

Electro-initiated cationic polymerization of α -methylstyrene by direct electron transfer

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Electro-initiated cationic polymerization of α -methylstyrene in a tetrabutylammonium fluoroborate–dichloromethane system has been investigated at various temperatures by constant potential electrolysis. It is established that polymerization occurs at low temperatures with higher yields. Apparent activation energy of the electro-initiated polymerization is $-64.3 \text{ kJ mol}^{-1}$.

(Keywords: α -methylstyrene; electro-initiation; poly(α -methylstyrene); direct-initiation; cyclic voltammetry; electrolysis)

INTRODUCTION

There have been several reports on the chemically-initiated polymerization of α -methylstyrene^{1–4}. Polymerization in an electric field has been studied also^{5–10}. Especially in the last decade, electro-initiated polymerization of olefins has been studied in detail. Electro-initiated anionic polymerization of α -methylstyrene has been reported by Yamazaki¹¹. The cyclic voltammogram of α -methylstyrene with one oxidation peak potential (E_{pa}) and no reduction peak potential (E_{pc}) within the range of the electrolyte–solvent system used, has been published previously⁵. Due to the absence of E_{pc} , direct anionic initiation by constant potential electrolysis (CPE) is not possible, which has been confirmed by Yamazaki¹². Cationic initiation via direct electron transfer by CPE should be possible, as any substrate apart from the monomer is electro-inert at E_{pa} of the monomer. Controlled-current electrolysis, however, is not selective at initiation as the electrolyte–solvent system may also be involved at the electro-initiation step.

EXPERIMENTAL

Materials

Purification of α -methylstyrene and tetrabutylammonium fluoroborate (TBAFB) has been described previously¹³. Dichloromethane (DM) was dried and distilled over CaH_2 .

Cyclic voltammetry

The cyclic voltammetry system had been discussed previously⁵. The reference electrode in the three electrode system was a $\text{Ag}^\circ/\text{Ag}^+$ electrode which was 0.01 M in silver fluoroborate and 0.10 M in tetrabutylammonium fluoroborate. The reference electrode was isolated from the cell by a tube which had a Luggin capillary tip and was filled with 0.10 M electrolyte. Cyclic voltammograms of α -methylstyrene were obtained in dichloromethane at temperatures ranging from $+10^\circ\text{C}$ to -40°C .

Polymerization procedure

Polymerizations were carried out in divided cells at platinum foil electrodes (6 cm^2 each). Solvent and monomer were freshly distilled and transferred into the cell containing TBAFB while the cell was being purged with nitrogen. Electrolyses were carried out at pseudo-oxidation peak potential of the monomer to avoid the resistance due to the film formation of the polymer on the anode. Samples ($40 \mu\text{l}$) for analysis of monomer concentrations were removed with syringes from both compartments at definite time intervals and transferred into 1 ml methanol. For the first 2 min samples were taken every 15 s. Unreacted monomer concentrations were determined by gas chromatography. A column (2.80 m) packed with 1.5% Apiezon L on 80–100 mesh size chromosorb was used. Indene was the internal standard for gas chromatography measurements.

Intrinsic viscosities of the polymers were measured at 30°C in benzene and the molecular weights were determined from the equation given in literature⁹. The necessary amount of polymers for viscometric studies were collected from several repeated experiments at each temperature.

RESULTS AND DISCUSSION

For analysis of reacted monomer concentrations, $40 \mu\text{l}$ aliquots were taken from both compartments and transferred into 1 ml of methanol containing $10 \mu\text{l}$ of indene as internal standard. Samples which were taken only from one compartment (anolyte) gave misleading results in the gas chromatography analysis of the solutions due to the diffusion of the monomer through the sintered disc of the cell. Whenever a certain amount of monomer was consumed, equilibrium was being established quickly between the two compartments by means of diffusion due to the concentration gradient. This difficulty was eliminated by taking aliquots from both compartments and transferring them into 1 ml of methanol. There was no polymerization in the cathode compartment and the only con-

sumption of monomer in the cathode compartment was due to negligible electrolytic destruction. Therefore, the average disappearance of monomer was assumed to be by polymerization in the anode compartment only.

The cyclic voltammogram of α -methylstyrene¹³ shows that it could be polymerized cationically by a direct electron mechanism if the electrolysis was carried out at CPE at $E_{p,a}$ (+1.85 V) of the monomer. Oxidation peak potential ($E_{p,a}$) measured in dichloromethane at 20°C is +1.60 V versus $\text{Ag}^\circ/\text{Ag}^+$ reference electrode, which shifts to +2.20 V at -40°C (Figure 1).

As seen in Figure 1, shifts in oxidation peak potential of α -methylstyrene were observed due to the film coating on the working electrode at low temperatures. This behaviour can not be attributed to a decrease in temperature. When the surface of electrode was cleaned and flamed before each CV measurement, the effect of the temperature on $E_{p,a}$ was not easily detectable. Even at room temperature, after few cycles, the working electrode was still coated by a film which caused the $E_{p,a}$ to shift to more anodic potentials than +1.60 V. Electrolyses carried out at the oxidation peak potential of α -methylstyrene ($E_{p,a} = +1.60$ V) had very low yields due to the film formation on the anode surface which prevented the necessary current passing through the system. Therefore, polymerizations of α -methylstyrene were carried out at a potential above the $E_{p,a}$ of α -methylstyrene measured on a freshly cleaned electrode. The potential for the polymeri-

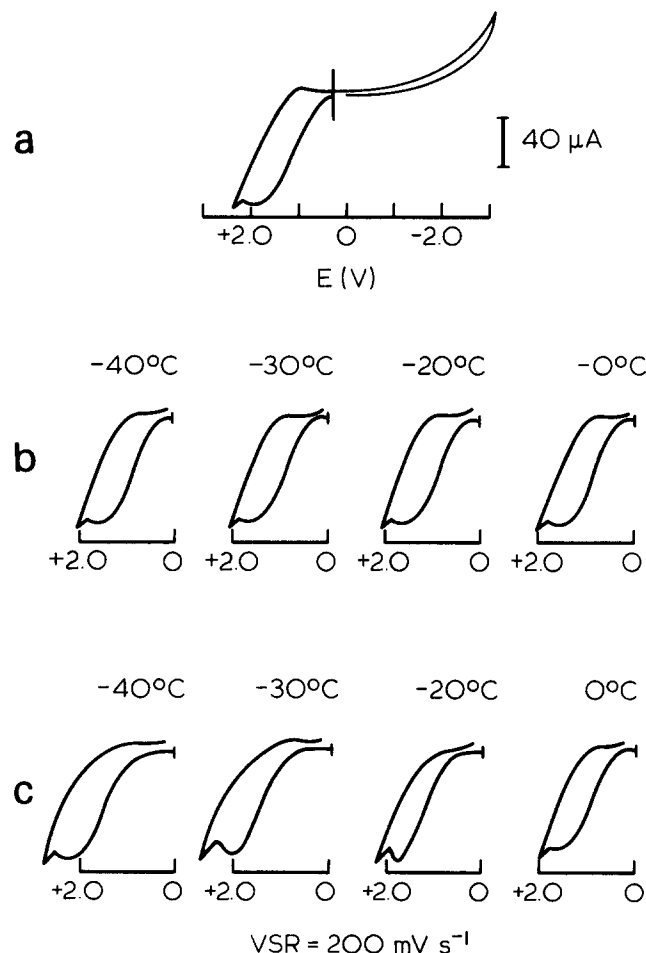


Figure 1 Cyclic voltammogram of α -methylstyrene (10^{-3} M) obtained on a Pt° wire versus $\text{Ag}^\circ/\text{Ag}^+$. (a) Measured in acetonitrile; (b) measured in dichloromethane. Electrode surface flamed before each run; (c) measured in dichloromethane via successive runs without clearing the electrode surface

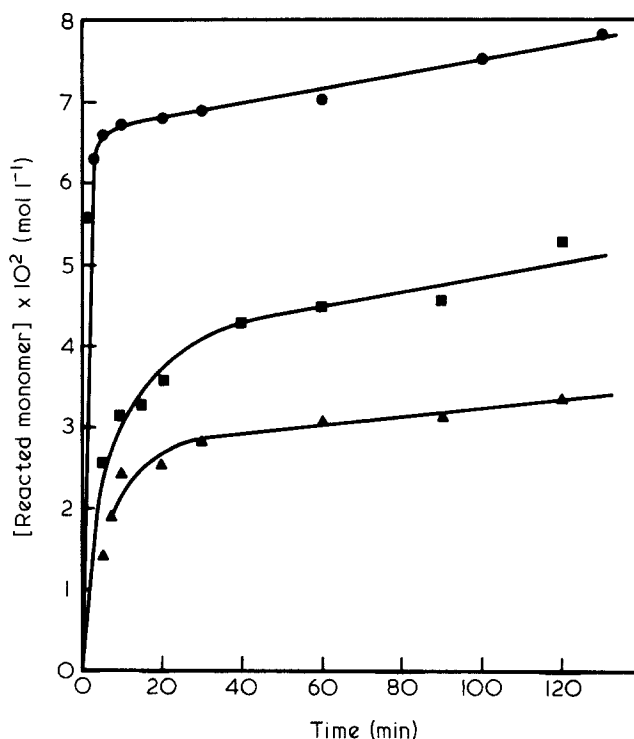


Figure 2 Electro-initiated cationic polymerization of α -methylstyrene at three different temperatures. Eight points corresponding to the sampling at every 15 s for the first 2 min are not shown. \bullet , -40; \blacksquare , -30; \blacktriangle , -20°C

Table 1 Polymerization of α -methylstyrene carried out in dichloromethane by constant potential electrolysis

T (°C)	Yield ^a (%)	$MW \times 10^{-3}$	Initial rate $\times 10^5$ ($\text{mol l}^{-1} \text{s}^{-1}$)	$E_{p,a}^b$ (V)	E_p^c (V)
-40	1.74	16.5	58.30	+1.6	+2.2
-30	0.82	3.4	7.41	+1.6	+2.2
-20	0.39	2.7	4.14	+1.6	+2.2
+10	No polymer	—	—	+1.6	+2.2

^a Polymer obtained by precipitation in methanol

^b Measured in dichloromethane at platinum electrodes versus $\text{Ag}^\circ/\text{Ag}^+$ reference electrode

^c Electrolysis potential which is maintained constant during the polymerization reaction

zation of α -methylstyrene was chosen as +2.20 V versus $\text{Ag}^\circ/\text{Ag}^+$.

α -Methylstyrene was cationically polymerized in TBAFB-DM solution at -20°, -30°C and -40°C. No polymer was obtained at +10°C. For each polymerization temperature the plots of reacted monomer concentration versus time are given in Figure 2. Polymerization of α -methylstyrene (0.63 M) was carried out at +2.20 V versus $\text{Ag}^\circ/\text{Ag}^+$ in unstirred solutions. The retarding effect of stirring solutions has been discussed previously⁵.

Apparent activation energy of the polymerization was -64.3 kJ mol^{-1} . Polymerization rates, at low temperatures, had decreased almost to zero at room temperature (Table 1). At low temperatures, higher molecular weight polymers were obtained. Similar results for chemically-initiated polymerization of α -methylstyrene at low temperatures have been reported¹⁴. Figure 2 shows that the rate of conversion decreases rapidly which may be due to

the formation of a thin polymer film on the anode surface reducing the current and, hence, the initiation rate. This behaviour confirms the CV results shown in *Figure 1*. No differences were observed in the i.r. spectra of polymers obtained electrochemically or by chemical initiation. Dichloromethane was more suitable than acetonitrile as the chain transfer constants are minimal¹⁵.

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