Electroinitiated copolymerization of α-methylstyrene and isoprene in the presence and absence of ultrasound

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(Received 1 July 1985; revised 11 September 1985)

Electroinitiated cationic copolymerization of isoprene with α-methylstyrene was achieved by constant potential electrolysis both in the absence and presence of ultrasound. The copolymerizations were carried out at different potentials. The effects of polymerization potential and ultrasound on the rate of polymerization, copolymer composition and reactivity ratios were investigated. In the absence of ultrasound critical copolymer potential was found to be +3.00 V *versus* Ag^0/Ag^+ at which $r_1 = r_2$ and mole per cent of both monomers in the copolymer become equal.

(Keywords: electroinitiation; constant potential electrolysis; reactivity ratios; copolymerization; ultrasound)

INTRODUCTION

Most of the previous studies on electroinitiation in polymerization use constant current electrolysis, in which the potential cannot be held constant[1]. This is mainly due to lack of measurements of the oxidation–reduction peak potentials of monomers. The polymerization mechanism is complex as the initiation step cannot be deduced easily. Also in studies of copolymerization involving an ionic mechanism, copolymer composition as well as reactivity ratios are strongly dependent on experimental conditions. This variable phenomenon is also true for electroinitiated polymerizations, so that the properties of copolymers produced in constant current electrolysis are not predictable.

In some recent studies, the use of constant potential electrolysis is discussed in terms of copolymer composition and reactivity ratios[2–5]. It was reported that polymerization potential affects the rate of polymerization, composition of copolymers and reactivity ratios. In this type of polymerization the electrode potential is controlled and kept at a suitable value depending on the electrochemical behaviour of the substrate. As a result of this, oxidation or reduction remains monomer-selective.

Copolymerization potentials have to be kept above oxidation peak potentials of both monomers[2–5]. This is due to shielding of electrode by formation of a thin polymeric film which creates a resistance and prevents the passage of sufficient current to effect polymerization. Consequently the rate of polymerization decreases. This film coating on the electrode surface was eliminated mostly by ultrasound without the retarding effect of mechanical disturbance of the polymerization system. Ultrasound introduced to the polymerization system prevents the film coating on the electrode surface, thus enabling polymerization potentials comparable to the $E_{p,a}$ of monomers to be applied.

EXPERIMENTAL

Materials

Tetrabutylammonium fluoroborate (TBAFB) was prepared and purified as described previously[6]. Dichloromethane was dried over CaH_2 and distilled over fresh CaH_2 before use. Isoprene was distilled under atmospheric pressure. α-Methylstyrene was purified as described previously[7].

Apparatus

The cyclic voltammetry system[8] and constant potential electrolysis system[6] were described earlier. A Buehler ultrasonic cleaner operated at 25 kHz was used to achieve copolymerization with ultrasound.

Polymerization procedure

Fresh distilled dichloromethane and dry TBAFB were introduced into the cell while the cell was being purged with nitrogen. The monomers isoprene (0.6 M) and α-methylstyrene (0.6 M) were then added to the solution and the cell was blanketed with nitrogen. The potentiostat and ultrasonic cleaner were switched on the same time and the cleaning process was maintained throughout the polymerization. The monomer concentrations and temperature (−30°C) were kept the same for each polymerization. The kinetics of the copolymerizations were followed by gas chromatographic (g.c.) analysis of samples removed from the polymerization cell. At definite time intervals 40 μl portions from each compartment were transferred into methanol containing an internal standard and analysed on a 2.0 m column packed with 20 M carbowax on 80–100 mesh Chromosorb.

The reactivity ratios were determined from the g.c. analyses of the polymer solutions by using the integrated Lewis–Mayo equation[9]. The per cent mole compositions of copolymers were determined from their i.r. spectra.

The intrinsic viscosities of copolymers were obtained in benzene at 25°C.

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0032-3861/86/050803-04$03.00

For polymerizations carried out with vibration, the polymerization cell was placed in an ultrasonically vibrated ethanol bath.

Copolymerization of isoprene with α-methylstyrene in the absence of ultrasound was achieved at four different potentials (i.e. +2.40, +2.60, +2.80 and +3.00 V vs. Ag°/Ag^+). Copolymerization was carried out at −30°C at seven different potentials (i.e. +1.80, +2.00, +2.20, +2.40, +2.60, +2.80 and +3.00 V vs. Ag°/Ag^+) in the presence of ultrasound.

RESULTS AND DISCUSSION

The anodic peak potential ($E_{p,a}$) of isoprene was measured as +2.00 V vs. Ag°/Ag^+ in acetonitrile–TBAFB system. The same value was obtained from the measurement made in dichloromethane. The anodic peak potential of α-methylstyrene is reported[7] as +1.60 V vs. Ag°/Ag^+ in dichloromethane–TBAFB system. Unreacted monomer concentrations were determined by g.c. analysis of samples removed from the cell. It was observed that in the absence of ultrasound the concentration of reacted isoprene decreased with increasing polymerization potential whereas that of reacted α-methylstyrene remained almost constant. The slope of concentration of reacted isoprene vs. E_{pol} was higher than that of reacted α-methylstyrene (*Figure 1*); this behaviour persists throughout the polymerization, and is related to film formation on the electrode surface. At lower E_{pol} values, the formation of thin polymeric film requires a longer time than at high E_{pol} values. Substrate present around the electrode surface and in the bulk should have more time and opportunity to cover the electrode surface at low than at high values of E_{pol}. On the other hand, at high E_{pol} values, rapid film formation on the electrode shields the surface and reduces the potential in the solution. Consequently oxidation of monomer which moves from the bulk to the electrode surface becomes difficult. However in the presence of ultrasound, which brings about rapid adsorption–desorption, the electrode surface was kept clean to almost the end of the electrolysis. As a result a slight increase in the reacted isoprene and α-methylstyrene concentrations vs. E_{pol} was observed. The total per cent conversion was plotted *versus* time for each potential separately both with and without ultrasound (*Figures 2* and *3*).

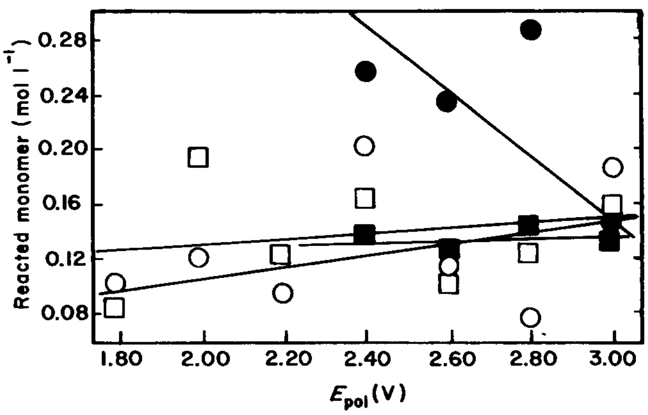

Figure 1 Effect of polymerization potential on the reacted monomer concentration in the copolymerization of isoprene with α-methylstyrene at −30°C. ●, Reacted isoprene concentration without ultrasound; ○, reacted isoprene concentration with ultrasound; ■, reacted α-methylstyrene concentration without ultrasound; □, reacted α-methylstyrene concentration with ultrasound

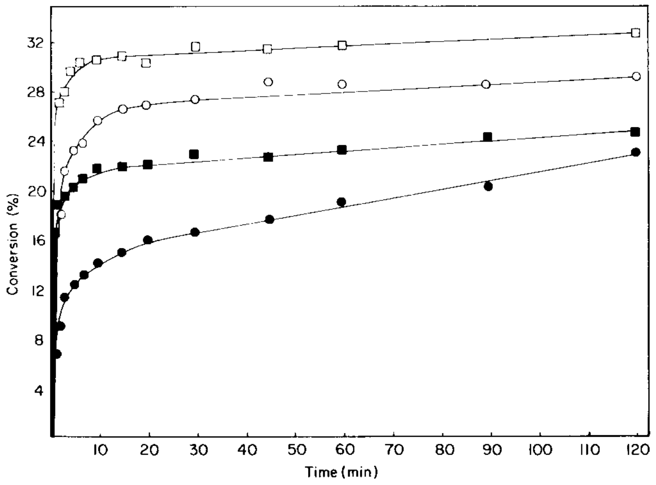

Figure 2 Conversion–time plots for electroinitiated cationic copolymerization of isoprene with α-methylstyrene without ultrasound at −30°C. □, +2.40 V; ○, +2.60 V; ■, +2.80 V; ●, +3.00 V

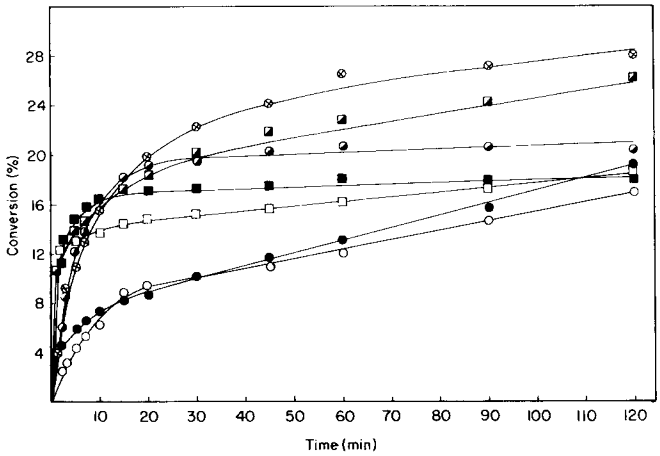

Figure 3 Conversion–time plots for electroinitiated cationic copolymerization of isoprene with α-methylstyrene with ultrasound at −30°C. □, +1.80 V; ◪, +2.00 V; ●, +2.20 V; ⊗, +2.40 V; ○, +2.60 V; ■, +2.80 V; ◑, +3.00 V

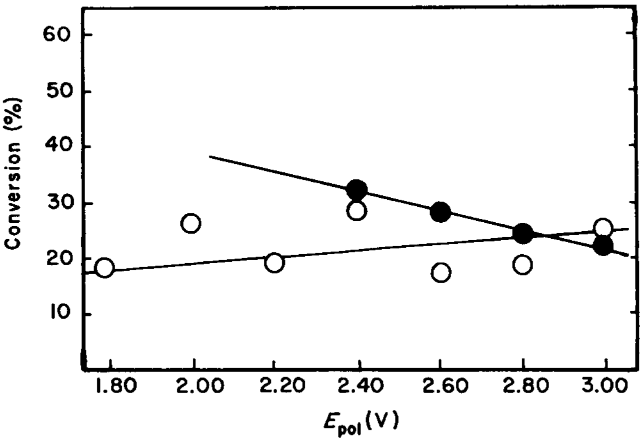

Figure 4 Effect of polymerization potential on percentage conversion in electroinitiated copolymerization of isoprene with α-methylstyrene. ●, without ultrasound; ○, with ultrasound

The effect of polymerization potential on the total percentage conversion at the end of 2 h is shown in *Figure 4*. It is seen from both *Figures 2* and *4* that the total percentage conversion decreases with increasing polymerization potential. Since the total percentage

Table 1 Effect of polymerization potential on electroinitiated cationic copolymerization of isoprene with α-methylstyrene without ultrasound at −30°C

E_{pol} (V)	Composition[a] (mol%)		Reactivity ratio		Conversion[b] (%)	Yield[a] (%)	$[\eta]$[a] (dl g^{-1})
	isoprene	α-methylstyrene	isoprene	α-methylstyrene			
+2.40	33.0	67.0	0.26±0.02	0.19±0.02	32.8	0.4	0.112
+2.60	36.0	64.0	0.36±0.01	0.23±0.01	28.8	3.3	0.110
+2.80	39.5	60.5	0.48±0.01	0.50±0.01	24.5	5.5	0.098
+3.00	50.0	50.0	0.80±0.01	0.75±0.01	22.9	14.4	0.044

[a] Calculated for 5 h of electrolysis
[b] Calculated for 2 h of electrolysis

Table 2 Effect of polymerization potential on electroinitiated cationic copolymerization of isoprene with α-methylstyrene with ultrasound at −30 C

E_{pol} (V)	Composition[a] (mol%)		Reactivity ratio		Conversion[b] (%)	Yield[a] (%)	$[\eta]$[a] (dl g^{-1})
	isoprene	α-methylstyrene	isoprene	α-methylstyrene			
1.80	34.0	66.0	0.53±0.01	0.62±0.01	18.4	3.9	0.051
2.00	44.5	55.5	0.97±0.01	0.72±0.01	26.2	36.7	0.046
2.20	43.5	57.0	0.94±0.03	0.89±0.03	19.3	23.6	0.045
2.40	44.0	56.0	0.81±0.01	0.78±0.01	28.4	21.7	0.049
2.60	53.5	46.5	0.77±0.02	0.77±0.02	17.1	34.9	0.057
2.80	38.0	62.0	0.70±0.02	0.98±0.02	18.3	41.5	0.045
3.00	42.0	58.0	0.95±0.01	0.97±0.01	20.5	36.9	0.050

[a] Calculated for 5 h of electrolysis
[b] Calculated for 2 h of electrolysis

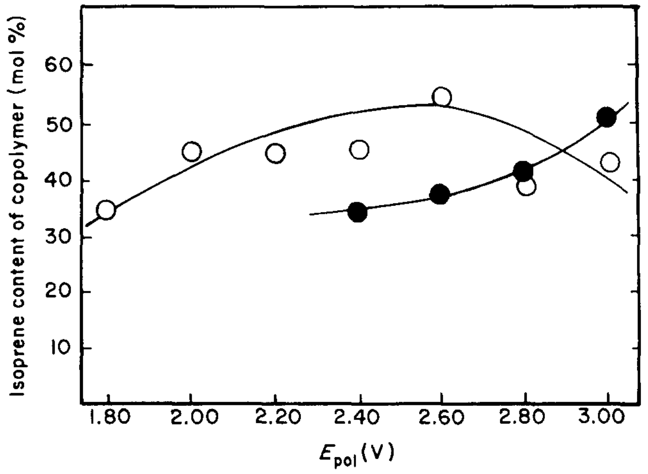

Figure 5 Effect of polymerization potential on the isoprene content (mol%) of electrochemically obtained isoprene–α-methylstyrene copolymers. ●, without ultrasound; ○, with ultrasound

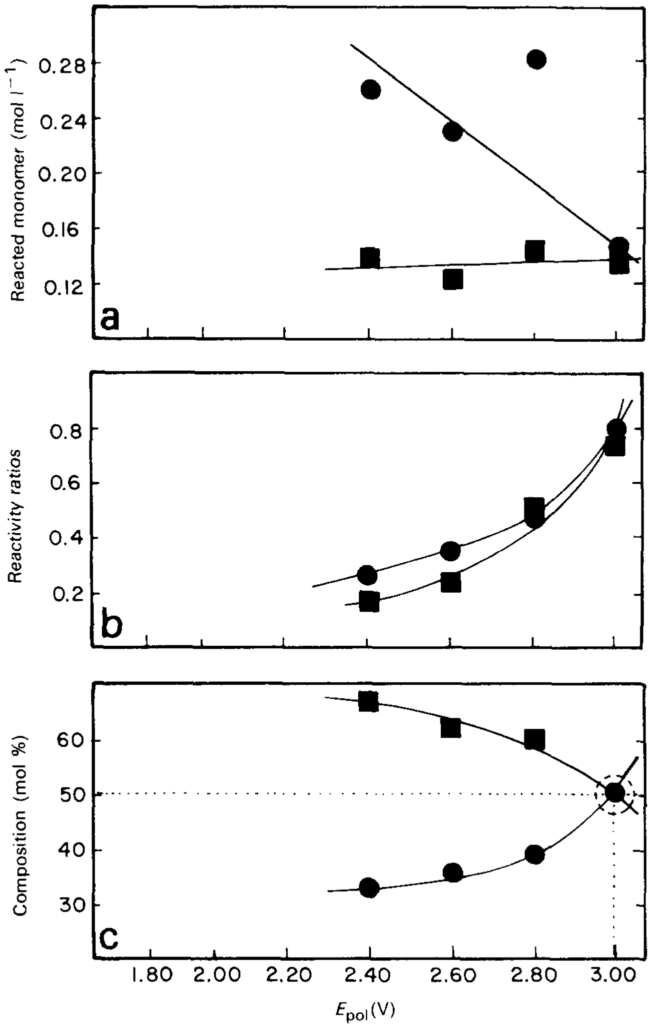

Figure 6 Effect of polymerization potential (a) reacted monomer concentration; (b) reactivity ratio; mole percentage composition in the copolymerization of isoprene (●) with α-methylstyrene (■) without ultrasound

conversion was calculated from reacted isoprene and α-methylstyrene concentrations (reacted monomer concentration decreases with increasing E_{pol}), the total percentage conversion decreases, as expected. On the other hand with ultrasound the total percentage conversion after 2 h shows a slight increase with increasing E_{pol} owing to the clear electrode surface.

It was observed that the polymerization potential also affected the copolymer composition, as reported previously[10,11]. The proportion of α-methylstyrene ($E_{p,a} = +1.60$ V) in the copolymer decreased with increasing polymerization potential owing to increase in incorporation of isoprene (+2.00 V), as seen in *Table 1* and *Figure 5*. When $E_{p,a}$ values of monomers are considered, increase of polymerization potential enhances incorporation of isoprene in copolymers and causes a decrease in the α-methylstyrene content, as expected. At the lowest polymerization potential (+2.40 V) isoprene content was 33.0%, which increased to 50.0% at $E_{pol} = +3.00$ V. However this trend with ultrasound does not continue at higher E_{pol} values. Up to a certain E_{pol} ($E_{pol} = +2.60$ V) isoprene content in copolymer increases gradually from 34.0% to 53.5% in the potential range of +1.80 to +2.60 V. Above +2.60 V, however, isoprene content of the copolymer decreases.

The reactivity ratios were also found to be affected by polymerization potential. Reactivity ratios for copolymerizations carried out without ultrasound increase with increasing polymerization potential. However, it was also observed that ultrasound affects the reactivity ratios as well as E_{pol}. The relation of E_{pol} and r_1, r_2 values disappeared with ultrasound (*Tables 1* and *2*).

The effects of E_{pol} on reacted monomer concentration, reactivity ratios and composition of copolymers in the absence of ultrasound are illustrated in *Figure 6*. Reacted isoprene and α-methylstyrene concentrations decrease with increasing E_{pol}, with a changed slope. They have a convergence point at $E_{pol} = +3.00$ V, which may be called the critical polymerization potential (*Figure 6a*). Reactivity ratios increase with increasing E_{pol} and converge at the same critical E_{pol} (*Figure 6b*). The percentage composition of copolymers determined by i.r. analysis at various E_{pol} shows that at the critical E_{pol} (+3.00 V) the composition of copolymer is 50 mol% for each monomer. In these figures the existence of critical polymerization potential suggests that the reactivity ratios and copolymer composition can be controlled by choice of E_{pol}.

ACKNOWLEDGEMENT

The authors thank Tubitak for supporting this research.

REFERENCES

1 Funt, B. L. and Rybicky, J. *J. Polym. Sci. A-1* 1971, **9**, 1441

2 Akbulut, U., Eren, S. and Toppare, L. *Br. Polym. J.* 1984, **16**, 71

3 Akbulut, U., Eren, S. and Toppare, L. *Polymer* 1984, **25**, 1655

4 Toppare, L., Eren, S. and Akbulut, U. *J. Polym. Sci., Polym Chem. Edn.* 1984, **22**, 2941

5 Toppare, L., Eren, S. and Akbulut, U. *Br. Polym. J.* 1984, in press

6 Akbulut, U., Eren, S. and Toppare, L. *J. Macromol. Sci. Chem.* 1984, **A21**(3), 335

7 Akbulut, U., Efen, S. and Toppare, L. *Polymer* 1984, **25**, 1028

8 Akbulut, U., Toppare, L., Önal, A. and Usanmaz, A. *Macromol. Chem., Rapid Comm.* 1983, **4**, 259

9 Meer, R. V., Linssen, H. N. and German, A. L. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **26**, 2915

10 Toppare, L., Eren, S. and Akbulut, U. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 303

11 Toppare, L., Eren, S., Özel, Ö. and Akbulut, U. *J. Macromol. Sci. Chem.* 1984, **A21**(10), 1284