

Electroinitiated Copolymerization of *N*-Vinylcarbazole and α -Methylstyrene in a Mixed Biphasic Medium

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Synopsis

The electroinitiated copolymerization of *N*-vinylcarbazole and α -methylstyrene has been studied using a mixed biphasic system in which formamide together with some added electrolyte has been used as the polar phase and the monomer in bulk form or its solution in a nonpolar solvent as the nonpolar phase. The copolymer has been characterized by elemental analysis, and infrared and nuclear magnetic resonance spectroscopy. Molecular weights obtained from gel permeation chromatography were in the range of $20\text{--}25 \times 10^3$. Generally the copolymer yield increased with increased applied current density. The effect of various other parameters such as dependence of copolymer yield on concentration of electrolyte and comonomer, temperature, and time of electrolysis have also been examined. The locus of polymerization is the anode compartment and a plausible mechanism based on the electrochemical formation of a radical-cation and a dication has been suggested.

INTRODUCTION

Although there have been numerous reports on the electroinitiated homopolymerization starting with the pioneering work of Wilson in 1949,¹ yet study of copolymerization using this technique is of recent origin.² Furthermore, in all the studies to date, the general tendency has been to use a monophasic system. Recently, however, it has been reported from this laboratory³ that electrohomopolymerization can be rather more conveniently achieved using a biphasic system, made of a polar phase containing a polar solvent with added electrolyte(s), and a nonpolar phase in the form of either the bulk monomer itself or its solution in a nonpolar solvent. The advantage of such a technique is that the presence of the polar phase mostly containing the electrolyte allows easy passage of the electrolytic current whereas the nonpolar phase functions as the main medium for the polymerization reaction. It further facilitates the dissolution of the polymer or the copolymer formed, thus making the electrode surface free of any polymer coating. The present work therefore constitutes an attempt to carry out the electroinitiated copolymerization of *N*-vinylcarbazole (NVC) and α -methylstyrene (α -MS) following this new technique.

Formamide, a solvent with a high dielectric constant (109.5 at 298.15 K) which can be deoxygenated easily and has been found to be a good polar solvent for biphasic electropolymerization studies reported from this laboratory earlier⁴ was used as the polar phase together with a suitable electrolyte, and the nonpolar phase consisted of either a solution of NVC in α -MS (a

liquid monomer) or the solutions of both the monomers, namely, NVC and α -MS in a nonpolar liquid such as toluene, benzene, xylene, or cyclohexane. Several salts such as chloride, bromide and acetate of zinc, sodium nitrate, ferric chloride, and tetrabutyl ammonium perchlorate were used as electrolytes to study their relative efficacies.

EXPERIMENTAL

Materials

Formamide (BDH, LR) was purified following the procedure described by Nayak et al.⁵ It was made free from any dissolved oxygen by passing purified and dried nitrogen gas through it for an hour. The final product was stored in an air-tight bottle at a temperature below 283.15 K.

α -Methylstyrene was freed from the inhibitor after washing with 10% sodium hydroxide solution several times. It was washed with distilled water until free from alkali and then dried over fused calcium chloride. It was subsequently distilled under reduced pressure and stored below 283.15 K (b.p. 331.15 K/15 mm).

N-vinylcarbazole was recrystallized from *n*-hexane⁶ and was dried in vacuum at 303.15 K for two days (m.p. 337.35 K). The sample was stored in the absence of light in a vacuum desiccator prior to its use.

Toluene (BDH, AR); benzene (BDH, AR); xylene (BDH, AR) were made free from thiophene and dried properly by following the standard procedure.⁷

Tetrabutyl ammonium perchlorate (Fluka, Ag, Chem, Fabrik) and anhydrous ferric chloride (Sarabhi. M. Chemicals) were used without further purification. These were always stored in a vacuum desiccator to avoid any contact with moisture. Zinc acetate (E. Merck proanalysis); zinc bromide (BU & Co); zinc chloride (TB & Co); sodium nitrate (BDH, AR) were dried under vacuum before use.

Apparatus and Polymerization Procedure

Generally, a single compartment electrolysis/reaction cell without any separation between the cathode and anode compartments was used to carry out the electrochemical polymerizations. For reactions which required the contents of the cathode and anode compartments to be analyzed separately, a split cell with compartments separated by means of a sintered glass disk of fine porosity was employed. The platinum electrodes ($1 \times 1 \text{ cm}^2$) were set 2.5 cm apart in the cell.

During electrolysis, 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 to the solutions in order to bring the two phases into intimate contact. All experiments were conducted at 313.15 K except as otherwise indicated. A variable direct current power supply unit (Aplab, model 7331) with provisions for the measurement of current and voltage drop through the cell was used to provide the required direct current.

After filling the cell with the polar phase (12 cm^3) with or without the electrolyte which together formed the lower layer, and the solution of mono-

mers which formed the upper layer, nitrogen gas was slowly bubbled through the cell for 30 minutes prior to electrolysis. After the polymerization reaction, the copolymer was precipitated by pouring the contents of the cell into excess of methanol. Finally the product was weighed after washing with methanol and drying under vacuum. The blank experiments which were carried out in the absence of current, however, did not yield any polymeric product. The copolymeric product obtained through electrolysis was further tested for the presence of any homopolymer.

The copolymerization runs were fairly reproducible, the copolymer yields varying in duplicate experiments by $\pm 5\%$.

Analysis

Since α -MS alone did not produce any polymerization under the conditions of electrolysis, the presence of poly (α -MS) was consequently ruled out. Further various fractions of the original polymeric product collected by fractional precipitation in toluene medium by the addition of methanol yielded the same infrared (IR) spectrum (in CHCl_3) which was different from that of poly (NVC). This clearly showed that the initial polymeric product was a copolymer of NVC and α -MS uncontaminated with any homopolymer.

Besides the IR spectra, the copolymer was further characterized by its nuclear magnetic resonance (NMR) spectra taken in CDCl_3 . Molecular weight of the polymer as found by gel permeation chromatography (GPC) technique in toluene was found to be in the range of $20\text{--}25 \times 10^3$.

RESULTS AND DISCUSSION

Preliminary experiments showed that the passage of electric current in the presence of an electrolyte was necessary to initiate the copolymerization reaction. No copolymer formed in the absence of any electric current. From GPC analysis the copolymer was found to be almost monodispersed with a dispersity value of 1.09.

The formation of copolymer of α -MS with NVC was confirmed through its NMR and IR spectra as well as its elemental composition. The NMR spectrum of the copolymer [Fig. 1(a)] shows broad resonances in the range δ 1.2 to δ 2.4 which are associated with aliphatic protons and again between δ 6.5 and δ 8.9 due to aromatic protons. In contrast, poly (NVC) gives relatively sharp resonances due to its aliphatic protons at δ 1.2 and δ 1.6 [Fig. 1(b)] and broad resonances in the range δ 7.5 to δ 8.2 due to its aromatic protons. Similarly the homopolymer poly (α -MS) which is not obtainable electrochemically but could be prepared using γ -radiations gave resonance peaks, for its aliphatic protons at δ 1.5 and for its aromatic protons in the range δ 6.9 to δ 7.1 [Fig. 1(c)].

The infrared spectrum of the copolymer is shown in Figure 2. The spectrum does not show the typical vinyl bands at 930 cm^{-1} and 975 cm^{-1} due to C—H bending although elemental analysis clearly indicate the presence of nitrogen (Table I) in the copolymeric product. This coupled with the fact that the spectrum shows a band at 1600 cm^{-1} which is characteristic of styrene moiety conclusively proves that the product is a copolymer of α -MS and NVC where the N-vinyl groups participated in the copolymerization process.

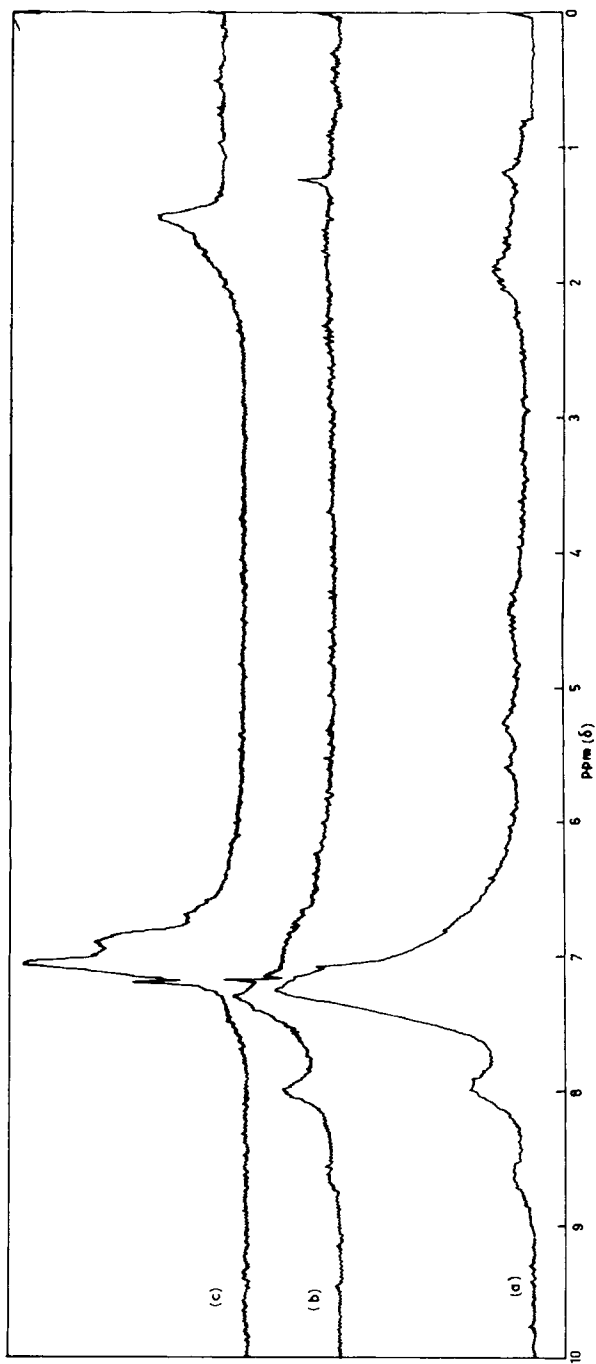


Fig. 1. NMR spectra of (a) the copolymer of NVC and α -MS; (b) homopolymer of NVC; (c) homopolymer of α -MS (solvent CDCl_3 , at 90 MHz).

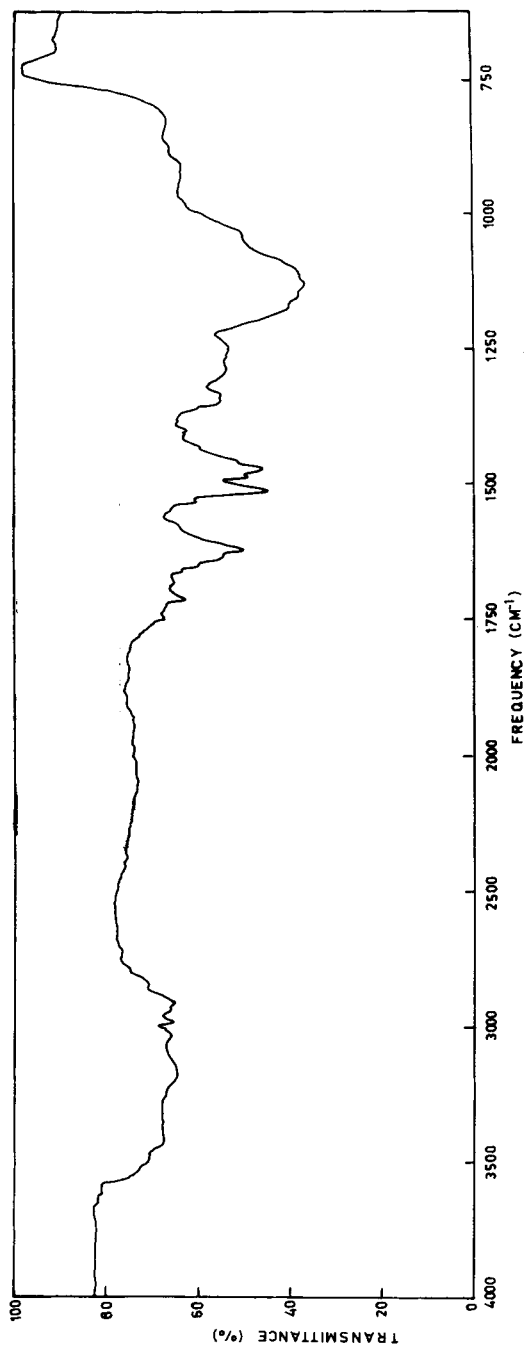


Fig. 2. IR spectrum of copolymer of NVC and α -MS in CHCl_3 solution.

TABLE I
Nitrogen Content of Copolymers of NVC and α -MS Obtained Electrochemically

NVC in g	α -MS in g	Mole ratio of α -MS : NVC	Copolymer yield (g)	% Nitrogen in copolymer
0.078	2.725	1 : 0.015	0.0401	4.78
0.120	2.725	1 : 0.027	0.0621	4.50
0.372	2.725	1 : 0.072	0.0332	6.54
0.466	2.725	1 : 0.090	0.0357	5.23
0.621	2.725	1 : 0.119	0.0226	5.37

Mole ratio of formamide : FeCl_3 , 20 : 0.12.

Time of electrolysis, 5 h; current, 15 mA; temperature, 313.15 K.

TABLE II
Effect of Various Added Electrolytes on the Electrocopolymerization of NVC and α -MS in Mixed Biphasic Medium

Electrolyte	Moles of electrolyte used	Copolymer yield (g)	Rate of copolymer formation. (Copolymer yield/h).
Zinc bromide	1.79×10^{-3}	0.0255	5.10×10^{-3}
Zinc chloride	1.74×10^{-3}	0.0293	5.86×10^{-3}
Ferric chloride	1.75×10^{-3}	0.0621	12.42×10^{-3}
Zinc acetate	1.75×10^{-3}	—	—
Sodium nitrate	1.84×10^{-3}	0.0035	7.00×10^{-4}
Tetrabutyl ammonium perchlorate	1.75×10^{-3}	0.0123	2.46×10^{-3}

Feed composition (mole ratio) : formamide : NVC : α -MS, 20 : 0.04 : 1.52; time of electrolysis, 5 h; temperature, 313.15 K; current, 15 mA.

The copolymer yield as well as its composition depends on various factors such as the current strength, comonomer concentrations, concentration of electrolyte, duration of electrolysis, temperature, and finally whether the cell contents are adequately stirred or not.

Addition of certain electrolytes into the medium increases the copolymerization reaction, the results of which are given in Table II. Among the electrolytes, ferric chloride is found to be the most effective in producing copolymers with higher yield.

The effect of comonomer ratio on the rate of copolymer formation, that is, the total weight (in grams) of copolymer formed per hour was studied keeping all other variables constant. The results are summarized in Table III which shows that with the increase of the mole ratio, NVC : α -MS, the rate of copolymer formation increases up to a certain value and then it decreases with the further increase of the said mole ratio. This is true irrespective of whether the mole ratio is changed by changing the moles of NVC while keeping the moles of α -MS constant or the vice versa.

The effect of the concentration of ferric chloride on the rate of copolymer formation has been studied at a fixed current strength (i.e., 15 mA shown in

TABLE III
Effect of the Comonomer Ratio and the Volume of Comonomer on the
Rate of Copolymer Formation

Volume of α -mS (mL)	Mole ratio of α -MS : NVC	Yield of copolymer (g)	Rate of copolymer formation. (copolymer yield/h)
3	1:0.007	0.0248	4.96×10^{-3}
3	1:0.015	0.0401	8.02×10^{-3}
3	1:0.027	0.0621	12.42×10^{-3}
3	1:0.058	0.0389	7.78×10^{-3}
3	1:0.072	0.0332	6.64×10^{-3}
3	1:0.090	0.0357	7.14×10^{-3}
3	1:0.119	0.0226	4.52×10^{-3}
1	1:0.081	0.0283	5.66×10^{-3}
2	1:0.041	0.0326	6.52×10^{-3}
3	1:0.027	0.0621	12.40×10^{-3}
4.5	1:0.018	0.0510	10.20×10^{-3}
6	1:0.013	0.0435	8.70×10^{-3}

Mole ratio of formamide: FeCl_3 , 20:0.12.

Time of electrolysis, 5 h; current, 15 mA; temperature, 313.15 K.

Fig. 3). It is found that the copolymer yield increases with the increase in the concentration of the electrolyte up to a limiting concentration and then it gradually decreases with further increase of electrolyte concentration.

The dependence of the copolymer formation on the magnitude of electrolytic current as observed over a fixed period of electrolysis at three different electrolyte concentrations is shown in Figure 4 where the abscissa shown in terms of quantity of electricity passed indirectly represents the magnitude of the current. It is to be noted that at low electrolytic concentration, the

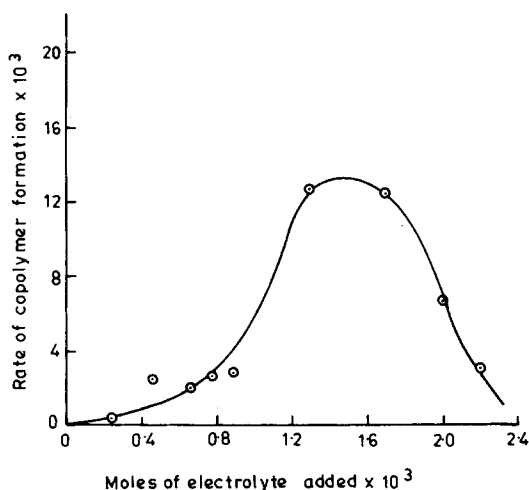


Fig. 3. Effect of electrolyte concentration on the rate of copolymer formation. Feed composition (mole ratio); formamide: NVC: α -MS, 20:0.04:1.52; time of electrolysis, 5 h, temperature, 313.15 K; current, 15 mA.

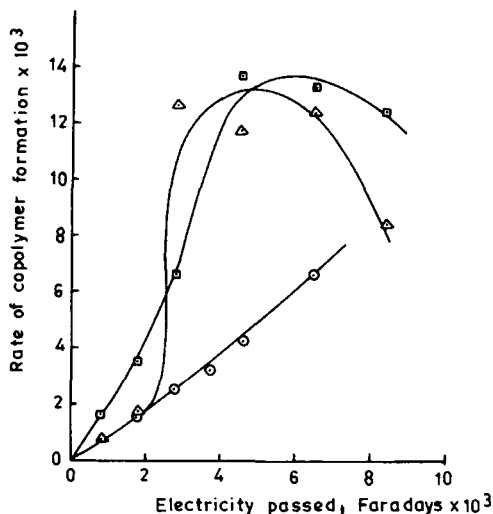


Fig. 4. Rate of copolymer formation as a function of current, i.e., quantity of electricity passed at three different concentrations of electrolyte. Feed composition (mole ratio); formamide : NVC : α -MS, 20 : 0.04 : 1.52; time of electrolysis, 3 h; temperature 313.15 K; FeCl_3 : \circ 8.8852×10^{-3} mole, \blacktriangle 1.3115×10^{-3} mole, \square 2.0402×10^{-3} mole.

copolymer formation is rather slow initially and then increases linearly throughout with the current. However, at higher electrolytic concentration, a peculiar trend is noticed. After the initial slow increase, the copolymer yield increases sharply with current, reaches a maximum, and then decreases with the further increase of the current.

Copolymer yield as a function of the time of electrolysis, at three different current strengths, is shown in Figure 5. It is to be noted that at lower values of current (i.e., 5 mA) the yield increases linearly with time. But at higher current strengths (i.e., 15 mA and 35 mA) the copolymer yield increases with

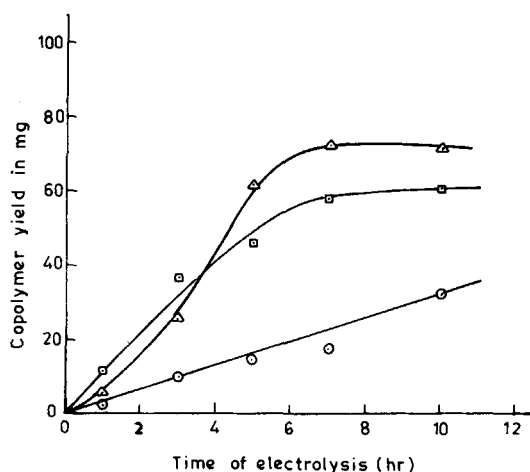


Fig. 5. Copolymer yield as a function of time and current in the electroinitiated reaction. Feed composition (mole ratio); formamide : NVC : α -MS : FeCl_3 , 20 : 0.04 : 1.52 : 0.12; temperature, 313.15 K; current, \circ 5 mA, \blacktriangle 15 mA, \square 35 mA.

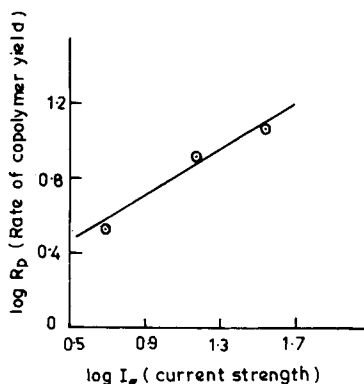


Fig. 6. Determination of current exponent in the rate equation, $R_p = k(I_e)^n + C$.

time at first, but subsequently assumes a constant value. No induction period is found to be present in any of the three cases.

From the plot in Figure 5, the initial rate of copolymer formation (R_p) can be calculated in principle, and this should satisfy the Eq. (8)

$$R_p = k(I_e)^n + C \quad \dots \quad (1)$$

The overall R_p corresponding to a 3 hour reaction period was calculated at different current strengths and it is found that such values satisfy Eq. (1) as shown by the linearity of the plot of $\log R_p$ versus $\log I_e$ in Figure 6. By taking C to be zero, as there was no polymerization in the absence of the current, k was evaluated from the intercept and was found to be 2.75 g/h and the current exponent calculated from slope was 0.621.

Figure 7 shows correlation of copolymer yield with the total charge transfer through the solution based on two different sets of experiments such as (a) by varying the current while fixing the time of electrolysis constant and (b) by varying the time period of electrolysis at a fixed value of the current. Although the points seem to be somewhat scattered, yet there appears to be a significant correlation between the copolymer yield and the total electricity passed. Copolymer yield seems to increase at first with the quantity of electricity passed through the cell but subsequently it becomes insensitive toward the same.

The effect of temperature on the copolymer yield with respect to time period of electrolysis has been presented in Figure 8. The results show that increase of temperature as expected, produces an enhancing effect on copolymer yield.

The effect of various biphasic systems on the copolymerization process has been shown in Table IV. It is to be noted that when formamide was replaced by water fully or partially, it produced the unexpected effect of inhibiting the copolymerization process. Again when the nonpolar phase was composed essentially of the solution of the comonomers in solvents such as toluene, benzene, xylene, and cyclohexane, instead of the solution of NVC in α -MS, the copolymer yield was generally found to decrease, the order of decrease for

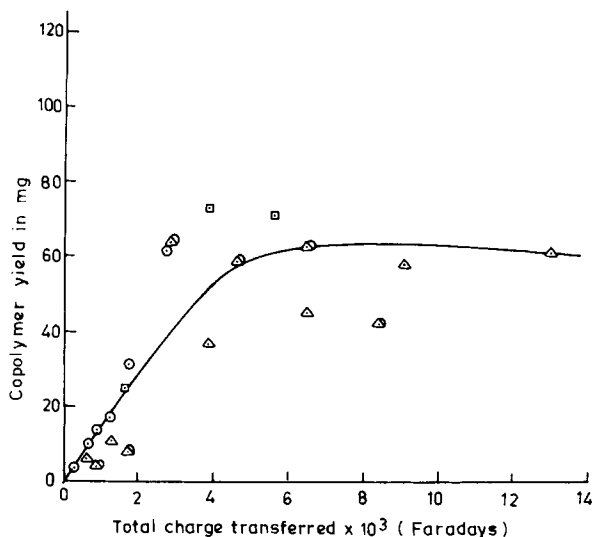


Fig. 7. Rate of copolymer formation as a function of the total charge transferred into the system. Feed composition (mole ratio); formamide : NVC : α -MS : FeCl_3 , 20 : 0.04 : 1.52 : 0.12; temperature; 313.15 K.

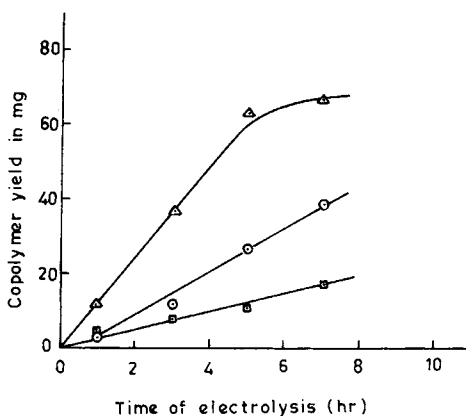
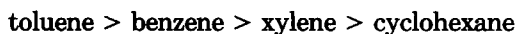


Fig. 8. Copolymer formation as a function of the time of electrolysis and temperature. Feed composition (mole ratio); formamide : NVC : α -MS : FeCl_3 , 20 : 0.04 : 1.52 : 0.09; current, 15 mA; temperature, ○ 303.15 K; ▲ 313.15 K; ◻ 323.15 K.

these solvents being,



Further, there was no significant postelectrolysis polymerization effect in this system as can be seen from the data presented in Table V. Stirring is found to be essential for this electrocopolymerization process, as in the absence of stirring no polymerization takes place. Introduction of hydroquinone, a radical quencher, produces a partial inhibiting effect on the copolymerization process and a similar effect is seen in the presence of air or oxygen. But

TABLE IV
Effect of the Composition of the Biphasic System on the Rate of Copolymer Formation of NVC and α -MS

Biphasic system	Mole ratio of polar solvent: α -MS : NVC : nonpolar solvent	Copolymer yield (g)	Rate of copolymer formation (yield/h)
Formamide + α -MS + NVC	20 : 1.52 : 0.04 : 0	0.0621	12.42×10^{-3}
Formamide + α -MS + NVC + toluene	20 : 1.52 : 0.04 : 1.86	0.0436	8.72×10^{-3}
Formamide + α -MS + NVC + benzene	20 : 1.52 : 0.04 : 2.24	0.0361	7.22×10^{-3}
Formamide + α -MS + NVC + xylene	20 : 1.52 : 0.04 : 1.62	0.0128	2.56×10^{-3}
Formamide + α -MS + NVC + cyclohexane	20 : 1.52 : 0.04 : 1.84	0.0100	2.00×10^{-3}
Water + α -MS + NVC	44.4 : 1.52 : 0.04 : 0	—	—
Water + formamide + α -MS + NVC	22.2 : 10.1.52 : 0.04	—	—

Moles of FeCl_3 , 0.1465×10^{-3} /ml; temperature, 313.15 K; current, 15 mA; time of electrolysis, 5 h.

TABLE V
Postelectrolysis Polymerization Effect on the Copolymer Formation of NVC and α -MS in Mixed Biphasic Medium

Time of the current flow (h)	Time allowed for polymerization in absence of current flow (h)	Copolymer yield (g)
3	—	0.0253
3	2	0.0282
3	4	0.0285
3	7	0.0294

Feed composition (mole ratio); formamide : NVC : α -MS : FeCl_3 , 20 : 0.04 : 1.52 : 0.12; temperature, 313.15 K; current, 15 mA.

pyridine, an inhibitor for cationic polymerization process when added to the system had a drastic inhibiting effect on the copolymer formation.

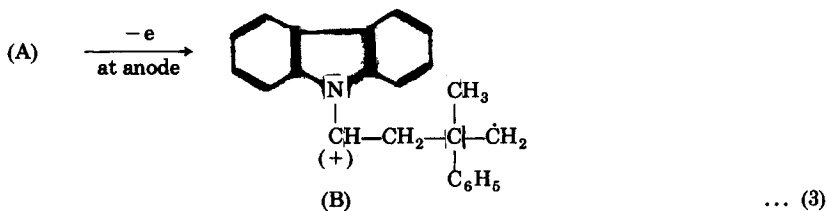
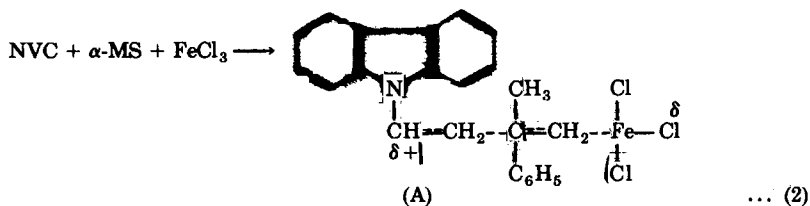
From split-cell experiments the locus of copolymerization was found to be the anode compartment.

MECHANISM

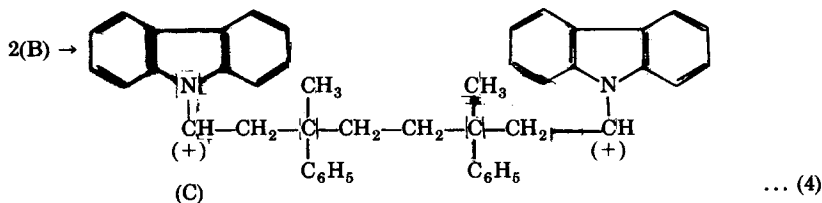
The mechanism of the copolymerization appears to be somewhat complex, as it is inhibited by both radical and cation quenchers to different extents. However, the mechanism appears to be predominantly cationic as pyridine had a more drastic effect on the copolymer yield than hydroquinone.

Considering all the observed facts, the following tentative mechanism may be proposed.

It is believed that initially NVC, α -MS, and FeCl_3 combine to form a loose complex as represented by (A). The complex (A) then undergoes the electrode reaction at the anode giving rise to a radical-cation (B).



The radical-cation is likely to be short lived as it would dimerize to give the dication (C).



Both the radical-cation (B) and dication (C) can further propagate polymerization reactions, the former by both cationic and radical mechanisms and the latter through cationic mechanism alone. Because of the ionic nature of these intermediates, it is further believed that they would mostly concentrate at the interface of polar and nonpolar phases and the polymerization would occur mostly at the interface of the minute droplets of the nonpolar phase dispersed in the polar phase. Thus the role of the biphasic system in this case appears to be twofold. (1) The polar phase mainly acts as the solvent medium for electrolyte, namely, ferric chloride, and thus increases the current flow. It also promotes the formation of the polar complex (A) as well as its ionic oxidation products at the interface with the nonpolar phase, that is, at the surface of the minute droplets of the nonpolar phase dispersed in the polar phase. (2) The nonpolar phase, on the other-hand, acts as the reservoir of the reacting monomers which take part in the propagation steps. This mechanism would explain the most salient feature of these studies, namely that α -MS can undergo electrocopolymerization with NVC while it cannot itself take part in the electrohomopolymerization process. This would also explain why a cation quencher like pyridine will be more effective in inhibiting the copolymerization reaction than a radical quencher such as hydroquinone or oxygen.

CONCLUSION

The electroinitiated copolymerization of *N*-vinylcarbazole and α -methylstyrene based on novel techniques (i.e., electrolysis in a biphasic system is described). The copolymer yield is found to be a function of current, time of electrolysis, and concentration of electrolyte. Among the various added electrolytes, ferric chloride is found to have the maximum effect in promoting copolymerization. The copolymer obtained is, however, of low molecular weight in the range of $20\text{--}25 \times 10^3$. The copolymerization appeared to be proceeding both through radical and cationic mechanisms, the latter being the more dominant one.

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