

Photosensitized cationic polymerization of cyclohexene oxide: a mechanistic study concerning the use of pyridinium-type salts

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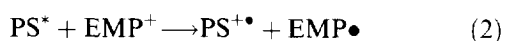
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The photoinitiation of the polymerization of bulk cyclohexene oxide (CHO) containing *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$) and either anthracene or thioxanthone (TX) at $\lambda_{\text{inc}} > 340 \text{ nm}$ was studied. Regarding the action of anthracene it is notable that upon u.v. irradiation of a CHO solution of poly(tetrahydrofuran) bearing terminal anthryl groups a block copolymer, poly(tetrahydrofuran-*block*-cyclohexane oxide), is formed. The optical absorption spectrum of the block copolymer does not possess bands characteristic for anthracene. Therefore, the following mechanism is postulated: electron transfer from singlet excited anthracene molecules to EMP^+ ions results in the formation of anthracene radical cations that react with ethoxyl radicals stemming from the decomposition of EMP^\bullet radicals. 9-Ethoxy-9,10-dihydroanthryl ions generated in this way react with CHO thus initiating its polymerization. Regarding the action of TX it seems that the polymerization of CHO is essentially initiated by protons. The generation of protons has been evidenced. In propylene carbonate solution protons are generated with $\Phi(\text{H}^+) = 0.27$ whereas $\Phi(-\text{TX}) = 0.028$. The postulated mechanism is based on the reaction of triplets, $^3\text{TX}^*$, with both CHO ($k_{\text{RH}} = 3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$) and EMP^+ ions ($k_{\text{ET}} = 4 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$). At low concentration of $\text{EMP}^+\text{PF}_6^-$ ($6.8 \times 10^{-4} \text{ mol l}^{-1}$) $^3\text{TX}^*$ molecules react almost exclusively (93%) with CHO and it appears that ketyl radicals thus formed react with EMP^+ ions, a process eventually resulting in the formation of protons and the regeneration of TX. At relatively high concentration of $\text{EMP}^+\text{PF}_6^-$ ($6.8 \times 10^{-3} \text{ mol l}^{-1}$), thioxanthone triplets are largely (47%) deactivated by electron transfer to EMP^+ ions. The importance of this reaction with respect to its contribution to the initiation of the polymerization of CHO has not yet been revealed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cationic polymerization; cyclohexene oxide; pyridinium ions)

INTRODUCTION

N-Alkoxy-pyridinium and *N*-alkoxy-quinolinium salts are effective photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide, or of vinyl ethers such as *n*-butyl vinyl ether^{1–4}. The application of these salts is limited to the wavelength range $\lambda \lesssim 350 \text{ nm}$, since they are transparent at longer wavelengths. To overcome this problem photosensitizers absorbing light at longer wavelengths, e.g. anthracene, perylene, phenothiazine and thioxanthone were employed successfully and flash photolysis studies revealed that pyridinium ions readily undergo electron transfer reactions with several electronically excited photosensitizers (PS) as depicted by reactions (1) and (2)⁵:



where EMP^+ represents the *N*-ethoxy-2-methyl-pyridinium ion.

Since our former investigations did not give an answer to the question of whether radical cations $\text{PS}^{\bullet+}$ formed according to reaction (2) react directly with the monomers and, in this way, start their polymerization, or whether another initiation mechanism prevails, the present study with anthracene and thioxanthone was performed. These compounds are considered to represent two families of sensitizers, namely polynuclear aromatic compounds and aromatic carbonyl compounds, respectively.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF; E. Merck) was dried over potassium hydroxide and distilled from sodium wire prior to use. Anthracene and 9-anthryl methanol (Aldrich) were recrystallized from ethanol. Thioxanthone (Fluka) was recrystallized from *n*-hexane. Cyclohexene oxide (CHO) was distilled from CaH_2 under argon. 2,6-Di-*tert*-butyl-4-methylphenol (DBMP; Aldrich) was dried overnight at 50°C. Triflic anhydride, NaH (80% dispersion in mineral oil) and (\pm) propylene

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