Electroinitiated cationic copolymerization by direct electron transfer

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Electroinitiated cationic copolymerizations of indene-4-methoxystyrene and indene-β-bromostyrene monomer couples were investigated in dichloromethane by constant potential electrolysis. Copolymer compositions were determined by i.r. spectroscopy and reactivity ratios for the monomers were calculated according to integrated Lewis–Mayo equation. The composition of copolymers and the reactivity ratios were discussed in terms of anodic peak potentials of monomers.

(Keywords: electroinitiation; electro-copolymerization; indene; 4-methoxystyrene; β-bromostyrene; copolymerization-potential)

INTRODUCTION

Electroinitiated copolymerizations, by constant current electrolysis in the presence of donor-acceptor complexes, have been reported by various authors[1–4]. Constant potential electrolysis (CPE) on the other hand, enables polymerization via direct electron transfer[5,6]. Copolymerization by CPE can be achieved at a given applied voltage provided that the oxidation peak potentials $(E_{p,a})$ of the monomers are known. The copolymer compositions, then, may be expected to depend on the applied copolymerization potential (E_{pol}) due to the differences in the $E_{p,a}$ of the monomer couples.

When E_{pol} is kept at a potential higher than $E_{p,a}$ of both monomers, the monomer with the lower $E_{p,a}$ (M_1) should produce more cations (or radical cations) than the other monomer (M_2). Therefore, most of the polymer chains should be activated by the M_1 cation. If M_1 is copolymerized by another monomer with the same $E_{p,a}$ (M_3) then upon electroinitiation (at E_{pol}) both monomers, M_1 and M_3 should produce approximately the same amount of cations (or radical cations). The polymer chains therefore should be activated by both M_1 and M_3 cations equally. As a result in the case of M_1–M_2 copolymerization, more of M_1 is expected to be incorporated into the copolymer as compared with the M_1–M_3 case.

EXPERIMENTAL

Materials

The purifications of tetrabutylammonium fluoroborate (TBAFB) and acetonitrile have been described previously. Dichloromethane was dried and distilled over CaH_2. Indene was washed with 6 M HCl, then with 40% NaOH and stirred on CaH_2 for 12 h. The dried monomer was distilled over fresh CaH_2 at 24°C at 5 mm Hg pressure.

4-Methoxystyrene was washed with 10% NaOH and stirred on CaH_2 for 12 h. It was distilled at 40°C at 4 mm Hg pressure. β-Bromostyrene was distilled at 46°C at 5 mm Hg and stored in dark condition till use.

Cyclic Voltammetry

The cyclic voltammetry system had been discussed previously[8]. Cyclic voltammograms were taken in acetonitrile at room temperature.

Procedure

The CPE system and the electrodes were discussed earlier[8]. Solvent and indene (0.64 M) and β-bromostyrene (0.28 M) monomers were freshly distilled and transferred into the divided cell containing TBAFB and the cell was purged with nitrogen. 40 µl samples for monomer concentration analysis were removed with styringes from both compartments at specific time intervals into methanol (1 ml). Unreacted monomer concentrations were determined by gas chromatography with a column (2.80 m) packed with 1.5% Apiezon L on 80–100 mesh size chromosorb. α-Methylstyrene was employed as the internal standard. Intrinsic viscosities of the copolymers were measured at 30°C in benzene.
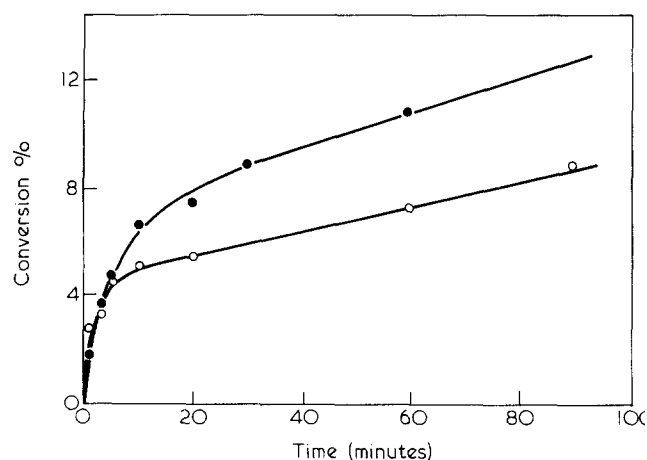

Figure 1 Total conversions of copolymers as measured by gas chromatography. Calculated from $\{[M_1]_t + [M_2]_t\}/\{[M_1]_0 + [M_2]_0\}$: (●) Indene-4-methoxystyrene copolymerization; (○) Indene-β-bromostyrene copolymerization

Table 1 Copolymerization of indene and β-bromostyrene by constant potential electrolysis at 20°C

E_{pol}[a] (V)	% Composition[b]		% Conversion[c]	Reactivity ratios		$[\eta]$[d] (dl/g)
	Indene	β-BrSt		Indene	β-BrSt	
+2.50	89.5	11.5	8.8	0.88 ± 0.01	0.90 ± 0.01	0.0172

[a] Copolymerization potential *versus* Ag^0/Ag^+ reference electrode
[b] Calculated by i.r. spectroscopy
[c] Calculated by gas chromatography after 150 min
[d] Measured in benzene at 30°C

Table 2 Copolymerization of indene and 4-methoxystyrene by constant potential electrolysis at 20°C

E_{pol}[a] (V)	% Composition[b]		% Conversion[c]	Reactivity ratios		$[\eta]$[d] (dl/g)
	Indene	4-MeoSt		Indene	4-MeoSt	
+2.50	58.0	42.0	13.3	0.84 ± 0.01	0.84 ± 0.01	0.1745

[a] Copolymerization potential *versus* Ag^0/Ag^+ reference electrode
[b] Calculated by i.r. spectroscopy
[c] Calculated by gas chromatography after 150 min
[d] Measured in benzene at 30°C
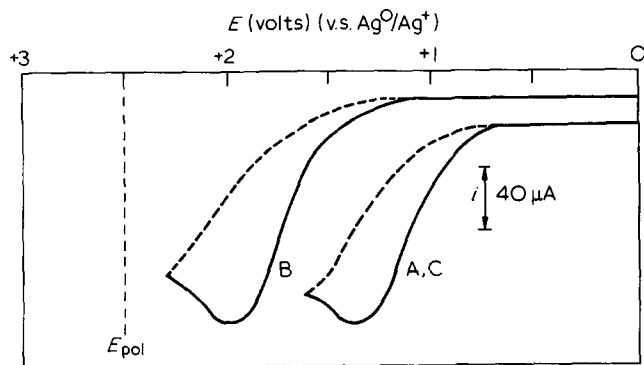
Figure 2 Cyclic voltammograms of indene (A), β-bromostyrene (B) and 4-methoxystyrene (C)

RESULTS AND DISCUSSION

Anodic peak potential $(E_{p.a})$ of indene was previously given as +1.40 V[8]. $E_{p.a}$ values of β-bromostyrene and 4-methoxystyrene are +2.00 V and +1.40 V respectively *versus* Ag^0/Ag^+ reference electrode.

The total conversion with respect to time for indene-4-methoxystyrene and indene-β-bromostyrene copolymerizations are given in *Figure 1*.

As can be seen in *Tables 1* and *2* at the same temperature and applied copolymerization potential (E_{pol}) the compositions of the two copolymers differ greatly. In the case of indene (M_1)–β-bromostyrene (M_2) copolymerization the amount of M_1 in the copolymer is much higher than that of M_2. Since there is a large difference between the oxidation peak potentials $(E_{p.a})$ of monomers M_1 $(E_{p.a} = +1.40$ V) and M_1 $(E_{p.a} = +2.00$ V), the observed percentage composition of 89.5 to 11.5 is not surprising. However, when the $E_{p.a}$ values for both monomers are identical as in the case of M_1–M_3 (4-methoxystyrene) copolymerization, the incorporation of both monomers is comparable. Percentage composition of the copolymer is 58.0 to 42.0 with respect to M_1 and M_3, as given in *Table 2*.

The above mentioned observations can be explained by the $E_{p.a}$ values of the monomers. As can be seen in *Figure 2* when E_{pol} is kept at +2.50 V in the case of M_1–M_2 copolymerization, more M_1 will be converted to cations (or radical cations) than M_2, thus more M_1 can be incorporated into the copolymer. In the second case however equal amounts of M_1 and M_3 cations will be produced and be incorporated in similar amounts to the copolymer.

Reactivity ratios were calculated from the integrated Lewis–Mayo equation[9] as 0.88 and 0.90 for the M_1–M_2 copolymerization and 0.84 and 0.84 for the M_1–M_3 copolymerization.

In conclusion we have shown that copolymer compositions depend on the $E_{p.a}$ values of monomers in electroinitiated copolymerizations.

ACKNOWLEDGEMENT

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