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Redox-initiated cationic polymerization: the pyridinium salt/ascorbate redox couple

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Pyridinium salts undergo copper catalysed reduction in the presence of ascorbic acid. This system can be used for cationic ring opening polymerizations. The cationic polymerization of cyclohexene oxide, was studied using pyridinium salt/ascorbate redox couple. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

We have recently developed alkoxy pyridinium salts as a new class of photoinitiators for cationic polymerization of cyclic ethers such as cyclohexene oxide (CHO) and alkyl vinyl ethers such as butyl vinyl ether. These salts generate reactive cations directly and indirectly via electron transfer mechanism. Indirect initiators which were successfully employed include various free radical sources, aromatic carbonyl compounds, sensitizers such as perylene, anthracene, substituted vinyl halide and polysilanes[1–5].

Crivello and Lam[6] reported the diaryliodonium salt–ascorbate redox system as an alternative method of initiating the cationic polymerization of appropriate monomers. It seemed therefore suitable to apply the ascorbate reducing agent to pyridinium salts. As it will be shown below, in addition to previously described various methods for pyridinium salts activation, the ascorbate–pyridinium salt redox couple readily initiates cationic polymerization of CHO.

EXPERIMENTAL

Materials

N-ethoxy-2-methyl pyridinium hexafluorophosphate ($EMP^+PF_6^-$) was prepared according to a procedure described previously[7]. Cyclohexene oxide (CHO) and dichloromethane were dried over calcium hydride and then fractionally distilled. Copper(II) benzoate (Pfalz and Bauer), copper(I) benzoate (Aldrich) and ascorbyl-6-hexadecanoate (Aldrich) were of reagent grade and used without further purification.

Initiator studies

The reaction of 2.43×10^{-5} mol EMP^+ with 2.43×10^{-5} mol ascorbyl-6-hexadecanoate and 6.14×10^{-6} mol Cu(II) benzoate was carried out in CH_2Cl_2 under argon atmosphere. After stirring the mixture for 2 h at 25°C a small amount of *n*-hexane was added to the reaction mixture to precipitate unreacted EMP^+ and ascorbyl-6-hexadecanoate. The mixture was analysed by gas chromatography (g.c.) in conjunction with mass spectroscopy (m.s.) (Varian 3700 GC equipped with quartz capillary column, permaphase PVMS/54, length 25 m, i.d. 0.3 mm connected to a Varian MAT-44 mass spectrometer).

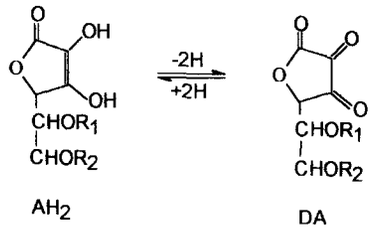
Polymerizations

Glass ampoules containing bulk monomer, a known amount of EMP^+, Cu(II) benzoate and ascorbyl-6-hexadecanoate was flushed with argon, sealed and placed in a constant temperature bath at a given temperature. At the end of a given time, the reaction mixtures were poured into a tenfold excess of methanol and the precipitated polymers were filtered off and dried.

RESULTS AND DISCUSSION

Ascorbic acid (AH_2) and its 5- and 6-acyl derivatives are known as suitable reducing agents due to their slightly acidic character. The acidity (pK_1 4.17, pK_2 11.57) and the reducing properties of AH_2 is attributed to the enediol structure[8].

To determine whether ascorbic acid and derivatives



(1)

$R_1, R_2 = H$ Ascorbic acid

$R_1 = H$, $R_2 = -\overset{O}{\overset{\|}{C}}-(CH_2)_{14}-CH_3$ Ascorbyl-6-hexadecanoate

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are capable of reducing pyridinium salts, the reaction mixture was analysed by g.c.-m.s., with identifications by comparison of the mass-spectral fragmentation patterns of the products with those of known compounds. Reduction of EMP^+ was confirmed by formation of 2-methyl pyridine. First step in the mechanism involves the reduction of Cu(II) to Cu(I) by ascorbic acid or its derivatives (ascorbyl-6-hexadecanoate) giving dehydroascorbic acid and weak acid HY [equation (2)].

$$AH_2 + 2CuY_2 \longrightarrow DA + 2CuY + 2HY \quad (2)$$

$$EMP^+X^- + CuY \longrightarrow CuXY + 2\,\text{  } + C_2H_5OH \quad (3)$$

$$AH_2 + 2CuXY \longrightarrow DA + 2CuY + 2HX \quad (4)$$

$$nM + HX \longrightarrow H(M)_{n-1}M^+X^- \quad (5)$$

When copper(II) compounds are mixed in aqueous solution with AH_2 in the absence of EMP^+, the initial blue colour due to the copper(II) compound is discharged producing an isolable colourless copper(I) ascorbate complex[9].

Copper(I) compounds are efficient reducing agents for the EMP^+ as shown in equation (3). The mixed copper(II) salt CuXY, containing the non-nucleophilic anion X^- is then reduced by ascorbate [equation (4)] producing the strong Brönsted acid HX. Subsequent attack of this acid on the monomer initiates the cationic polymerization. In this process the initial state of the copper compound was reported to have no importance[10] and similar behaviour was observed in the polymerization of CHO when Cu(I) benzoate was used instead of Cu(II) benzoate in this study.

The overall redox reaction can be represented as shown in equation (6).

$$AH_2 + 2EMP^+PF_6^- \longrightarrow DA + 2\,\text{  } + C_2H_5OH + HPF_6 \quad (6)$$

Cu(II) benzoate and ascorbyl-6-hexadecanoate were preferred in this study due to their much better solubility in organic solvents and monomer.

Figures 1–4 give the results of a study of the polymerization of CHO. Increase in the concentration of copper(II) benzoate effects the percent conversion of CHO only to some extent (*Figure 1*), then it remains stable and does not show a dependence to cupric benzoate concentration which indicates the catalytic role of cupric benzoate in the redox system. The conversion of CHO *versus* reaction time is shown in *Figure 2*. It was observed that conversion of CHO increases up to 30 min, then reaches a level off. This behaviour may be explained in terms of competitive attack of monomer and liberated free 2-methyl pyridine group formed according to reaction (6) on the cationic propagating end. During the propagation, monomer rapidly reacts with the growing end in the beginning of the polymerization, whereas competitive attack of 2-methyl pyridine group increases as the monomer concentration decreases. Obviously, this would result in the formation of dead-end which cannot reinitiate the polymerization. Similar behaviour was observed in N-benzyl pyridinium salt initiated systems in which free pyridine was liberated[11].

Figure 3 shows that the per cent conversion to polymer

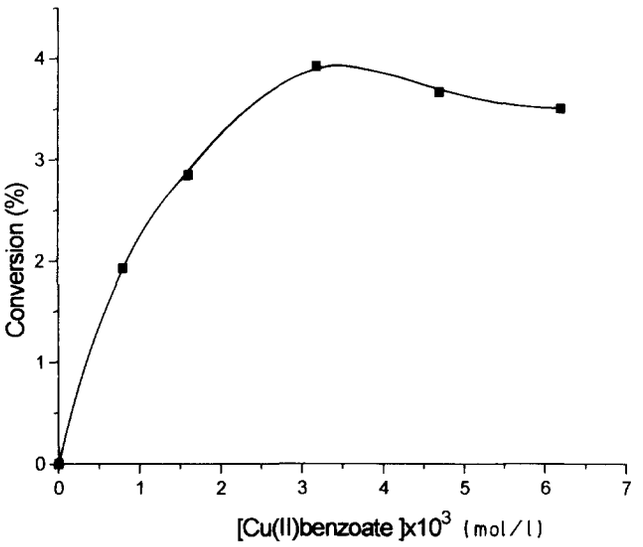

Figure 1 Effect of copper(II) benzoate concentration on the polymerization of 9.88 mol l^{-1} CHO in the presence of 1.2×10^{-2} mol l^{-1} ascorbyl-6-hexadecanoate and 1.2×10^{-2} mol l^{-1} EMP^+ at 25°C, for 40 min

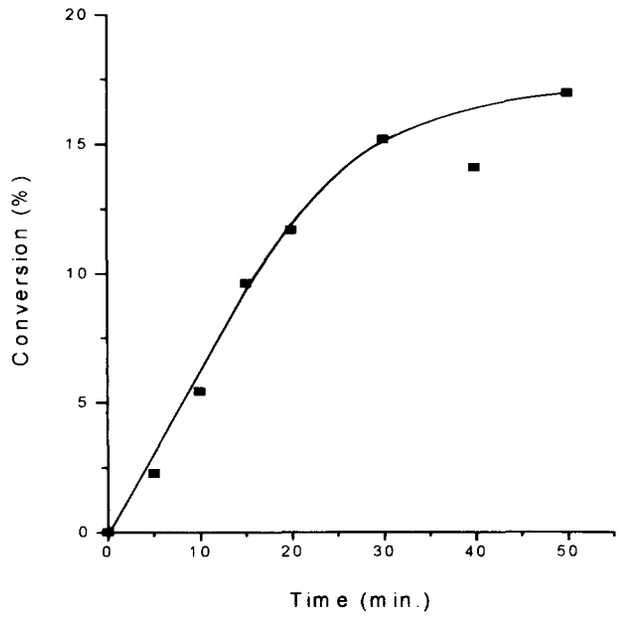

Figure 2 Redox cationic polymerization of 9.88 mol l^{-1} CHO at 25°C, using 2.43×10^{-2} mol l^{-1} EMP^+, 7.4×10^{-2} mol l^{-1} ascorbyl-6-decanoate and 6.1×10^3 mol l^{-1} cupric benzoate at 25°C

is also very low at very low concentrations of the EMP^+ and increases with increasing EMP^+ concentration. This may be due to the fact that the cationic species capable of initiating polymerization is continuously produced from the pyridinium salt, the polymerization does not stop until the initiator is completely consumed or the amount of 2-methyl pyridine exceeds the amount of the initiator unreacted.

Effect of ascorbyl-6-hexadecanoate concentration on the per cent conversion of CHO was also studied. *Figure 4* shows that maximum conversions are obtained when the molar ratio of EMP^+ to ascorbyl-6-hexadecanoate is approximately 1/6. As the temperature of the polymerization increased there is not a certain change at the rate

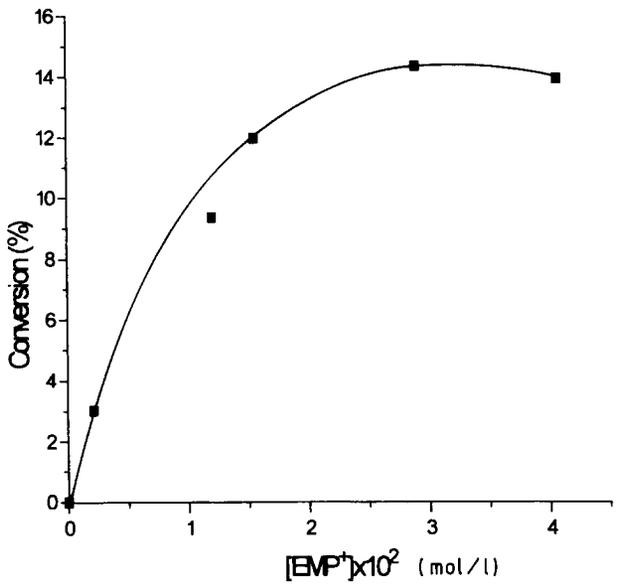

Figure 3 Effect of EMP^+ concentration on the polymerization of 9.88 mol l^{-1} CHO in the presence of 7.4×10^{-2} mol l^{-1} ascorbyl-6-hexadecanoate and 6.1×10^{-3} mol l^{-1} cupric benzoate at 25°C for 50 min

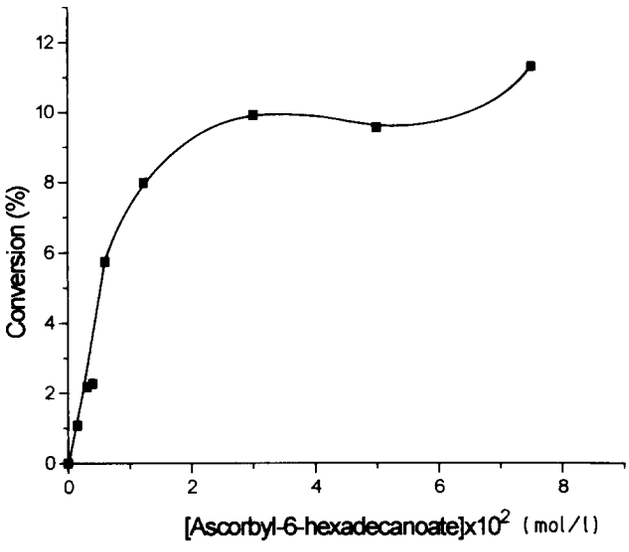

Figure 4 Effect of ascorbyl-6-hexadecanoate concentration on the polymerization of 7.88 mol l^{-1} CHO in the presence of 9.75×10^{-3} mol l^{-1} EMP^+ and 2.45×10^{-3} mol l^{-1} cupric benzoate in CH_2Cl_2 at 25°C for 1 h

Table 1 Polymerization[a] of CHO by using different salts

Salt	$E_{1/2}^{red}$ (V) vs SCE[b]	Conversion (%)
EMP^+	−0.7	17.1
EIQ^+	−0.4	16.0
EPP^+	−0.46	10.2
Ph_2I^+	−0.2	33.0
Ph_3S^+	−1.06	6.6

[a] Ascorbyl-6-hexadecanoate, 7.48×10^{-2} mol l^{-1}; copper(II) benzoate, 6.1×10^{-3} mol l^{-1}; salt, 2.43×10^{-2} mol l^{-1}; CHO, 9.88 mol l^{-1}; temperature, 25°C; time, 40 min

[b] Standard calomel electrode

of monomer consumption up to 60°C, but at 80°C there is a corresponding increase in the extent of polymerization since the rate of decomposition of the pyridinium salt may be increased at high temperatures.

Apart from EMP^+ ions, two other salts namely, N-ethoxy-*p*-phenyl pyridinium hexafluorophosphate ($EPP^+PF_6^-$) and N-ethoxy isoquinolinium hexafluorophosphate ($EIQ^+PF_6^-$) were also examined with respect to their participation in similar redox reactions. For comparison, diphenyl iodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) and triphenyl sulfonium hexafluorophosphate ($Ph_3S^+PF_6^-$) was also included. As can be seen from *Table 1*, Ph_2I^+, which has more favourable reduction potential, is the most efficient reducing agent and pyridinium salts exhibit intermediate behaviour.

In conclusion, cationic polymerization of CHO has been achieved with the ternary system consisting of EMP^+, copper(II) benzoate and ascorbyl-6-hexadecanoate. Copper salt acts as an electron carrier for the reduction of EMP^+ by ascorbate. Protonic acids generated by this way are responsible for the initiation of cationic polymerization.

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