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Electroinitiated polymerization of maleic anhydride with 1,4-dimethylpyridiniumiodide—kinetics of polymerization

Uma S. Sahu

Department of Chemistry, Ranchi College, Ranchi, Bihar, India

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Abstract

The polymerization of maleic anhydride was investigated under constant current electrolysis in a simple H-type divided cell with 1,4-dimethylpyridiniumiodide as supporting electrolyte. The polymer formation depends on polymerization time, current intensity and on the nature of the supporting electrolyte. The polarographic measurements showed that the reduction potential of the supporting electrolyte is less than that of the monomer or the solvent. The product of the electrolysis arising from the supporting electrolyte initiates the polymerization. The mechanism of polymerization is assumed to be an anionic one. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electroinitiation; Kinetics

1. Introduction

There appear to be only two reports on the electrochemical polymerization of maleic anhydride (MA) [1,2]. Bhadani et al. reported on investigation of electrochemically initiated polymerization in dimethylformamide and acetic anhydride using 1-methylpyridiniumiodide as supporting electrolyte. The present article reports a detailed investigation of the electrochemically initiated polymerization of MA in DMF with 1,4-dimethylpyridiniumiodide as supporting electrolyte. 1,4-dimethylpyridiniumiodide has not been employed before for electrochemical polymerization.

2. Experimental

1,4-dimethylpyridiniumiodide was prepared by mixing equimolar amounts of anhydrous r-picoline with methyliodide. The pale yellow precipitate was washed several times with dry benzene to yield a white salt which was dried at 50°C [3]. Toluene, r-picoline and dimethylformamide were purified by standard methods. Electrolysis was carried out in a simple H-type glass cell with two platinum electrodes [2]. The polarograms of the solution were recorded on Hungarian polarograph model OHO11/1. The viscosity measurements were carried out in a Ubbelohde dilution viscometer immersed in a constant temperature bath at 30°C and the concentration of the polymer was 0.50 g per 100 ml DMF.

3. Results and discussion

The electrointiated polymerization of the maleic anhydride (MA) with 1,4-dimethylpyridiniumiodide as supporting electrolyte in DMF occurred exclusively in the cathode compartment. The polymerization did not take place if the

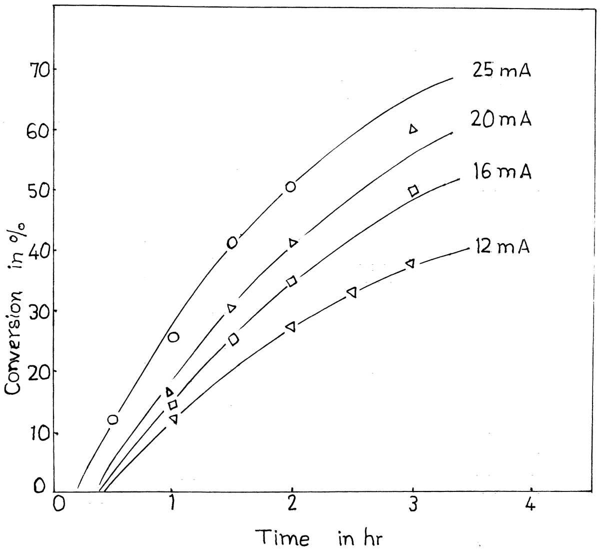

Fig. 1. Polymerization of MA (conc: 0.816 mol.l^{-1}) in DMF with 1,4-dimethylpyridiniumiodide (conc: 0.082 mol.l^{-1}) as a function of current intensity, as indicated by the curves at 30°C.

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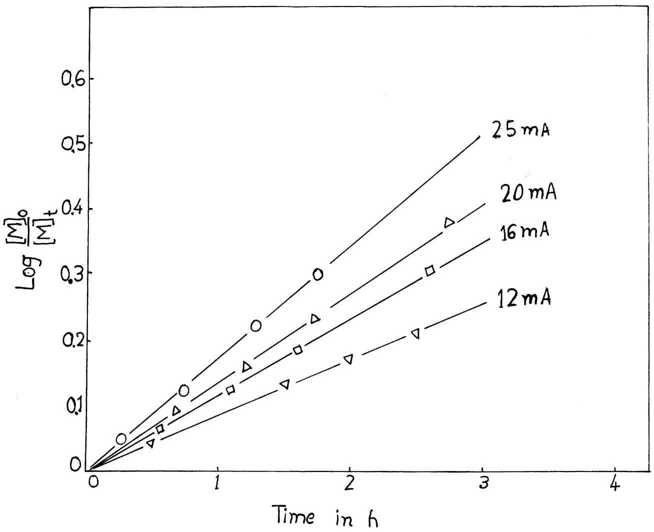

Fig. 2. First-order plots of the conversion curves of Fig. 1.

solution was not subjected to electrolysis. The orange yellow catholyte gradually turned to red brown. On pouring the catholyte obtained after electrolysis into toluene, polymers precipitated as a dark-brown or black mass. Some carbon dioxide gas evolved during polymerization.

Fig. 1 shows the conversion time curves for the polymerization of maleic anhydride with current intensity as parameters and fixed initial concentration of monomer and of 1,4-dimethylpyridinium iodide. A systematic increase in polymer formation with current intensity is observed. The induction period decreases with increasing current intensity and may be due to residual impurities present in the solution. The data presented in Fig. 1 may be treated as for a first-order reaction:

$$\log_{10}[M]_o/[M]_t = 1/2.303\, K_p[I].t$$

where $[M]$ is the monomer concentration (index ‘o’ indicates initial concentration when t = o), $[I]$ is the current intensity, and K_p overall rate constant.

The plot of $\log_{10}[M]_o/[M]_t$ verses polymerization time is indeed linear (Fig. 2), the inhibition period being disregarded. The rate constants obtained from the slopes of Fig. 2 show that the rate constant increases with current intensity (Fig. 3). Polymer formation increase with

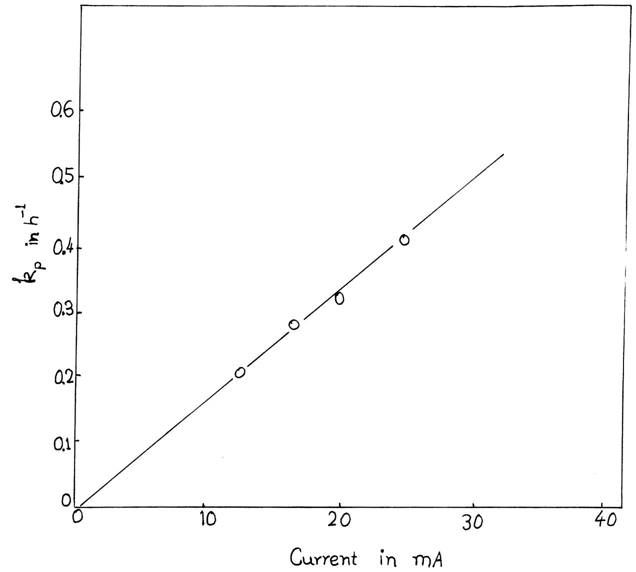

Fig. 3. Influence of current intensity in the cathodic polymerization of MA (conc: 0.816 mol.l^{-1}) in DMF solution of 1,4-dimethylpyridiniumiodide (conc: 0.082 mol.l^{-1}) at 30°C.

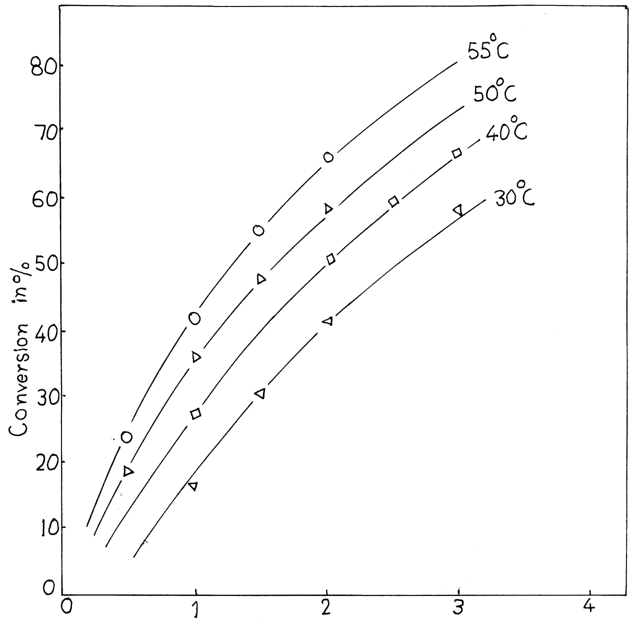

Fig. 4. Effect of reaction temperature on the cathodic polymerization of MA (conc: 0.816 mol.l^{-1}) in DMF solution of 1,4-dimethylpyridiniumiodide (conc: 0.082 mol.l^{-1}) at 20 mA.

Table 1
The rate constants and viscosity number of polymerization of maleic anhydride in the presence of 1,4-dimethylpyridinium iodide (0.082 mol.l^{-1}) in DMF at 30°C

Current in MA	[MA] mol.l^{-1}	Rate constant K_p in h^{-1}	Viscosity number $n_{sp/c}$ dl.g^{-1}
12	0.816	0.016	0.120
16	0.816	0.017	0.122
20	0.816	0.016	0.120
25	0.816	0.016	0.125
20	0.632	0.016	0.166
20	2.041	0.016	0.126

increasing temperature with time at a constant current of 20 mA, initial monomer concentration (0.816 mol.l^{-1}) and concentration of supporting electrolyte (0.082 mol.l^{-1}) is shown in Fig. 4. The overall apparent activation energy is found to be equal to 4.20 kcal.mol^{-1}. (17.60 kJ.mol^{-1}). The viscosity number (0.12 dl/g) is nearly independent of current intensity and of monomer concentration, similar to other photochemically initiated polymerization [4] as summarized in Table 1.

The viscosity numbers of the polymers obtained with 1,4-dimethylpyridiniumiodide suggest that the average molecular weights of the polymer are independent of the concentration of monomer and current intensity.

During the course of electrolysis the applied voltage increased as shown in Fig. 5. The depletion of charge carrier ions, coating of the electrode with a thin polymer film and the presence of resulting polymers might have caused the increase in electrical resistance of the polymerizing solution which enhanced the applied voltage.

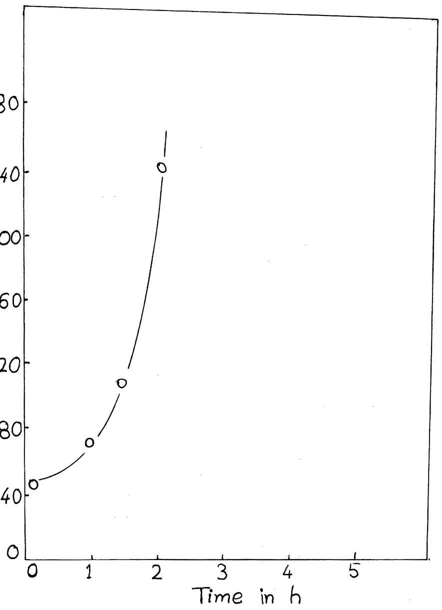

Fig. 5. Influence of supporting electrolyte on the applied voltage during the course of the cathodic polymerization of MA (conc: 2.041 mol.l^{-1}) with 1,4-dimethylpyridiniumiodide (conc: 0.082 mol.l^{-1}) at 20 MA at 30°C.

The polarographic measurements show that the reduction potential of 1,4-dimethylpyridinumiodide is less negative than that of maleic anhydride or the solvent, as shown in Fig. 6. The polarographic results under constant current electrolysis suggest that the polymerization is plausibly initiated by the product of electrolysis arising from supporting electrolytes, although the initiation by direct electron transfer from cathode to monomer cannot be ruled out completely [5,6]. The electrochemical polymerization of MA also took place with decarboxylation, as confirmed by the

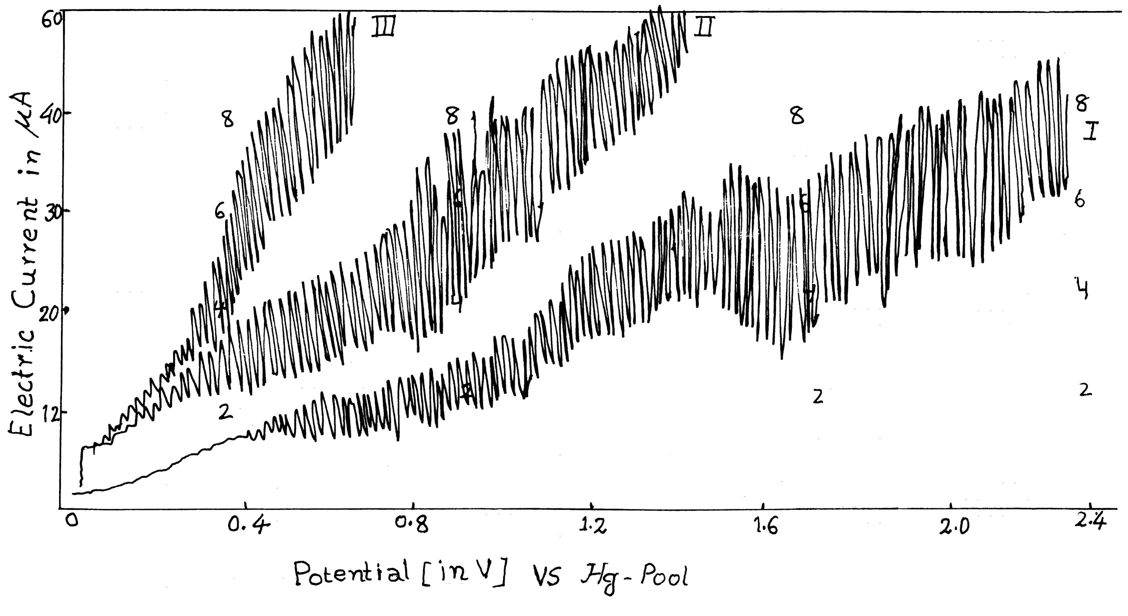

Fig. 6. Polarograms in dimethyl formamide of (I) Saturated tetramethyl chloride as supporting electrolyte; (II): maleic anhydride (0.816 mol.l^{-1}); and (III) 1,4-dimethylpyridiniumiodide (0.082 mol.l^{-1}).

change in colour which suggests that the polymerization mechanism is possibly anionic [7–9].

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