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Electroinitiated Cationic Copolymerization of Styrene and 4-Methoxystyrene

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ABSTRACT

The copolymerization of styrene and 4-methoxystyrene by constant potential electrolysis in 1,2-dichloroethane was achieved at three different potentials. Amounts of the monomers in the resulting copolymers were found to be potential-dependent. The effect of polymerization potential on copolymer composition was also found to be related to anodic peak potentials ($E_{p,a}$) of the monomers.

Monomer reactivity ratios were found with the integrated Lewis-Mayo equation.

INTRODUCTION

Electroinitiated copolymerization studies have been reported [1-4]. These describe cationic polymerization via constant current electrolyses in the presence or absence of donor-acceptor complexes.

We have shown that direct initiation of polymerization processes can be achieved by constant potential electrolysis [5]. Copolymeriza-

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tion under controlled potential conditions has not been reported yet, thus investigation of the effect of the applied potential on copolymer composition is a new approach.

The monomer reactivity ratios of various monomers under different reaction conditions have been reported by Tobolsky [6]. The direct initiation technique requires only the activation of monomers in contrast to the constant current method in which any component of a polymerization solution may be involved in the polymerization process. Therefore, the reactivity ratios of monomers found upon constant potential electrolysis should represent more accurate values as far as electrochemical initiation is concerned.

EXPERIMENTAL

Materials

Tetrabutylammonium fluoroborate (TBAFB) was prepared and purified as described previously [7].

1,2-Dichloroethane was dried over CaH_2 for 12 h and later distilled over fresh CaH_2 under nitrogen atmosphere.

Purification of styrene was also reported previously [7].

4-Methoxystyrene was distilled over CaH_2 at $40^\circ\text{C}/4$ mmHg pressure.

Procedure

The controlled potential electrolysis system was described earlier [8]. In the case of polymerization, equal amounts of recrystallized and freshly dried TBAFB were placed in both cell compartments. The cell was purged with nitrogen and later distilled dichloroethane and the monomers, styrene (0.32 M) and 4-methoxystyrene (0.28 M), were introduced into the cell. Before controlled potential electrolysis was started, the solution in each compartment of the cell was equilibrated and the cell was placed in a constant temperature bath. The solution was blanketed with nitrogen, and 40 μL aliquots were transferred from each compartment into 1 mL of methanol containing 10 μL indene as the internal standard for the gas chromatographic analyses of the solutions.

During electrolysis, at definite time intervals 40 μL samples from each compartment for analysis of monomer concentration were transferred into 1 mL methanol. Samples were removed from both compartments to eliminate the effect of diffusion of monomers from the cathode compartment to the anode compartment. It was assumed that the electrolytic decomposition of monomers in catholyte solution was negligible.

Unreacted monomer concentrations were determined by gas chroma-

tography (GC) with a column of 2.80 m packed with 1.5% Apiezon L on 80-100 mesh-size Chromosorb.

Copolymerization was carried out at three different potentials at 0°C. The polymers were precipitated by pouring the anolyte into excess methanol. The viscosity measurements were made in benzene at 30°C. Composition analyses of copolymers were made by IR spectroscopy with a Perkin-Elmer 177 instrument.

RESULTS AND DISCUSSION

Cyclic voltammograms of the monomers obtained in acetonitrile at room temperature have been reported [8]. During copolymerizations, the total monomer consumptions were obtained and plotted versus time for each potential (Fig. 1).

Composition analyses of copolymers show that at low electrolysis potential (i.e., +2.00 V) the contribution of styrene decreases in the co-

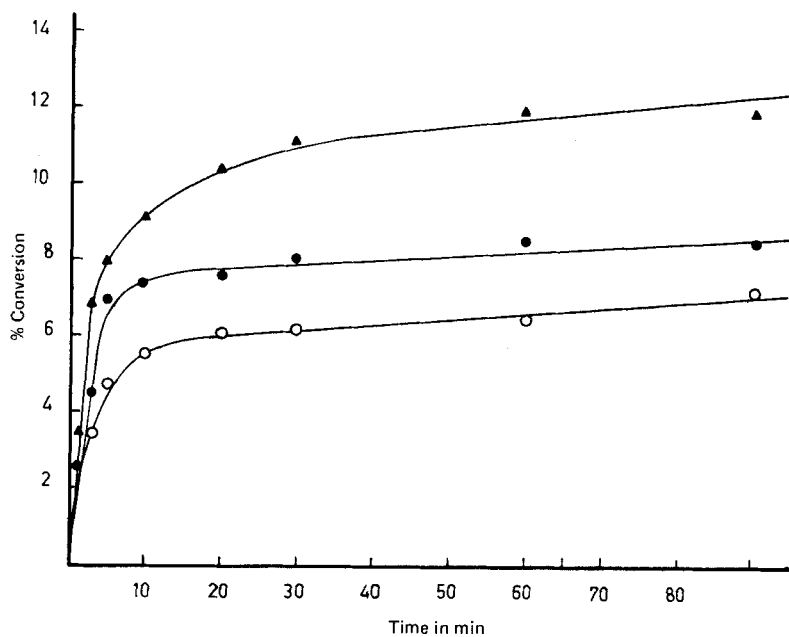


FIG. 1. Electroinitiated cationic copolymerization of styrene and 4-methoxystyrene at 0°C in 1,2-dichloroethane at (▲) +2.00 V, (●) +2.20 V and (○) +2.50 V.

TABLE 1. Electroinitiated Copolymerization of Styrene-4-methoxystyrene at Different Applied Voltages^a

E_{pol}^b (V)	% Composition		Total ^e conversion (%)	r_1^f 4-MOS	r_2 ST	η^g (dL/g)
	4-MOS ^c	ST ^d				
+2.00	71.5	28.5	17.44	0.88 ± 0.01	0.67 ± 0.01	0.017
+2.20	67.5	32.5	10.88	0.80 ± 0.01	0.42 ± 0.01	0.168
+2.50	57.5	42.5	7.25	1.59 ± 0.02	2.50 ± 0.02	0.190

^a $E_{\text{p,a}}$ of styrene is +1.80 V and that of 4-methoxystyrene is +1.40 V.

^bElectrolysis potential versus Ag^0/Ag^+ reference electrode.

^c4-Methoxystyrene.

^dStyrene.

^eMeasured by GC analyses of electrolysis solutions at the end of 150 min of electrolysis, calculated from $([\text{M}]_t + [\text{M}_2]_t)/([\text{M}]_0 + [\text{M}_2]_0) \times 100$.

^fCalculated by the integrated Lewis-Mayo equation.

^gMeasured in benzene at 30°C.

polymer composition because the oxidation peak potential of styrene (+1.80 V versus Ag^0/Ag^+ reference electrode) is higher than that of 4-methoxystyrene (+1.40 V versus Ag^0/Ag^+). Increasing the applied voltage causes an increase in the styrene content in the copolymer composition (Table 1).

These observations are expected because more of the monomer with a lower oxidation peak potential (4-methoxystyrene) will be converted to radical cation in comparison to the one with a higher oxidation peak potential (styrene). The monomer with the lower oxidation peak potential should have a smaller HOMO (highest occupied molecular orbital) energy, as reported previously [9], and thus it will lose electrons more easily than the monomer with a higher oxidation peak potential. It is also known that in any electrolysis system, more of the substrate with the lowest oxidation potential oxidizes on the electrode compared to the other species. This introduces a method for external control of the composition of the copolymer produced if the electrochemical conditions are suitable. Even for monomers which have very high oxidation potentials i.e., higher than the value of the solvent-electrolyte couple (+3.50 V) [8], it will still be possible to initiate copolymerizations via the activation of the other monomer which must have a reasonably low oxidation potential in the limits of the electrolysis system.

The integrated Lewis-Mayo equation [10] for the calculation of monomer reactivity ratios was used to determine the straight lines in an r_1 - r_2 diagram for each experiment based on GC measurements.

As seen from Table 1, the reactivity ratios are also affected by the copolymerization potential. This leads to the conclusion that in the case of a constant current approach where the potential may vary over a wide range of values during electrolysis, the computation of the reactivity ratios will not be very accurate and can only represent an average value.

In the present work it is shown that electroinitiation by constant potential electrolysis can be utilized for copolymerizations. The variation of the applied potential allows external control of the copolymer composition and the reactivity ratios, which is not possible in the case of chemical initiation or by constant current electrolysis.

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