Electroinitiated copolymerization of indene with β-methoxystyrene

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Electroinitiated copolymerization of indene with β-methoxystyrene was carried out at 0°C and five different potentials. Monomer consumption was studied by cyclic voltammetry. It is known that, when the difference between oxidation potentials of two monomers is large, polymerization potential affects copolymer composition. In the present study indene and β-methoxystyrene were selected because their oxidation potentials are almost equal, *ca.* +1.40 V. The effect of polymerization potential on copolymer composition was studied. The copolymer composition did not change with polymerization potential, a novel result, for these monomers with almost equal oxidation peak potentials. The total reacted monomer concentration did not change with polymerization potential either. The amount of precipitated polymer, however, increased with polymerization potential.

(Keywords: electroinitiation; copolymerization; indene; β-methoxystyrene)

INTRODUCTION

Selective activation of the monomer by constant potential electrolysis (c.p.e.) is one of the most attractive features of electrochemical polymerization. Constant current[1–6] and constant potential electrolysis have been successfully used to polymerize various monomers[1–8]. As well as in homopolymerization, c.p.e. has been used in copolymerization of different monomers[9,10]. During such studies copolymer composition was observed to depend on polymerization potential[9,10]: when two monomers of different oxidation potentials ($E_{p,a}$) are electrochemically polymerized the monomer with higher oxidation potential is incorporated more into the copolymer than the other, with increasing polymerization potential (E_{pol}).

This interesting behaviour begged the question whether this is peculiar to monomers with different oxidation potentials. To clarify this, two monomers of almost the same oxidation potentials were copolymerized at different potentials. Indene ($E_{p,a} = +1.40$ V *versus* Ag^0/Ag^+) and β-methoxystyrene ($E_{p,a} = +1.35$ V *versus* Ag^0/Ag^+) were selected to be copolymerized electrochemically. In an earlier publication[10], indene was copolymerized with isoprene ($E_{p,a} = +2.00$ V *versus* Ag^0/Ag^+) and it was found that incorporation of indene, with lower $E_{p,a}$ than isoprene, decreases as the potential is increased. In the present work, the effect of E_{pol} on copolymerization of indene with β-methoxystyrene was investigated.

EXPERIMENTAL

Materials

Tetrabutylammonium fluoroborate (TBAFB) was purified according to the method given earlier[11]. Dichloromethane was dried and distilled over CaH_2. Acetonitrile was dried over CaH_2 overnight, refluxed for 6 h and then fractionally distilled under dry N_2 atmosphere. Indene was washed with 6 M HCl, then with 40% NaOH aqueous solution and finally with distilled water. It was dried and distilled over CaH_2 at 24°C and 5 mmHg (0.7 kPa). The middle fraction was used freshly. β-Methoxystyrene was distilled under reduced pressure and the middle fraction was used.

Cyclic voltammetry

Details of the cyclic voltammetry (c.v.) system have been given previously[12]. In the present work monomer consumption was followed by c.v. For this purpose a specially designed c.v. cell with 3 ml capacity was used (*Figure 1*). The working electrode was a Pt bead, 1 cm

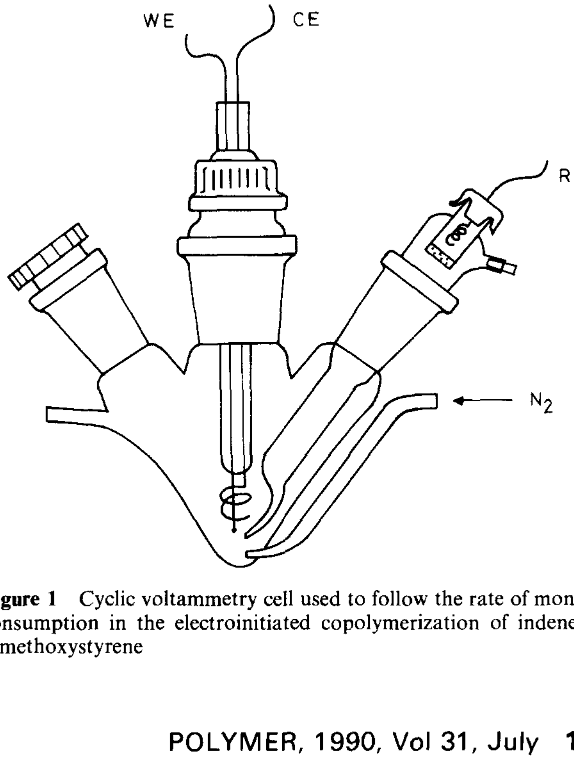

Figure 1 Cyclic voltammetry cell used to follow the rate of monomer consumption in the electroinitiated copolymerization of indene and β-methoxystyrene

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long; the counter electrode was Pt wire, 3 cm long, coiled around the working electrode; and the reference electrode was Ag^0/Ag^+ (0.01 M). During the electrolysis, 40 μl samples from each compartment of the electrolysis cell were transferred to 3 ml of acetonitrile and were later analysed for unreacted monomer concentrations by c.v. Calibration curves (concentration *versus* peak current) for both of the monomers were prepared in advance, for determination of unknown samples drawn from the electrolysis cell at certain time intervals. A cyclic voltammogram of each sample withdrawn was taken individually at room temperature.

Electroinitiated copolymerization

Dichloromethane (30 ml) and 0.1 M TBAFB were used as the solvent–electrolyte couple. The solution was ≈0.014 M in indene and 0.013 M in β-methoxystyrene. The electrolysis cell used for this purpose was H shaped, as used in previous studies[10]. The two compartments were isolated by a fine porosity sintered disc. The working and counter electrodes were 1 cm^2 platinum foils. The reference electrode was Ag^0/Ag^+. The solution was purged with dry nitrogen before electrolysis started. The cell and contents were allowed to attain thermal equilibrium at 0°C before the electrolysis was triggered. The electrolysis was carried out at 0°C and at five different potentials: 1.40–2.20 V at intervals of 0.20 V, all anodic with respect to the Ag^0/Ag^+ reference electrode. The solution in the anodic part of the cell was kept quiescent during the 2 h of electrolysis and kept under nitrogen throughout this period. The reaction was followed for up to 2 h by withdrawing 40 μl samples from each of the anode and cathode compartments and analysing for unreacted monomer concentration by cyclic voltammetry.

The yield was determined by precipitating the cell content in an excess of methanol, filtering, washing, drying and weighing the copolymer obtained. The composition of the copolymer was determined by infrared (i.r.) analysis.

RESULTS AND DISCUSSION

Cyclic voltammograms of β-methoxystyrene (BMS) and indene (In) are given in *Figure 2*. The monomers have irreversible anodic peaks at +1.35 V (BMS) and +1.40 V

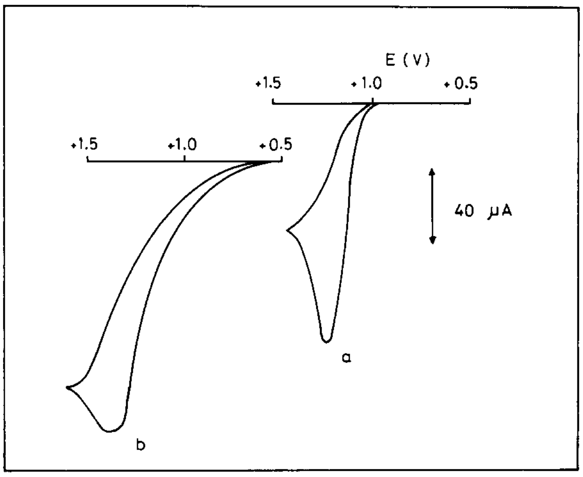


Figure 2 Cyclic voltammograms of (a) β-methoxystyrene and (b) indene obtained in CH_3CN–TBAFB *versus* Ag^0/Ag^+ reference electrode

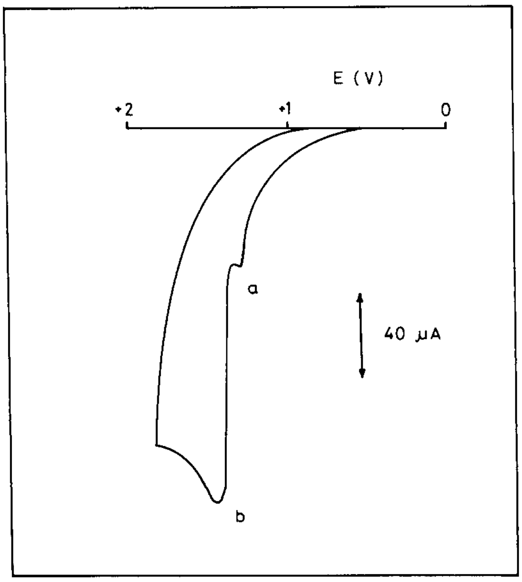


Figure 3 Cyclic voltammogram of β-methoxystyrene–indene mixture

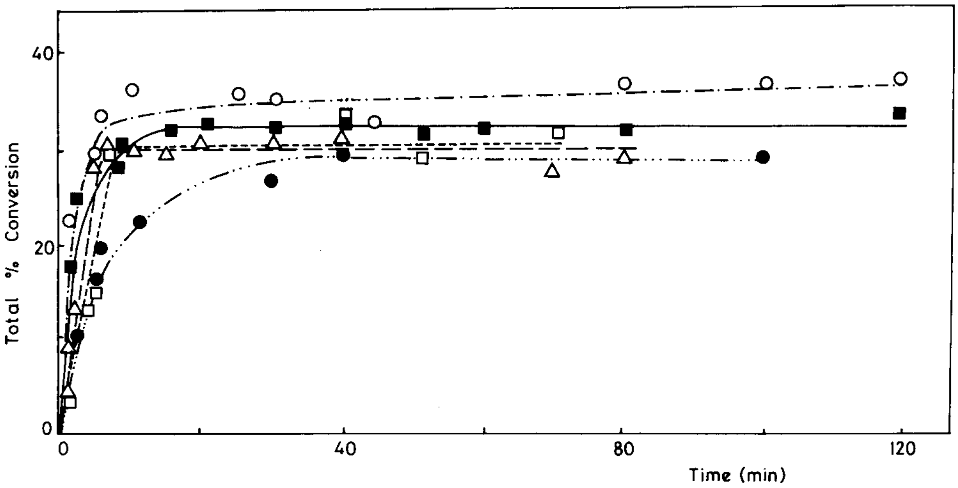


Figure 4 Total percentage conversion *versus* time for indene–β-methoxystyrene copolymerization at various polymerization potentials. ○, —·—·—, 1.4 V; △, ———, 1.6 V; □, -----, 1.8 V; ●, —··—··, 2.0 V; ■, ——, 2.2 V

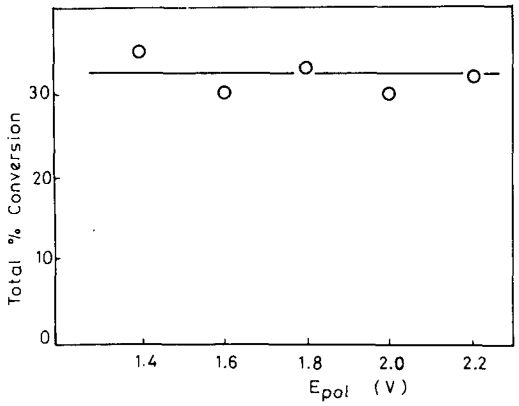
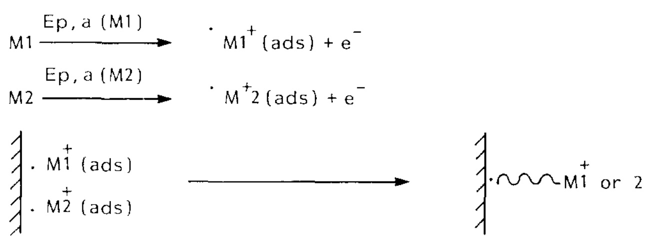


Figure 5 Total percentage conversion *versus* polymerization potential for electroinitiated copolymerization of indene with β-methoxystyrene

(In) *versus* the Ag^0/Ag^+ reference electrode in the CH_3CN–TBAFB system. A cyclic voltammogram of indene–β-methoxystyrene mixture is shown in *Figure 3*. For the calibration curve, different amounts of the two monomers were mixed in CH_2Cl_2 and c.v.s were taken. Straight lines were obtained by plotting concentration *versus* peak current for each monomer. The percentage conversion *versus* time plots are shown in *Figure 4*. The conversion–time plots assume asymptotic shapes after the first few minutes of electrolysis. Furthermore, total percentage conversions changed little with polymerization potential, as seen in *Figure 5*. *Table 1* shows that the total conversion fluctuates around an average value of 32% for various E_{pol} values.

The copolymer composition as determined by i.r. analysis was found to be 16.4% in BMS (*Table 1*). Within experimental error, the percentage composition remained unchanged as the polymerization potential was increased. This is a novel result for electrochemical copolymerization systems. Previous studies had shown that the composition of the monomer with higher oxidation potential increases with polymerization potential, whereas the reverse is true for the other monomer. In the present study it is established that, when the two monomers have almost equal oxidation potentials, their composition in the copolymer does not change with polymerization potential (*Figure 6*).



In electroinitiated copolymerization where the oxidation potentials of the two monomers are different, there will be competition between them on the anode to be adsorbed, oxidized and added to the growing end. At low polymerization potentials, if $E_{p,a}(M_1) \ll E_{p,a}(M_2)$, then the amount of the oxidized form of M_1 which is polarized and adsorbed on the anode should be much higher than that of M_2. Thus the contribution of M_1 to copolymerization will be greater than M_2. As the polymerization potential increases, however, the chance of adsorption and oxidation of M_2 on the anode should increase. Hence the contribution of M_2 to copolymerization increases as polymerization potential increases. On the other hand, for monomers with similar $E_{p,a}$ values, the monomers should be affected equally by the polymerization potential. Therefore, the composition of copolymer obtained at high potentials will be the same as that obtained at low potentials. This approach can be generalized to explain the effect of potential on electroinitiated copolymerization for monomers with similar or different $E_{p,a}$ values. Our previous and present experimental results are consistent with this generalization.

The yield is observed to increase with increasing polymerization potential (*Table 1* and *Figure 7*). The difference between total conversion calculated for disappearance of monomer and yield obtained from precipitated polymer can be explained by the formation of oligomers that cannot be precipitated from the electrolysis solution.

CONCLUSIONS

As established in earlier work[9,10], applied polymerization potential affects copolymer composition in electroinitiated polymerization. The extent of this effect depends greatly on the difference between the peak potentials of the monomers concerned. Thus a monomer couple with almost equal $E_{p,a}$ values yields the same composition even at different polymerization potentials.

Table 1 Copolymerization of indene with β-methoxystyrene at 0°C by c.p.e.

	Composition[b]			
E_{pol}[a] (V)	Indene (%)	BMS (%)	Total conversion (%)	Yield[c] (%)
+1.40	83.0	17.0	35	3.04
+1.60	86.8	13.2	30	5.04
+1.80	79.2	20.8	33	6.10
+2.00	83.5	16.5	30	7.11
+2.20	84.5	15.5	32	10.80
Average	83.4	16.4	32	–

[a] *Versus* Ag^0/Ag^+ (0.01 M) reference electrode
[b] Determined by i.r. analysis
[c] After 2 h of electrolysis

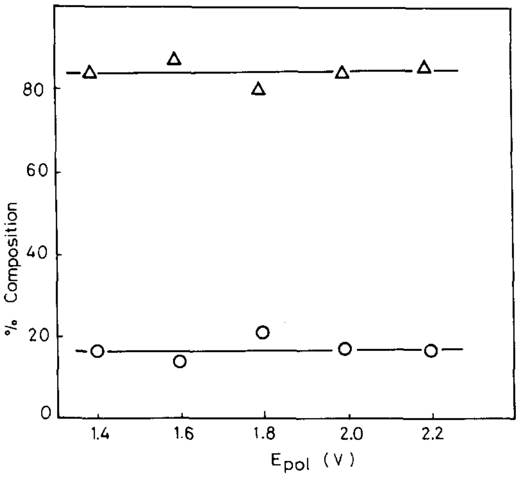


Figure 6 Percentage composition *versus* polymerization for (△) indene and (○) β-methoxystyrene

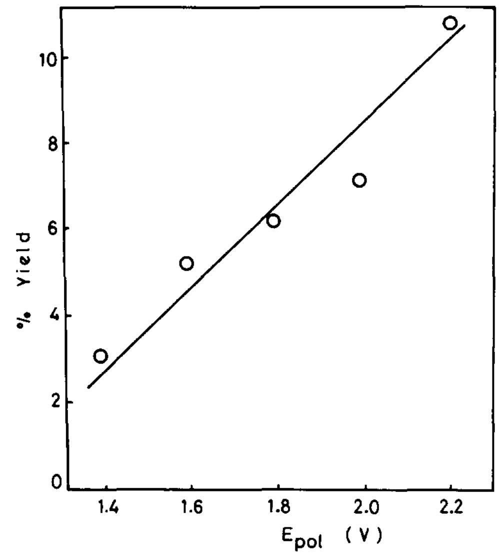


Figure 7 Total percentage yields (obtained by precipitation after 2 h electrolysis) *versus* polymerization potential

In this study it was also established that cyclic voltammetry is a useful tool for kinetic studies in electroinitiated polymerization and is a rapid, reproducible method.

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