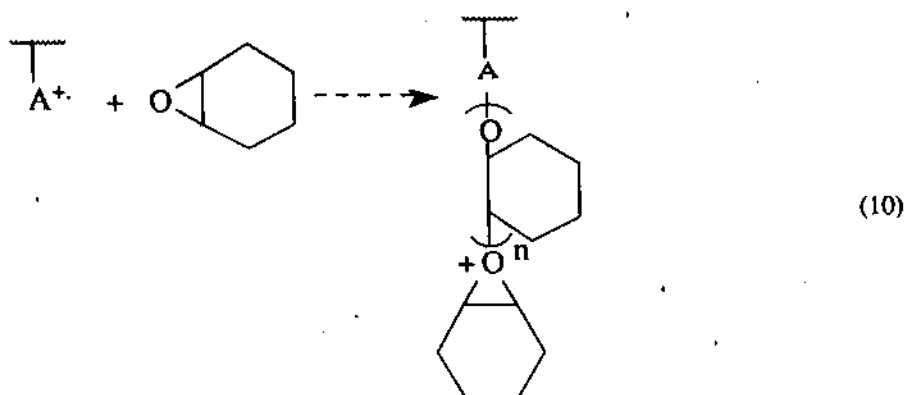


Figure 1. UV spectra of polymers with anthracene side groups (0.3 g/l) and $\text{EMP}^+\text{PF}_6^-$ ($5 \times 10^{-3} \text{ mol/l}$) in methylene chloride; (a) [PVAS 1], (b) [PVAS 2], (c) [PVAS 3] and $\text{EMP}^+\text{PF}_6^-$

It is assumed that in the system under consideration photoexcited anthracene groups undergo internal electron transfer reaction with the pyridinium salts



The resulting side chain anthracene radical cations initiate cationic polymerization of CHO.



The results of photosensitized polymerization of CHO by polymers with anthracene groups are summarized in Table 2. It is interesting to note that the overall conversion of CHO was low when the anthracene concentration was high, probably owing to total complete absorption of irradiation by chromophoric groups and self quenching process. The screening effect on the surface should also be considered since polymeric photosensitizers are employed. In these cases, however, the percentage grafting was higher, indicating that only a limited number of anthracene groups on the chain are yielding radical cations to initiate subsequent cationic polymerization. In addition to extraction experiments, successful grafting was also evidenced by spectral and g. p. c. investigations. The IR spectrum of *n*-hexane insoluble fraction show the characteristic ether bond of PCHO grafted segments at 1090 cm^{-1} in addition to characteristic PVA bands Figure 2.

Table 2. Photosensitized polymerization of CHO using VA-St copolymers in the presence of $\text{EMP}^+\text{PF}_6^-$

Photosensitizer	[PS] (g/l)	Conversion (%)	Grafting (%)
PVAS 1	33.3	40.9	34.58
PVAS 2	33.3	11	29.30
PVAS 3	33.3	14	45.14
PVA	33.3	16.36	37.15
PVA	16.6	20.89	14.00

$$^a[\text{EMP}^+\text{PF}_6^-] = 5.89 \times 10^{-3} \text{ mol/l, } \lambda > 340 \text{ nm, solvent } \text{CH}_2\text{Cl}_2, \text{ time} = 4 \text{ h.}$$

The g. p. c. chromatogram obtained with PVA irradiated by u. v. light in the presence of the pyridinium salt and CHO is shifted to the higher molecular weight range with respect to the chromatogram of the unirradiated polymer (Figure 3). All these results are in support of the proposed mechanism. In this connection it is worth mentioning the work of Crivello and Lee⁹ who used the perylene-sulphonium salt photosensitization system. These authors evidenced incorporation of perylene groups to the polymer backbone by u. v. spectral measurements, indicating direct initiation by photosensitizer radical cations.

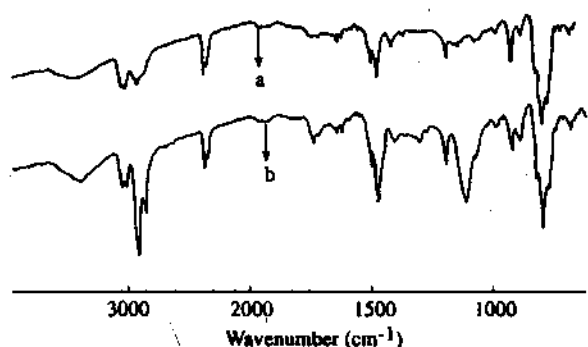


Figure 2. IR spectra of Poly (vinyl anthracene) before (a) and after grafting with cyclohexene oxide by photosensitization (b)

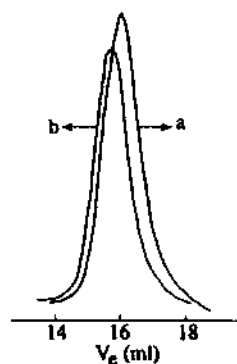


Figure 3. GPC traces of Poly (vinyl anthracene) before (a) and after grafting with cyclohexene oxide by photosensitization (b)

In conclusion these results indicate a useful polymerization process by means of which polymeric radical cations can ultimately be generated by photosensitization giving rise to the formation of graft copolymers.

Acknowledgement

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