

# Electroinitiated Polymerization of Commercial Divinylbenzene in Acetonitrile Medium

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## Synopsis

The electroinitiated polymerization of commercial divinylbenzene (DVB) containing *p*- and *m*-DVB and *p*- and *m*-ethylvinylbenzene (EVB) and traces of diethylbenzene has been studied in acetonitrile medium with an added electrolyte, namely, tetrabutylammonium fluoroborate (TBAFB). A white partially crosslinked polymer is formed only after the passage of an electrical current. The dependence of yields on parameters such as current strength, temperature, time of electrolysis, and stirring of the reaction mixture has been determined. A detailed IR analysis of the polymeric product has been made and the linear polymeric product is identified as poly(*p*-DVB-co-*m*-DVB-co-*p*-EVB-co-*m*-EVB). The electropolymer is thermally stable up to 645 K as found by its DTA, TG, and DTG studies and possesses partial crystallinity as indicated by the X-ray diffraction experiments. Experiments conducted with a split cell indicated the formation of the polymer in the anode compartment; hence the polymerization mechanism appears to be cationic in nature.

## INTRODUCTION

In an earlier communication from this laboratory<sup>1</sup> electroinitiated radical copolymerization of styrene and commercial divinylbenzene was reported. However, a search of literature revealed that there has been no previous report on electropolymerization of divinylbenzene, although there are several publications on the thermal polymerization of commercial divinylbenzene (DVB) initiated chemically.<sup>2-16</sup> In a recent study<sup>17</sup> we attempted to electropolymerize commercial divinylbenzene in a number of solvent-electrolyte systems where the solvents chosen were acetonitrile, tetrahydrofuran, *N,N*-dimethyl formamide, and some mixed solvent pairs, such as acetonitrile-tetrahydrofuran, acetonitrile-*N,N*-dimethylformamide, and the salts chosen were tetramethylammonium perchlorate (TMAP), tetrabutylammonium perchlorate (TBAP), tetrabutylammonium fluoroborate (TBAFB), and lithium perchlorate. Among the various solvent-electrolyte systems tried, acetonitrile-tetrabutylammonium fluoroborate was found to be the most effective. In our present work, an attempt has been made to make a more detailed investigation of the said electropolymerization, i.e., of commercial divinylbenzene in the acetonitrile-TBAFB system in order to study the effect of various parameters such as the current strength, time of electrolysis, temperature, and finally the stirring rate of the solution on the course of polymerization and its yield.

## EXPERIMENTAL

### Materials

Commercial divinylbenzene (Fluka) was freed from the inhibitor in the usual way by treating it with 5% sodium hydroxide solution and then by washing it with distilled water repeatedly. It was then dried over solid potassium carbonate and finally distilled under reduced pressure. The middle fraction boiling at 333 K and 5 mm Hg pressure was collected and stored at 273 K. Its composition was almost 50% *p*- and *m*-divinylbenzene and 50% *p*- and *m*-ethylvinylbenzene with traces of diethylbenzene by weight.

Acetonitrile (BDH, LR), which contained trace amounts of water, acetamide, ammonium acetate, and ammonia, was first partially dried over activated silica gel and then with calcium hydride until hydrogen evolution ceased. The solvent was then distilled at atmospheric pressure and the fraction collecting within the boiling range 354–355 K, was collected and stored at room temperature. Methanol (BDH, LR), anhydrous tetrabutylammonium fluoroborate (Fluka) and hydroquinone (BDH, LR) were used without further purification.

### Procedure

Generally, a single compartment cell without separation between the cathode and the anode compartments was used to carry out the electrochemical polymerization reaction. For reactions that required the cathode and the anode sections to be analyzed individually, a split cell, whose compartments were separated by a sintered glass disk of fine porosity, was employed. The cell was provided with arrangements for bubbling pure and dry nitrogen gas through the cell and for withdrawing samples from it. The platinum electrodes (1 cm<sup>2</sup>) were 1.5 cm apart in the single compartment cell; however, the distance was much higher (ca. 5 cm) in case of divided cell experiments. All experiments were conducted at 303 K except as otherwise mentioned. The temperature was maintained constant by means of a water bath, and the assembly consisting of the cell and the water bath was mounted on a magnetic stirrer to provide adequate stirring of the solution during electrolysis. Electrolysis was carried out in both stirred and unstirred mixtures.

After filling the cell with a solution containing the required amount of the monomer, electrolyte and the solvent, dry nitrogen gas was bubbled through the solution for 30 min prior to electrolysis. Though the passage of nitrogen gas was not absolutely needed, yet this was done to maintain the uniformity of the experimental conditions. A variable current power supply unit (Aplab, 7612) with provisions for the measurement of current and voltage drop through the cell was used to provide direct current. At the end of electrolysis, the polymeric product that contained both the linear and the crosslinked polymer was precipitated with large excess of methanol and subsequently dried under vacuum at room temperature (ca. 303 K).

Polymer yields were determined gravimetrically and the polymer was characterized from its IR spectrum. Thermal analysis (DTA, TG, and DTG) of the polymer were done by a Stanton Redcroft thermal analyzer (STA 781) in nitrogen atmosphere at a heating rate 10 K/min from ambient temperature to

948 K. The X-ray diffractogram was taken by a Phillips Diffractometer (PW 7001) using Ni-filtered Cu  $K_{\alpha}$  radiation.

## RESULTS AND DISCUSSION

The results of the electroinitiated polymerization studies of commercial divinylbenzene have been summarized in Tables I and II and also shown in Figures 1–6. Preliminary experiments showed that the flow of electrolytic current in the presence of a suitable electrolyte is necessary to initiate the polymerization reaction. The polymerization runs were fairly reproducible, the polymer yield varying in duplicate experiments by no more than 5%. In the case of successful polymerization, it is further noticed that the reaction mixture, which is colorless initially, gradually turns brown during electrolysis. In the split cell experiments the polymerization is found to occur in the anode compartment where the reaction mixture assumes only a faint yellow color, while the solution in the cathode compartment turns deep brown. In each of the experiments, the anode got coated with a thick white polymer that affected the current flow through the electrode on prolonged electrolysis. Hence to maintain the constant current flow throughout the reaction period, proper readjustment of the applied voltage was done from time to time during the electrolysis.

Table I summarizes the results of this preliminary set of experiments in the presence and absence of nitrogen atmosphere and the results show that these conditions have no profound effect on the polymerization rate. The results also show that, to initiate the polymerization reaction, the flow of current is not only necessary, but also the polymer yield is dependent on the current strength to some extent. Increase of time and temperature, however, has an enhancing effect on the polymerization yield.

TABLE I  
Conversion of Electroinitiated Polymerization of Commercial  
Divinylbenzene in Various Conditions<sup>a</sup>

Current passed (mA)	Temperature (K)	Time of electrolysis (h)	Conversion (%)	$R_p$ (%/h)
1	303	12	Nil	—
15	303	5 air	7.19	1.438
15	303	5 N <sub>2</sub>	7.51	1.502
25	303	5 air	10.98	2.196
25	303	5 N <sub>2</sub>	11.34	2.268
15	313	5	9.81	1.96
25	313	5	12.54	2.508
15	303	10	10.71	1.071
25	303	10	13.78	1.37
15	313	10	12.03	1.203
25	313	10	13.52	1.352
15	303	5 h + 12 h after electrolysis	7.81	1.562
25	303	5 h + 12 h after electrolysis	11.73	2.346

<sup>a</sup>Acetonitrile : DVB : TBAFB mole ratio 22.83:1.05:0.045.

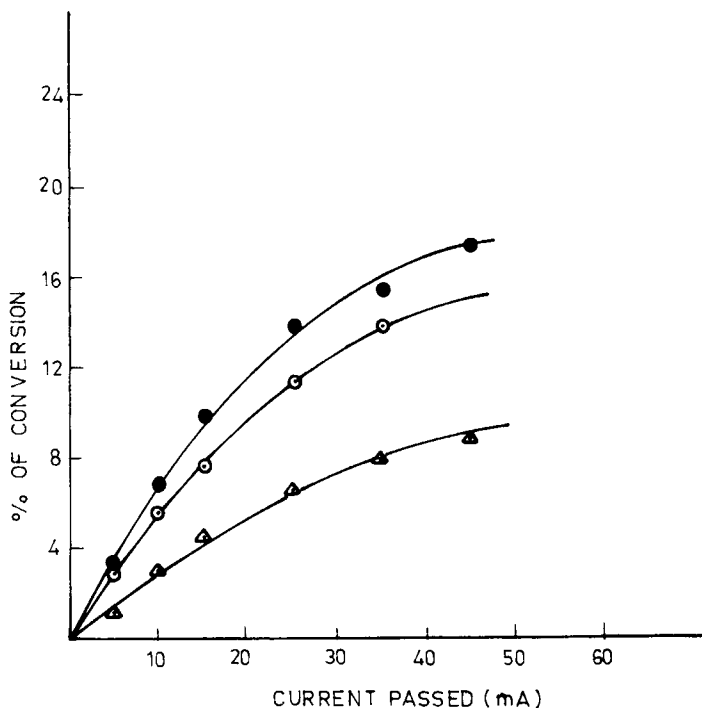


Fig. 1. Polymer formation as a function of current flow at different time intervals. Acetonitrile:DVB:TBAFB mole ratio 22.83:1.05:0.045; temperature 303 K; ( $\triangle$ ) 3 h; ( $\circ$ ) 5 h; ( $\bullet$ ) 8 h.

The effect of the current strength on the polymer formation as observed over a fixed period of electrolysis is shown in Figure 1. The figure shows that the polymer yield tends to increase with current almost proportionally at the lower value of the latter, but subsequently with the further increase of current it becomes gradually insensitive to it.

Polymer yield as a function of time of electrolysis at different current strengths is shown in Figure 2, which shows a linear variation of the yield with time at the lower current strength (i.e., 15 mA), but, at the higher current strengths (i.e., 25 and 45 mA), it shows a progressive deviation from the linearity as the time of electrolysis is increased.

When the logarithm of the rate of polymerization ( $R_p$ , i.e., percentage of conversion/h) measured as an overall rate over the initial 5 h of electrolysis (total conversion not exceeding 20%) is plotted against the logarithm of the current value ( $I_e$ ) in mA, a straight line is obtained (Fig. 3), showing that  $R_p$  is related to  $I_e$  through the usual equation

$$R_p = K(I_e)^n + C$$

From the slope of the line in Figure 3,  $n$  is calculated to be 0.89.

Stirring is found to be quite beneficial for polymer formation as can be seen from Table II; the polymer yield in every case goes up as the solution is stirred.

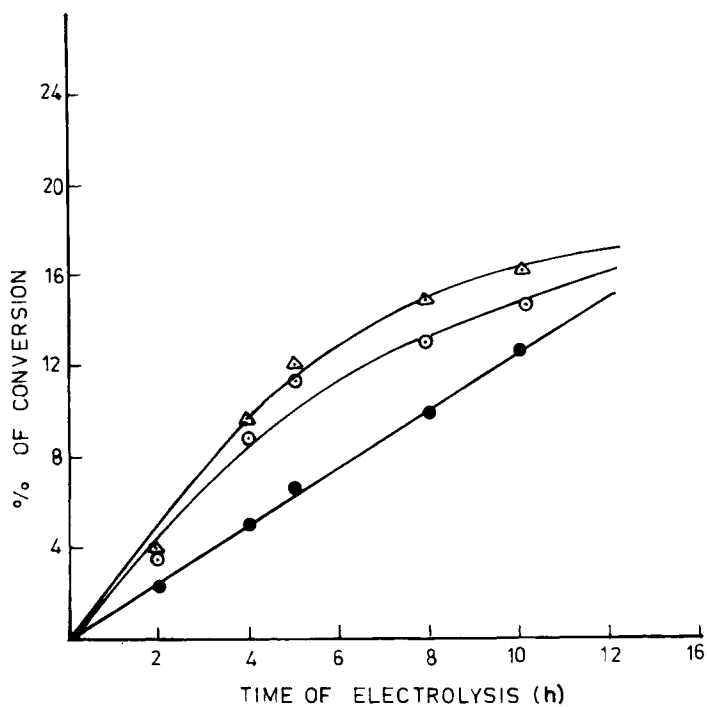


Fig. 2. Polymer formation as a function of time of electrolysis at different current strengths. Acetonitrile : DVB : TBAFB mole ratio 22.83 : 1.05 : 0.045; temperature 303 K; (—●—) 15 mA; (—○—) 25 mA; (—△—) 35 mA.

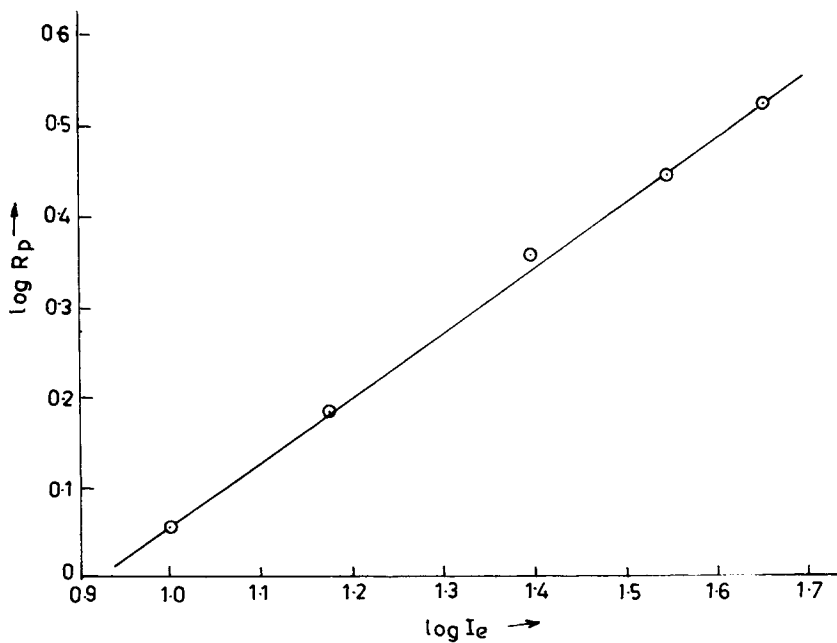


Fig. 3. Plot of  $\log R_p$  vs.  $\log I_e$ .

TABLE II  
Effect of Stirring on the Electroinitiated Polymerization  
of Commercial Divinylbenzene in Various Electrolytic Condition<sup>a</sup>

Current (mA)	Temperature (K)	Time of electrolysis (h)	Condition of electrolysis	Conversion (%)	$R_p$ (%/h)
15	303	5	Stirred	7.52	1.504
15	303	5	Unstirred	5.93	1.186
15	313	5	Stirred	9.81	1.962
15	313	5	Unstirred	7.82	1.562
15	313	10	Stirred	12.03	1.203
15	313	10	Unstirred	9.37	0.937
25	303	5	Stirred	11.34	2.268
25	303	5	Unstirred	8.84	1.768
25	313	10	Stirred	13.78	1.378
25	313	10	Unstirred	10.87	1.087
45	303	5	Stirred	16.48	3.296
45	303	5	Unstirred	12.53	2.506

<sup>a</sup>Acetonitrile : DVB : TBAFB mole ratio 22.83:1.05:0.045.

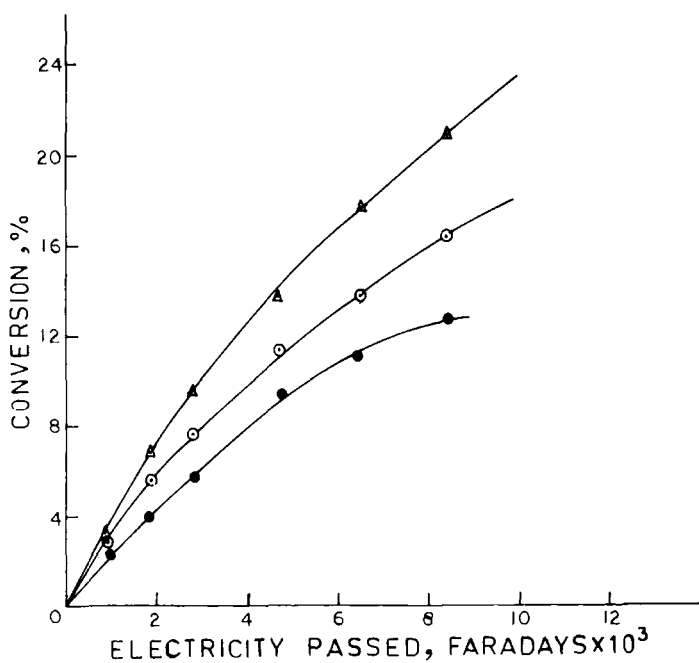


Fig. 4. Polymer formation as a function of quantity of electricity passed over 5 h at different monomer concentrations. Acetonitrile : TBAFB mole ratio 22.83 : 0.045; time of electrolysis 5 h; temperature 303 K; (—●—)  $7.017 \times 10^{-3}$  mol dm<sup>-3</sup>; (—○—)  $10.525 \times 10^{-3}$  mol dm<sup>-3</sup>; (—△—)  $17.524 \times 10^{-3}$  mol dm<sup>-3</sup>.

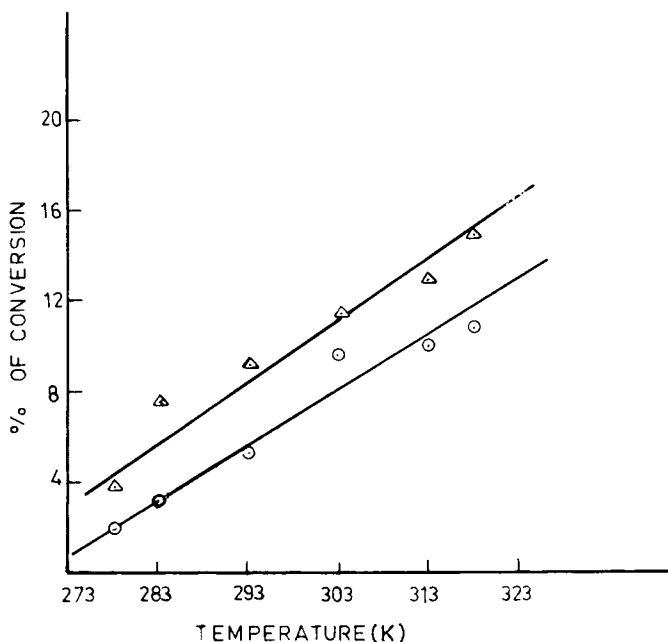


Fig. 5. Polymer formation as a function of temperature at different current flows. Acetonitrile:DVB:TBAFB mole ratio 22.83:1.05:0.045; time of electrolysis 5 h; (—○—) 15 mA; (—△—) 25 mA.

A plot of polymer yield as a function of total electricity passed at different monomer concentrations is shown in Figure 4. The yield increases for a given monomer concentration with the quantity of electricity passed but shows a gradual tendency to flatten out at the higher values of the latter. For a given quantity of electricity passed, the yield increases with the increase of monomer concentration.

From the blank experiments it was confirmed that no thermal polymerization occurs in the range of temperature 283–318 K. However, the results presented in Figure 5 show that increase of temperature produces an enhancing effect on the yield of electropolymerization at different current strengths, as expected.

The IR spectrum of the polymer formed electrochemically using KBr pellet technique is shown in Figure 6. The spectrum bears a close resemblance to that of the polymeric product obtained by Walczynski et al.<sup>18</sup> during the thermal polymerization of commercial divinylbenzene in toluene using benzoyl peroxide as the initiator. The linear polymeric product obtained by the thermal polymerization was identified to be mainly poly(*p*-DVB-co-*m*-DVB-co-*p*-EVB-co-*m*-EVB). We therefore believe that the electropolymer reported in the present studies has a similar structure. The major peaks of the IR spectrum in the range of 2000–600  $\text{cm}^{-1}$  may be assigned as follows: 1630  $\text{cm}^{-1}$  (C=C stretching vibration); 1505  $\text{cm}^{-1}$  (*para*-disubstituted phenyl ring,  $\nu_{\text{C}-\text{C}}$ ); 1410  $\text{cm}^{-1}$  (scissoring vibration of the terminal  $-\text{CH}_2$  of vinyl group,  $\delta_{\text{C}-\text{H}}$ ); 1015 and 990  $\text{cm}^{-1}$  (out of plane deformation of  $-\text{CH}$  in the vinyl group); 840  $\text{cm}^{-1}$  (out of plane deformation of  $-\text{CH}$

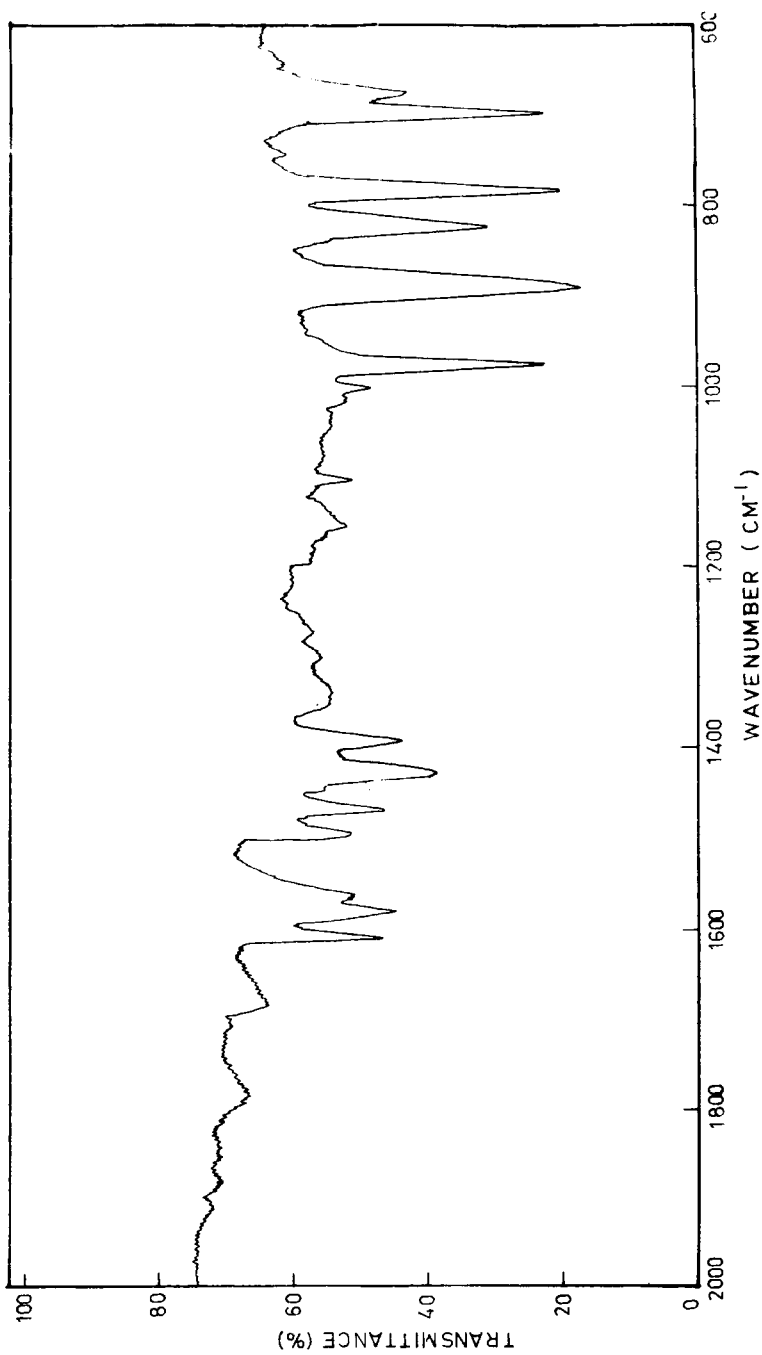


Fig. 6. IR spectra (in KBr pellet) of poly(*p*-DVB-co-*m*-DVB-co-*p*-EVB-co-*m*-EVB) obtained electrochemically.



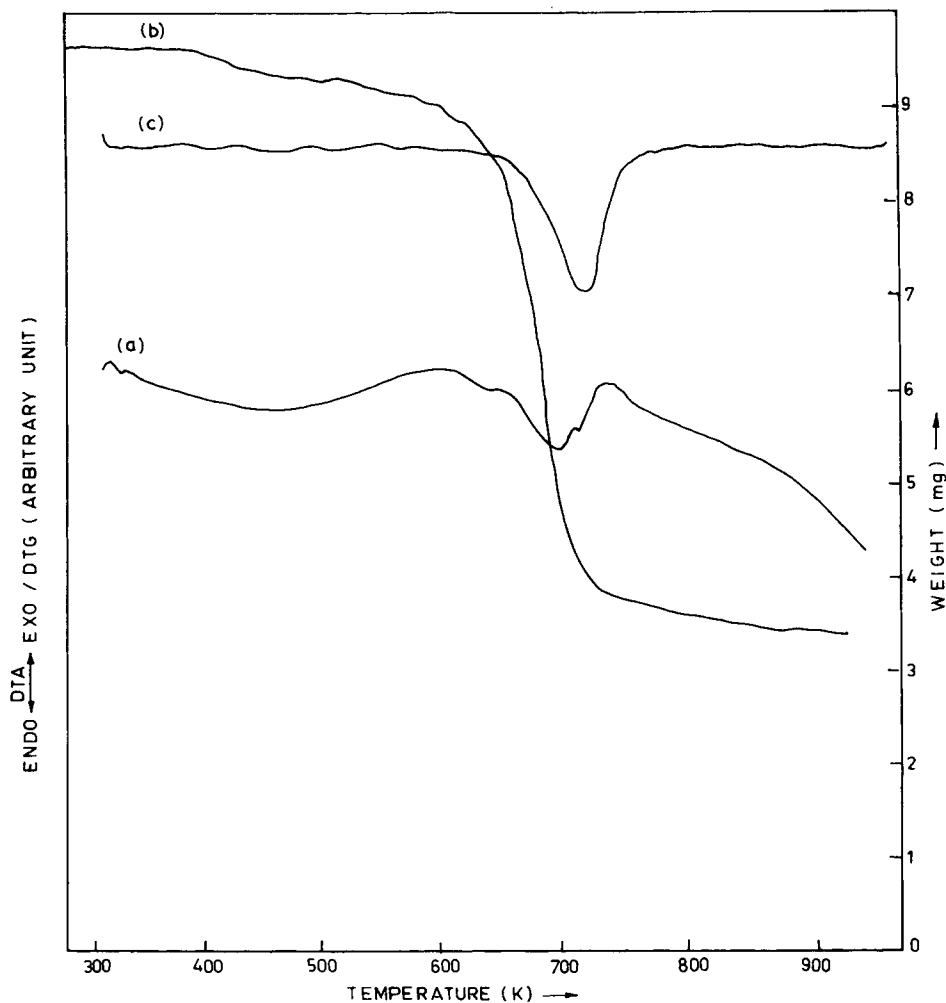


Fig. 7. (a) DTA, (b) TG, and (c) DTG curve of the polymer obtained electrochemically.

of the para-disubstituted phenyl ring); 795 and 700  $\text{cm}^{-1}$  (out of plane deformation of  $-\text{CH}$  of the meta-disubstituted phenyl ring).

The DTA, TG, and DTG curves of the polymer are shown in Figures 7(a), (b), and (c), respectively. The DTA curve shows a broad endothermic peak in the temperature range 458–638 K with a peak maximum at 573 K and a very prominent endothermic peak in the temperature range 638–733 K with a peak maximum at 695 K. Although no characteristic peak is observed beyond 733 K, yet a steady endothermic change is found to occur in this region up to the maximum temperature of study, i.e., 948 K. The first endothermic peak (i.e., 573 K) may be due to the elimination of low molecular weight impurities as well as the softening of the polymeric product. The second endothermic peak obviously corresponds to the thermal degradation of the polymer accompa-

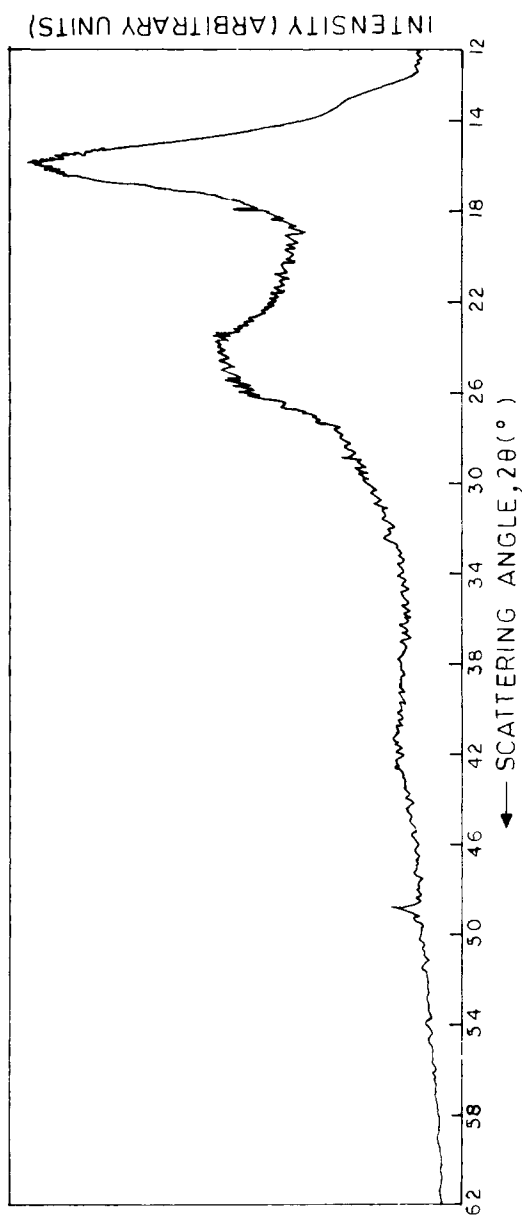


Fig. 8. X-ray diffraction (xrd) pattern of the polymer obtained electrochemically.

nied by the significant weight loss as can also be seen from the DTG and TG curves. The endothermic changes occurring beyond 733 K may be ascribed to further thermal degradation of the products of the first stage of degradation. Both from DTG and TG curves, it may be concluded that the polymer is thermally stable only up to the temperature 645 K.

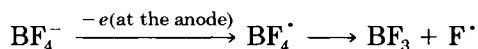
The X-ray diffractogram of the polymer is shown in Figure 8. The diffractogram shows a well defined peak at  $2\theta$  value  $16^\circ$  over a diffused background extending from  $13^\circ$  to  $28^\circ$  and a small peak of low intensity at  $49^\circ$ . These results are indicative of the fact that the electropolymer has partial crystalline character.

The polymer obtained is partially crosslinked as evidenced from its partial solubility in tetrahydrofuran and also loss of fluidity of the reaction mixture during electrolysis.

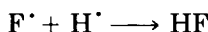
In the presence of hydroquinone, the polymer formation is not hindered. Similarly the presence of air in the system does not produce any inhibiting effect. These observations exclude the probability of any radical mechanism for the polymerization reaction and strongly suggest a cationic mechanism similar to that observed earlier in the case of styrene<sup>19</sup> and vinyl naphthalene<sup>20</sup> under certain experimental conditions using fluoroborate or perchlorate as the electrolyte. This is, however, in contrast to the radical, mechanism observed earlier<sup>1</sup> in the case of electrocopolymerization of styrene and commercial divinylbenzene under biphasic electrolysis technique.

Based on the experimental results and certain findings by earlier workers a tentative mechanism for the initiation process may be outlined as follows.

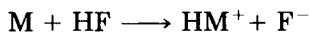
Tetrafluoroborate ( $\text{BF}_4^-$ ) ion is oxidized because of its high anodic discharge potential<sup>21</sup> at the anode to produce  $\text{BF}_4^\cdot$  radical:



The resulting  $\text{F}^\cdot$  radical may then abstract a hydrogen atom from the medium either from the solvent or from water molecules in the form of moisture present as impurities to form an acidic species<sup>22</sup> such as HF as shown below:



The acidic species then induces the cationic polymerization through the formation of  $\text{HM}^+$  through the reaction



Any radicals formed as a result of electrolysis or hydrogen atom abstraction from the medium are of little consequence in initiating polymerization reaction through a radical mechanism. Experimental evidence in support of this supposition is that the polymer formed was free of any boron and fluorine and that the medium which was neutral initially became acidic with the progression of electrolysis.

Trial experiments show that there is no post-electrolysis polymerization indicating the absence of any living propagating species after the termination of the current flow. Thus it appears that the propagating species have very short lifetimes.

Stirring of the solution increases the rate of polymerization probably due to the fact that the initiating species formed at the electrode or in the vicinity of the same get quickly dispersed in the bulk, thereby making polymer formation at the electrode and its consequent blocking less probable.

The slope of the curve,  $\log R_p$  vs.  $\log I_e$  (Fig. 3), clearly shows that, at the initial phase of electrolysis, the rate of polymerization is proportional to approximately the first power of the current.

The increase of polymer yield with the time of electrolysis is obviously due to the continuous formation of  $\text{BF}_4^-$  as well as that of  $\text{MH}^+$  and their cumulative effect on the polymerization process.

The effect of temperature on the electropolymerization reaction studies at relatively high electric current is well understood, as under this condition, diffusion of  $\text{BF}_4^-$  to the electrode will be a limiting factor and the increase of temperature would generally promote such diffusion facilitating the formation of  $\text{F}^-$ .

The constancy of the polymer yield at higher time period of electrolysis may be easily explained as due to the depletion of the monomer concentration on prolonged electropolymerization.

### References

1. P. K. Mahata and B. Nayak, *Polym. J.*, **19**, 1131 (1987).
2. B. F. Soper, R. N. Haward, and E. F. T. White, *J. Polym. Sci. (A-1)*, **10**, 2545 (1972).
3. D. J. Worsfold, *Macromolecules*, **3**, 513 (1970).
4. J. Malinsky, J. Klaban, and K. Dusek, *Coll. Czech. Chem. Commun.*, **34**, 711 (1969).
5. D. Y. D. Chung, M. Bartholin, and A. Guyot, *Angew Makromol. Chem.*, **103**, 109 (1982).
6. G. Hild, and P. Rempp, *Pure Appl. Chem.*, **53**, 1541 (1981).
7. R. H. Wiley, and E. E. Sale, *J. Polym. Sci.*, **42**, 491 (1970).
8. G. J. Schwachula, *J. Polym. Sci. Polym. Symp. Ed.*, **53**, 107 (1975).
9. K. Dusek, H. Galina, and J. Mikes, *Polym. Bull.*, **3**, 19 (1980).
10. H. Galina, and M. Gordon, *Proc. 12th Europhys. Conf. Molecular Mobility in Polymer Systems*, Leipzig, 1980, p. 50.
11. R. S. Whitney and W. Burchard, *Makromol. Chem.*, **181**, 869 (1980).
12. H. Kast, and W. Funke, *Makromol. Chem.*, **180**, 1335 (1979).
13. R. H. Wiley, J. Jin, and T. Ahn, *J. Makromol. Sci. Chem.*, **3**, 1543 (1969).
14. Y. Natadori, and T. Tsuruta, *Makromol. Chem.*, **179**, 2069 (1978).
15. B. T. Storey, *J. Polym. Sci. A*, **3**, 265 (1965).
16. T. Narita, T. Yamaguchi, and T. Tsuruta, *Bull. Chem. Soc. Jpn.*, **46**, 3825 (1973).
17. P. K. Mahata and B. Nayak, *Bull. Electrochem.*, **4**, 375 (1988).
18. B. Walczynski, B. N. Kolarz, and H. Galina, *Polymer Commun.*, **26**, 276 (1985).
19. U. Akbulut, J. E. Fernandez, and R. L. Birke, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 133 (1975).
20. D. C. Phillips, J. D. B. Smith, and D. H. Davies, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 1563 (1977).
21. M. Fleischmann, and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968).
22. B. M. Tidswell and A. G. Doughty, *Polymer*, **12**, 431 (1971).

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