Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Electroinitiated Polymerization of Styrene in a Mixed Two-Phase Medium

Remesh Ch. Bhakta[a]; Swati Sanyal[b]; Bimbadhara Nayak[b]
[a] Berger Paints India Ltd., Shibpur, Howrah, India [b] Department of Chemistry, Indian Institute of Technology, Kharagpur, India

To cite this Article Bhakta, Remesh Ch. , Sanyal, Swati and Nayak, Bimbadhara(1987) 'Electroinitiated Polymerization of Styrene in a Mixed Two-Phase Medium', Journal of Macromolecular Science, Part A, 24: 5, 493 — 505

To link to this Article: DOI: 10.1080/00222338708068136

URL: http://dx.doi.org/10.1080/00222338708068136

J. MACROMOL. SCI.–CHEM., A24(5), pp. 493-505 (1987)

ELECTROINITIATED POLYMERIZATION OF STYRENE IN A MIXED TWO-PHASE MEDIUM

REMESH CH. BHAKTA

Berger Paints India Ltd.
Shibpur, Howrah, India

SWATI SANYAL and BIMBADHARA NAYAK

Department of Chemistry
Indian Institute of Technology
Kharagpur 721302, India

ABSTRACT

In extension of our earlier work on electroinitiated polymerization in biphasic media, the electroinitiated polymerization of styrene has been studied using a mixed two-phase system in which formamide together with some added electrolyte is used as the polar phase and the monomer in the bulk form as the nonpolar phase. Among a series of zinc and ferric salts used as the electrolyte, $ZnBr_2$ was found to be the most effective. The polymer obtained has a molecular weight of 44-47 X 10^3. The effects of various other parameters, such as the dependence of polymer yield on current, the concentration of the electrolyte, the temperature, and the stirring, have also been examined, and a plausible mechanism based on the electrochemical formation of radicals involving a CT complex has been suggested.

INTRODUCTION

There have been several reports on the electroinitiated polymerization of styrene ever since the first such attempt, though unsuccessful, was made by Kolthoff et al. in 1951 [1]. It appears from these reports that, due to the low solubility of styrene monomer in aqueous medium and in other highly polar solvents, most of the electropolymerization had to be carried out in nonaqueous solvents of moderate polarity [2-9]. In almost all of these studies reported so far, only single-solvent systems forming a homogeneous solution of the monomer have been used. As pointed by us in a recent communication [10], the inherent difficulty is the rather difficult choice of the solvent. A nonpolar solvent which facilitates the dissolution of the polymer and thus keeps the electrode surface free of polymer coating produces poorly conducting solutions. On the other hand, a polar liquid might act as a solvent for the monomer and produce a more conducting solution, but it might be a nonsolvent for the polymer, leading to blocking of the electrode. To overcome these difficulties, we recently introduced a novel technique for electropolymerization in which we employed a two-phase medium consisting of a polar liquid containing the added electrolyte(s) and a nonpolar phase which consisted of either the bulk monomer or its solution in a nonpolar liquid. This technique, which was successfully applied to the electroinitiated polymerization of methyl methacrylate, was based on the principle that the more conductive polar phase would allow the passage of sufficient current and serve chiefly as the medium for electrolysis, while the nonpolar phase containing the bulk of the monomer will eventually trap most of the radicals and radical ions formed at the electrode and act as the polymerization medium. In view of the success achieved, we have considered it worthwhile to extend the technique to the electropolymerization of styrene.

In the present studies, electropolymerization was attempted in a two-phase system with styrene as the nonpolar phase and formamide containing some added electrolyte(s) as the polar phase.

EXPERIMENTAL

Formamide (BDH, LR) and styrene (Polychem) were purified by following the standard procedures [10, 11]. Anhydrous $FeCl_3$ (Sarabhai M. Chemicals), $Fe_2(SO_4)_3$ (SBP, LR), and toluene (BDH, AR) were used without further purification. $ZnCl_2$ (DDS, GDH) and $ZnBr_2$ (BB, LR) were dried at 423.15 K under vacuum for 10 h [12].

The electropolymerization was mostly carried out in a single-compartment electrolytic cell. The experimental procedure was similar to that described earlier [10]. The polystyrene was isolated from the reaction mixture by precipitation with excess acidified methanol. The polymer was characterized by IR and NMR spectroscopy with $CHCl_3$ and $CDCl_3$ as solvents, respectively. Viscosity-average molecular weights, $\overline{M}_v$, of the polymer were determined in toluene by the relation [13] $[\eta] = 1.10 \times 10^{-4} M_v^{0.725}$.

RESULTS AND DISCUSSION

A mixture of styrene and formamide with a molar ratio 5.2:60 at room temperature (298.15 K) separates into two layers, the upper layer (A) being mostly styrene and the lower (B) mostly formamide. It was found that the styrene content in its saturated solution in formamide was approximately 2.4 wt% and that of formamide in the styrene layer was close to 0.5 wt%. The conductance of the mixed phase (C) was found to be much higher than that of the nonpolar phase (A), but somewhat less than that of the polar phase (B) as was expected (see Table 1).

Preliminary experiments showed that the electrolysis carried out in (C) without any added electrolyte did not produce any polymerization. However, the addition of certain zinc and ferric salts not only increased the conductance of the medium but also initiated the polymerization reaction. Among the salts tried, $ZnBr_2$ was found to be the most effective in giving a better yield of the polymer (Table 2). Consequently, in subsequent experiments $ZnBr_2$ was used as the electrolyte in preference to other salts. To avoid the possibility of thermal polymerization, a low temperature around 313.15 K was used for most of the electropolymerization runs. During electrolysis the polarity of the electrode was reversed every hour to minimize the electrodeposition of metallic zinc. Such alternation had, however, very little effect on the polymer yield.

Stirring of the solution during the electrolysis was found to enhance the polymer yield, but the presence of air in the electrolytic cell produced a tremendous inhibiting effect. Electrolysis was therefore carried out in solutions under nitrogen atmosphere and under constant agitation.

It was found (Fig. 1) that the rate of polymerization rises sharply with current at both concentrations of the electrolyte up to a certain value of the current, and then remains virtually constant.

The effect of $ZnBr_2$ concentration on the rate of polymerization (Fig. 2) shows a particular trend: the polymerization rate first increases with electrolyte concentration, thereafter falls slowly, and ultimately reaches a constant value.

TABLE 1. Specific Conductance of Pure Liquids and Various Layers Involved

Description of the liquid/layer	Specific conductance at 298.15 K, mho/cm
Formamide (pure)	3.20×10^{-5}
Styrene (pure)	4.12×10^{-7}
Upper layer (A): Styrene saturated with formamide	5.07×10^{-7}
Lower layer (B): Formamide saturated with styrene	2.94×10^{-5}
Mixed two-phase system (C)	2.67×10^{-6}

It is found that at 15 mA the polymer yield increases linearly with the time of current flow (Fig. 3). However, at 2.5 mA there appears to be an induction period, after which the increases reach a linear time dependence.

It was found that no thermal polymerization occurred in the temperature range 293.15-323.15 K. Table 3 shows that increasing temperature, as expected, raises the polymer yield.

The polymer yield did not increase significantly after the cessation of the current. Polymer yield was also practically negligible in the presence of hydroquinone during electrolysis.

The molecular weight ($\overline{M}_v$) of the polymer was not determined in all cases, but $\overline{M}_v$ of the samples measured was 44 000-47 000.

The present study, though not exhaustive in view of the complex nature of the system, nevertheless permits some conclusions to be drawn with regard to the polymerization process, and in conjunction with experimental observation by earlier workers, these provide a basis for a mechanism to be developed.

The fact that the polymerization was inhibited by the presence of radical quenchers like hydroquinone or oxygen is suggestive of a radical mechanism. It is further corroborated from the fact that alternating copolymerization between styrene and methyl methacrylate results when methyl methacrylate was added to the system. The alternating copolymer was characterized by its solubility difference in cyclohexane and acetonitrile, good solvents for polystyrene and polyMMA, respectively, but nonsolvents for the copolymer. The NMR spectrum of the copolymer shows three distinct peaks of methoxy protons of MMA at δ 2.1-3.7 ppm instead of a single peak at δ 3.4-3.8 ppm along

TABLE 2. Effect of Various Added Electrolytes on the Electropolymerization of Styrene[a]

Electrolyte	Electrolyte used, mmol/12 mL	Time of electrolysis, h	Conversion, %	Polymerization efficiency
Ferric chloride	0.136	5	1.50	0.14
	0.136	3	0.70	0.11
Ferric sulfate	0.125	5	Nil	–
Zinc chloride	0.131	5	0.90	–
	1.75	5	1.30	0.12
Zinc bromide	0.111	3	1.14	0.18
	1.68	5	3.25	0.34
Zinc chloride + ferric chloride	1.75 + 0.136	5	0.80	–

[a] Formamide:styrene mole ratio, 60:5.2; current, 15 mA; temperature, 313.15 K.

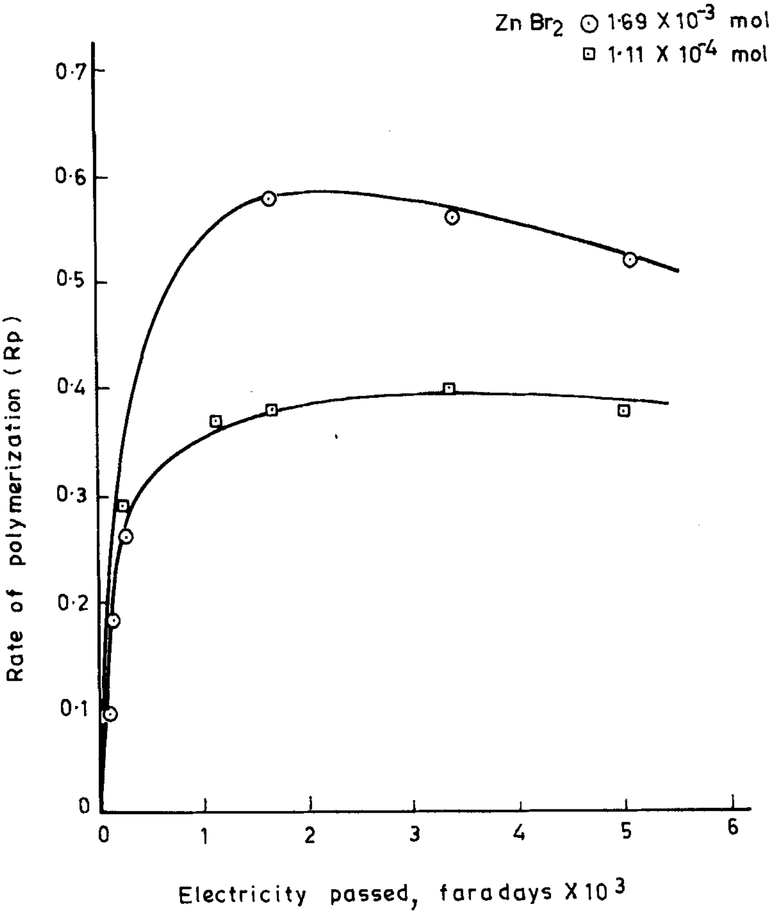


FIG. 1. Rate of polymerization as a function of current, i.e., quantity of electricity passed over 3 h at two different electrolyte concentrations. Formamide:styrene mole ratio, 60:5.2; time of electrolysis, 3 h; temperature, 313.15 K; $ZnBr_2$ added per 12 mL formamide, as indicated within drawing; $ZnBr_2$:formamide mole ratio, (○) 5.61 X 10^{-3} :1; (□) 0.37 X 10^{-3} :1.

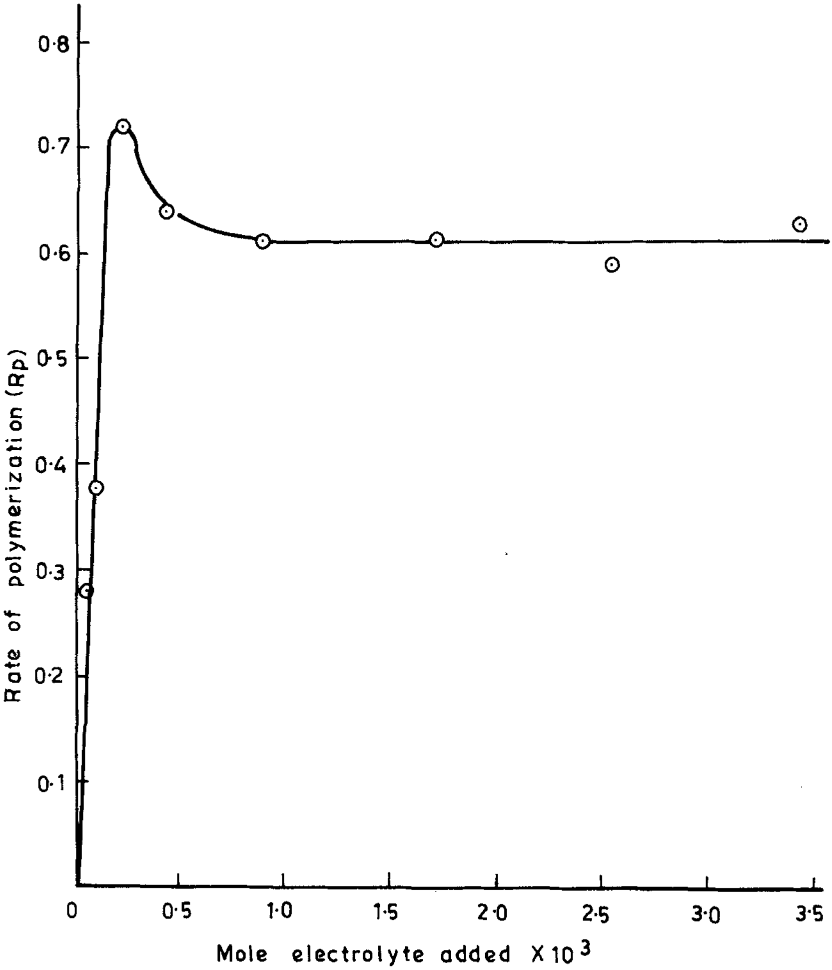


FIG. 2. Rate of polymerization as a function of quantity of electrolyte added per 12 mL formamide. Formamide:styrene mole ratio, 60:5.2; time of electrolysis, 3 h; temperature, 313.15 K; current, 15 mA.

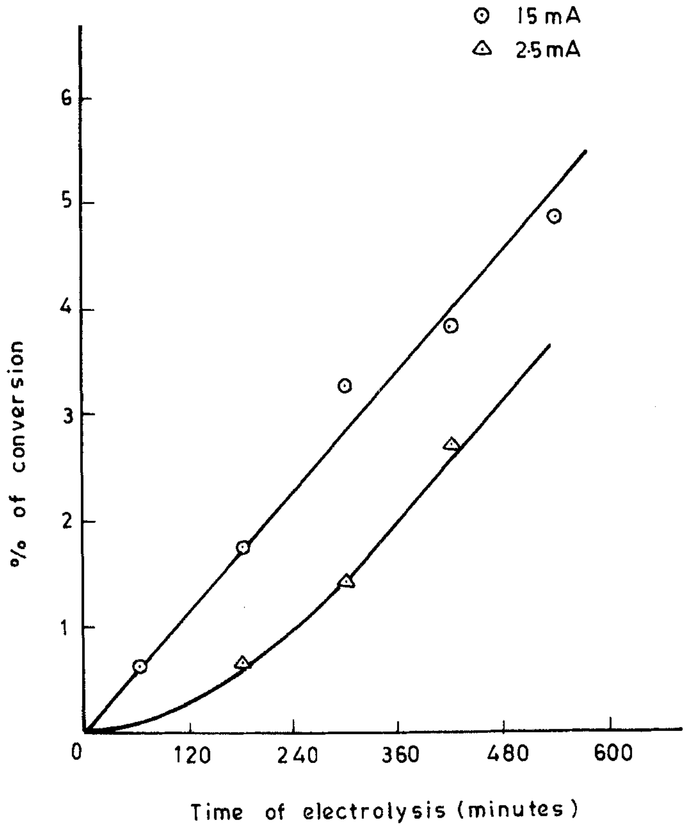


FIG. 3. Polymer yield as a function of time and current in the electroinitiated reaction. Formamide:styrene:$ZnBr_2$ mole ratio, 60:5.2:0.34; temperature, 313.15 K.

with the aromatic protons of styrene units at δ 6.4-6.9 ppm (Fig. 4) [14, 15].

The split-cell experiments showed that the polymerization occurs in both the cathode and the anode compartments, the former yielding overwhelmingly more polymer than the latter. This indicates that the radicals generated at the cathode are more effective in initiating the polymerization than those formed at the anode. As far as the anodic polymerization in the styrene-formamide-$ZnBr_2$ system is concerned, the formation of a charge transfer

TABLE 3. Effect of Temperature on the Electropolymerization of Styrene

Temperature, K	Conversion, %	R_p, %/h	Polymerization efficiency
293.15	0.77	0.26	0.12
303.15	1.36	0.45	0.21
313.15	1.74	0.58	0.27
323.15	2.69	0.89	0.42

[a] Formamide:styrene:$ZnBr_2$ mole ratio, 60:5.2:0.34; time of electrolysis, 3 h; current, 15 mA.

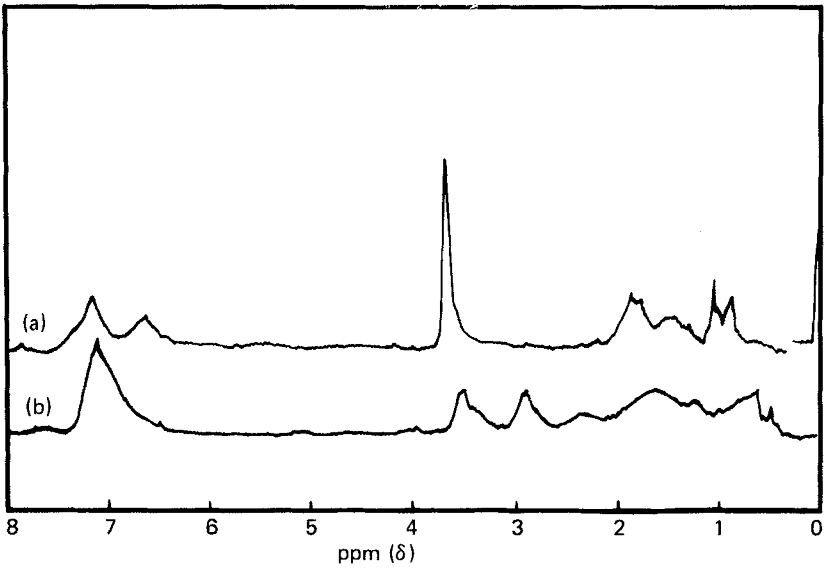
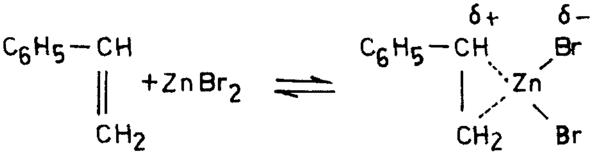


FIG. 4. NMR spectrum of (a) mixture of polyMMA and polystyrene, and (b) copolymer of styrene and MMA.

(CT) complex between styrene and zinc bromide is more likely [16-19] and the complex would get oxidized at the anode, giving rise to a radical cation. It is expected that such radical cations would initiate polymerization by both radical and cationic mechanisms, and we would not expect hydroquinone to inhibit such polymerization completely. Therefore, polymerization observed in a single-compartment cell, which is completely inhibited by hydroquinone and which yields an alternating copolymer in the presence of methyl methacrylate, would proceed only through a pure radical mechanism. Although radicals may be easily generated at the cathode through Reactions (1)-(4) in a single-compartment cell and cause initiation of the polymerization, there is a possibility that the radical cations generated at the anode may also contribute to the radical populations by migrating to the cathode and undergoing certain reactions there (Reactions 5-7).

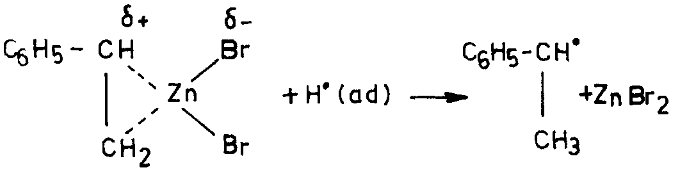
Considering all these aspects and taking into account the fact that no polymerization occurs in the absence of electrolytic current or the electrolyte, the following mechanism appears to be the most likely one for the electropolymerization:

$$2HCONH_2 \rightleftharpoons HCON\overset{+}{H}_3 + HCON\overset{-}{H} \qquad (1)$$



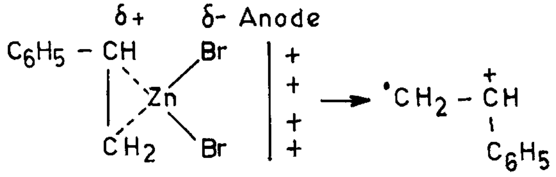
(2)

$$HCON\overset{+}{H}_3 + e \text{ (at cathode)} \longrightarrow HCONH_2 + H^{\bullet}\text{(ad)} \qquad (3)$$



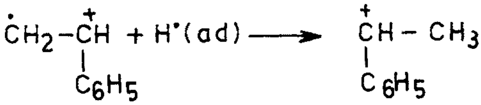
(4)

The formation of the radicals in the single-compartment cell by the anodic reactions may be visualized as follows, in accordance with the mechanism proposed by Murty and Nayak [9] but with some modifications:

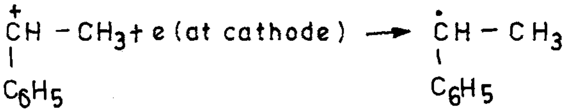


(5)

The radical cation then migrates to the cathode and there undergoes the following reactions:



$$\underset{\substack{|\\ C_6H_5}}{\overset{\bullet}{C}H_2-\overset{+}{C}H} + H^{\bullet}(ad) \longrightarrow \underset{\substack{|\\ C_6H_5}}{\overset{+}{C}H}-CH_3 \qquad (6)$$



$$\underset{\substack{|\\ C_6H_5}}{\overset{+}{C}H}-CH_3 + e\,(\text{at cathode}) \longrightarrow \underset{\substack{|\\ C_6H_5}}{\overset{\bullet}{C}H}-CH_3 \qquad (7)$$

The initiating radicals thus formed, either alone or in combination with zinc bromide, which might partially stabilize them, migrate to the nonpolar phase to propagate the polymerization process.

The mechanism postulated above can satisfactorily explain the various features of the present studies, such as the dependence of polymer yield on current, on concentration of the electrolyte, and on stirring. Stirring promotes diffusion of radicals from the polar phase to the nonpolar phase. Further, it helps the radical cations formed in the anodic region to be transported to the cathodic region where they are converted to pure radicals, thus increasing the overall concentration of radicals in the polar phase.

One aspect of the dependence of the polymer yield on the current might need further explanation, namely, the intensitivity of the polymerization rate to current at higher values of the latter. This may be because, at higher currents, the rate of formation of radicals in the medium depends on the rate of diffusion of CT complex from the bulk of the polar phase to the electrode surfaces. This, however, is not the case at lower currents where there will be no short supply of CT complexes near the cathode or at the anode and, hence, the rate of generation of radicals will be determined by the current flow only.

The peculiar trend of the polymerization rate with the concentration of the electrolyte can be explained as follows. When the concentration of the electrolyte in the medium increases, the formation of the CT complexes and the conductance of the medium as a whole increases. The former is unexpected to promote the rate of diffusion of the CT complex to the electrode surfaces. This, in turn, would increase the rate of polymerization. However, the increased conductance of the medium would decrease the polarization of the electrodes, and this may inhibit the adsorption of CT complexes on the electrode surfaces. This opposing effect will be less pronounced at lower concentrations of the electrolyte and, hence, the rate of polymerization increases sharply. But as the concentration of the electrolyte is gradually increased, the two opposing effects cause the polymerization rate to pass through a maximum and then decrease slowly to a constant value.

The linear variation of polymer yield with time of electrolysis at two different values of the current can be explained by the fact that with the progress of electrolysis, the total number of radicals diffusing into the nonpolar phase from the polar phase increases and hence the polymer yield is also enhanced. However, at a low electrolytic current, i.e., 2.5 mA, the formation of polymer during the initial phase is rather low (Fig. 3), which may be due to the presence of traces of moisture present as impurity in the reaction medium. The moisture produces a slight inhibiting effect, though indirectly, through one of its electrolysis products, oxygen. With the progress of electrolysis, however, such moisture is exhausted and, therefore, the radical generation takes the usual course and the polymer yield increases monotonically with time. That such an inhibiting effect is not observed at higher current (Fig. 3) may be because under this condition, exhaustion of moisture through electrolysis is quite rapid and the effect is not noticed.

The increase of polymer yield with temperature would also follow from the mechanism as this will be mostly due to the higher rate of diffusion of the radicals from the polar phase to the nonpolar phase.

REFERENCES

[1] I. M. Kolthoff and L. L. Ferstanding, *J. Polym. Sci., 5,* 563 (1951).
[2] B. L. Funt and F. D. Williams, *J. Polym. Sci., Part A-2,* 865 (1964).
[3] B. L. Funt, D. Richardson, and S. N. Bhadani, *Can. J. Chem., 44,* 711 (1966).
[4] B. L. Funt and D. Richardson, *J. Polym. Sci., Part A-1, 8,* 1055 (1970).
[5] B. L. Funt and T. J. Blain, *Ibid., 8,* 3339 (1970).
[6] B. M. Tidswell and A. G. Doughty, *Polymer, 12,* 760 (1971).
[7] B. M. Tidswell and A. G. Doughty, *Ibid., 12,* 431 (1971).

[8] J. D. B. Smith, D. C. Phillips, and D. H. Davies, *J. Polym. Sci., Polym. Chem. Ed., 15*(7), 1555 (1977).
[9] V. V. V. Murty and B. Nayak, *Eur. Polym. J., 17,* 151 (1981).
[10] B. Nayak and R. C. Bhakta, *J. Appl. Electrochem., 13,* 105 (1983).
[11] C. A. Barson, J. R. Knight, and J. C. Robb, *Br. Polym. J., 4,* 427 (1972).
[12] D. H. Davies, D. C. Phillips, and J. D. B. Smith, *J. Polym. Sci., Polym. Chem. Ed., 17,* 1153 (1979).
[13] F. Danusso and G. Moraglio, *J. Polym. Sci., 24,* 161 (1957).
[14] T. Ikegami and H. Hirai, *J. Polym. Sci., Part A-1, 8,* 195 (1970).
[15] M. Hirooka, H. Yabuuchi, J. Iseki, and Y. Nakai, *Ibid., 6,* 1381 (1968).
[16] B. L. Funt, I. McGregor, and J. Tanner, *J. Polym. Sci., Part B, 8,* 695 (1970).
[17] N. G. Gaylord and A. Takahashi, *Adv. Chem. Ser., 91,* 94 (1969).
[18] D. C. Phillips, J. D. B. Smith, and D. H. Davies, *J. Polym. Sci., Polym. Chem. Ed., 10,* 3267 (1972).
[19] D. C. Phillips, D. H. Davies, J. D. B. Smith, and S. Spewock, *Ibid., 15,* 1563 (1977).

Received January 9, 1986
Revision received April 19, 1986