(19) G. R. Hamed, presented at the Rubber Division Meeting, Fall 1980, Detroit, MI, Paper No. 38.
(20) R. P. Campion, *J. Adhes.* 7, 1 (1974).
(21) G. R. Hamed and C. H. Shieh, *J. Polym. Sci., Polym. Phys. Ed.*, 21, 1415 (1983).
(22) K. Jud, M. Kausch, and J. G. Williams, *J. Mater. Sci.*, 16, 204 (1981).
(23) S. Prager and M. Tirrell, *J. Chem. Phys.*, 75, 5194 (1981).
(24) Y. H. Kim and R. P. Wool, *Macromolecules*, 16, 1115 (1983).
(25) J. O. Tveekrem, unpublished results.

Electroinitiated Polymerization of *N*-Vinylcarbazole in Mixed Biphasic Media

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ABSTRACT: The electroinitiated polymerization of *N*-vinylcarbazole has been studied in an intimately mixed two-phase medium consisting of a polar phase, i.e., formamide with an added electrolyte, and a nonpolar phase formed by a solution of the monomer in a nonpolar liquid like toluene. Poly(*N*-vinylcarbazole) was obtained in good yield with the highest R_p of 3.1%/h and the highest polymerization efficiency of 28.4×10^{-3} mol/faraday. The polymer was characterized by its IR and NMR spectra, and its molecular weight was found to be in the range of $(10–15) \times 10^3$. Experiments conducted with a divided cell indicated the formation of the polymer in the anode compartment and hence a cationic mechanism has been suggested.

In an earlier communication from this laboratory,[1] the electroinitiated polymerization of methyl methacrylate using a novel technique was reported. The technique is based on using a two-phase system in the electrolytic cell in the place of a monophasic one used customarily. The biphasic system consisted of a polar phase containing a polar solvent with added electrolyte(s) and a nonpolar phase which could be either the bulk monomer itself or its solution in a nonpolar solvent. The polar phase being more conducting allows the passage of sufficient current and serves chiefly as the medium for electrolysis while the nonpolar phase containing the bulk of the monomer or its solution traps most of the radicals formed at the electrodes and acts as the chief medium for polymerization. The technique has the further advantage that it allows more electrolytic current to flow through the cell and also prevents the coating of the electrodes by the polymer as the polymer formed remains in a dissolved state in the nonpolar phase. In the present communication, an effort has been made to apply a similar biphasic technique to the electroinitiation polymerization of a solid monomer, namely *N*-vinylcarbazole (NVC). Although there have been a few reports on electropolymerization of NVC earlier,[2-6] in all these studies, the electropolymerization has been carried out by using a single homogeneous medium.

For carrying out the electropolymerization in the present studies, formamide has been used as the solvent for the polar phase because of its high dielectric constant (109.5 at 298.15 K). An added consideration was that it can be easily deoxygenated. The nonpolar phase consisted mostly of a solution of NVC in toluene. The two phases were almost immiscible with each other. To facilitate the transfer of initiating species from the polar phase to the nonpolar phase, the two phases were kept in intimate contact with each other by adequate stirring. Several salts such as zinc chloride, zinc bromide, ferric chloride, sodium nitrate, zinc acetate, and potassium acetate were used as electrolytes with a view to examining their efficiency in promoting the electropolymerization.

Experimental Section

Materials. Formamide (BDH, LR) was purified by following the procedure described by Nayak et al.[7] The solvent was then made free from any dissolved oxygen by passing through it purified and dried nitrogen gas for 1 h. The final product was stored in an airtight bottle at a temperature below 283.15 K.

NVC (BASF, West Germany) was recrystallized from *n*-hexane[3] and was dried under vacuum at 303.15 K for 2 days. The sample was stored in complete absence of light in a vacuum desiccator prior to its use.

Toluene (BDH, AR) and benzene (BDH, AR) were made free from thiophene and dried properly by following the standard procedures.[8] Zinc acetate (E. Merck pro-analysi), potassium acetate (BDH, AR), zinc bromide (BB, AR), sodium nitrate (BDH, AR), and zinc chloride (TB and Co., London) were each dried under vacuum before use. Anhydrous ferric chloride (Sarabhai M Chemicals) was used without further purification. It was always stored in a vacuum desiccator to avoid any contact with moisture.

Apparatus and Procedure. The electrochemical polymerizations were carried out mostly in a single-compartment electrolysis/reaction cell without any separation between the cathode and anode compartments. For reactions which required the cathode and anode sections to be analyzed individually, a split cell, whose compartments were separated by a sintered glass disk of fine porosity, was employed.

All experiments were conducted at 313.15 K except as otherwise indicated. 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 in order to bring the two phases into intimate contact during electrolysis. 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 the cell was filled with the polar phase (12 cm^3), with or without the electrolyte which together formed the lower layer, and then with the solution of the monomer which formed the upper layer, nitrogen gas was slowly bubbled through the cell for 30 min prior to electrolysis.

The polymer formed in the upper layer was collected by precipitating the same with an excess of acidified methanol and subsequently drying under vacuum. The polymer was characterized by IR and NMR spectroscopy using $CHCl_3$ and $CDCl_3$ as solvents, respectively. The viscosity average molecular weights ($\bar{M}_v$) of the polymer were determined in benzene by using the following relation:[9]

$$[\eta] = 3.35 \times 10^{-4} M_v^{0.58} \quad (1)$$

Results

Preliminary experiments showed that the flow of electrolytic current in the presence of an electrolyte was necessary to initiate the polymerization reaction. In the

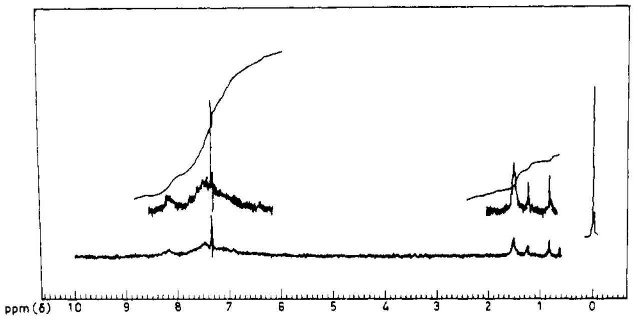

Figure 1. ^{1}H NMR spectra (90 MHz) of $CDCl_3$ solutions of poly(*N*-vinylcarbazole) obtained electrochemically in mixed biphasic media.

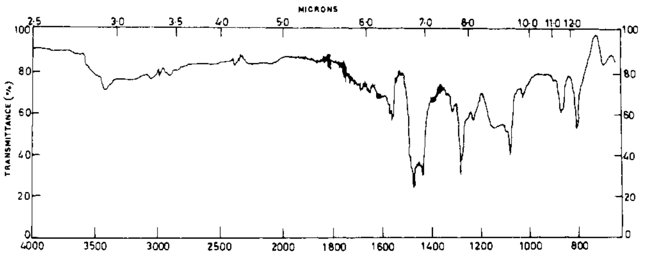

Figure 2. IR spectra of poly(*N*-vinylcarbazole) in $CHCl_3$ solution obtained electrochemically in mixed biphasic media.

case of successful polymerization, it was further noticed that a light yellow shade followed by a deep green color developed in the polar phase, and at the same time the nonpolar phase assumed a reddish tinge. In the case of split-cell experiments, such color development along with polymerization occurred only in the anode compartment.

The poly(*N*-vinylcarbazole) obtained by this novel technique was confirmed from its NMR and IR spectral data. The NMR spectrum of the poly(NVC) shows the presence of aromatic proton peaks at δ 8.2 and 7.5 and aliphatic proton peaks at δ 1.2 and 1.6 (Figure 1), which are close to those reported by Phillips et al.[3] The absence of the vinyl bands at 930 and 975 cm^{-1} as found in the IR absorption spectrum of the polymer (Figure 2) indicates that polymerization had occurred through the *N*-vinyl groups. Other absorption bands were almost identical with those quoted by Tazuke et al.[10]

The polymer yield obtained by this electrochemical method depended on various factors such as current strength, concentration of the electrolyte, time of electrolysis, temperature, monomer concentration, and finally whether the cell contents are adequately stirred or not. Although electropolymerization runs were carried out under nitrogen atmosphere, such a condition was, however, not absolutely necessary as air or oxygen had no effect on the polymerization process. The polymerization runs were fairly reproducible, the polymer yields varying in duplicate experiments by ±5%.

Addition of certain electrolytes into the medium not only increased the conductance of the medium but also initiated the polymerization reaction. The results, with various added electrolytes, are given in Table I. Among the electrolytes, ferric chloride is found to be the most effective in producing polymers with higher yield.

The effect of the magnitude of electrolytic current on the polymer formation as observed over a fixed period of electrolysis is shown in Figure 3. It is to be noted that the percentage conversion of monomer to polymer increases with the current at first, particularly over the lower current range, but at higher currents it tends to assume a constant value.

Table I
Effect of Various Added Electrolytes on the Electropolymerization of NVC in Mixed Biphasic Media[a]

electrolyte	10^3(mol of electrolyte)	conversn, %	R_p,[b] %/h	polymerizn efficiency, mol of NVC polymerized/faraday
zinc bromide	1.759	4.24	0.848	9.42×10^{-3}
zinc chloride	1.758	2.58	0.516	5.74×10^{-3}
ferric chloride	1.804	5.32	1.064	11.83×10^{-3}
zinc acetate	1.766	0.25	0.050	5.56×10^{-4}
potassium acetate	1.775	nil	nil	nil
sodium nitrate	1.912	3.28	0.656	9.12×10^{-3}

[a] Feed composition (mole ratio), formamide:toluene:NVC 20:1.86:0.04; time of electrolysis, 5 h; temperature, 313.15 K; current, 15 mA. [b] Rate of polymerization.

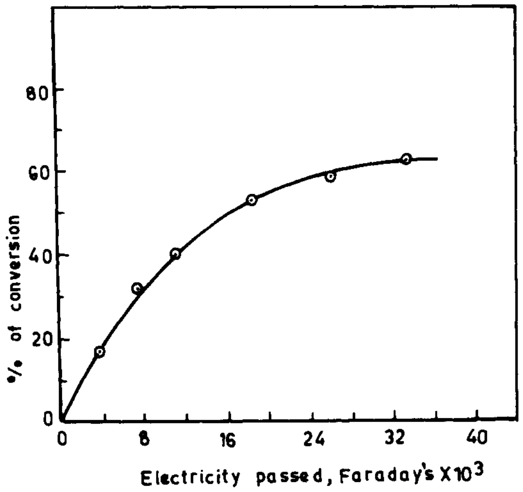

Figure 3. Polymer formation as a function of the charge passed: feed composition (mole ratio), formamide:toluene:NVC:$FeCl_3$ 20:1.86:0.04:0.12; time of electrolysis, 20 h; temperature 313.15 K.

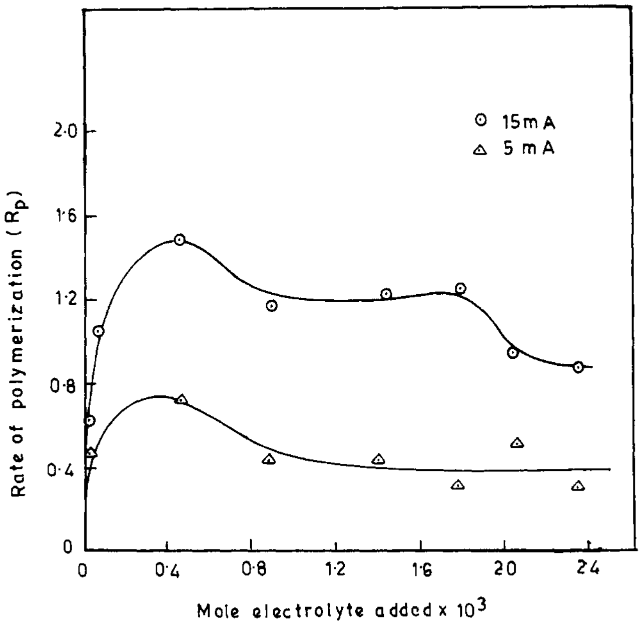

Figure 4. Rate of polymerization as a function of the quantity of electrolyte added and current in the electroinitiation reaction: feed composition (mole ratio), formamide:toluene:NVC 20:1.86:0.04; time of electrolysis, 10 h; temperature, 313.15 K.

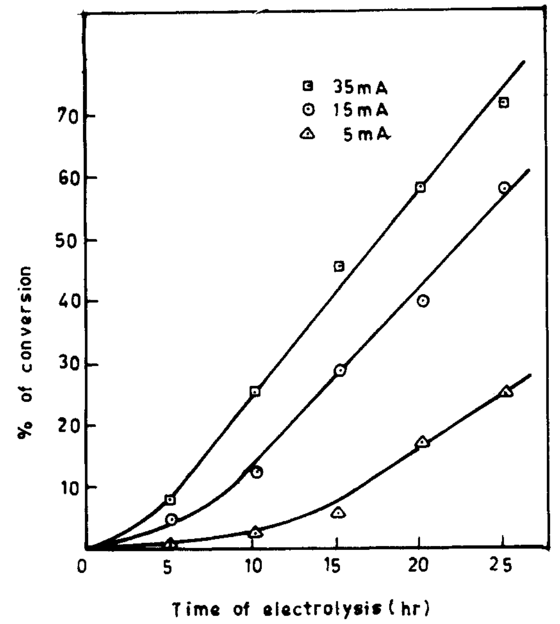

Figure 5. Polymer yield as a function of time and current in the electroinitiated reaction: feed composition (mole ratio), formamide:toluene:NVC:$FeCl_3$ 20:1.86:0.04:0.12; temperature, 313.15 K.

The effect of ferric chloride concentration on the rate of polymerization has been studied at two different current strengths, i.e., 5 and 15 mA shown in Figure 4. It is found that, at low current, the rate of polymerization first increases with the increase in the concentration of the electrolyte and then passes through a maximum before attaining finally a constant value at higher concentrations. Although a similar trend is also observed at a higher current, i.e., at 15 mA, in this case, in the range of the high concentration of the electrolyte, R_p shows a peculiar trend inasmuch as it shows two plateau regions instead of one.

The polymer yield as a function of the time of electrolysis, at three different current strengths, is shown in Figure 5. In all the cases, there appears to be an induction period over which the polymer yield is rather low and beyond which it increases and subsequently varies linearly with the time. The induction period is found to be more prominent at lower values of the current, i.e., 5 mA or so, but shrinks with increase in the current strength.

From the plots in Figure 5, the initial rate of polymerization, R_p, can be calculated in principle, and this should satisfy the equation

$$R_p = k(I_e)^n + C \qquad (2)$$

However, because of the occurrence of the induction period at the initial stage of polymerization, R_p values so obtained do not truly reflect the initial rate of polymerization in the absence of any inhibitors. To overcome this, the overall R_p corresponding to a 10-h reaction period was calculated at different current strengths and it is found that such values satisfy eq 2 as shown by the linearity of the plot of log R_p vs. log I_e in Figure 6. When we assumed 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 0.603 reaction %/h and the current exponent calculated from the slope was 0.687.

While studying the effect of temperature, we ascertained from the blank experiment that no thermal polymerization occurred in the range of temperature 301.15–323.15 K. The results presented in Figure 7 show that increase of temperature, as expected, produces an enhancing effect on the yield of the electropolymer.

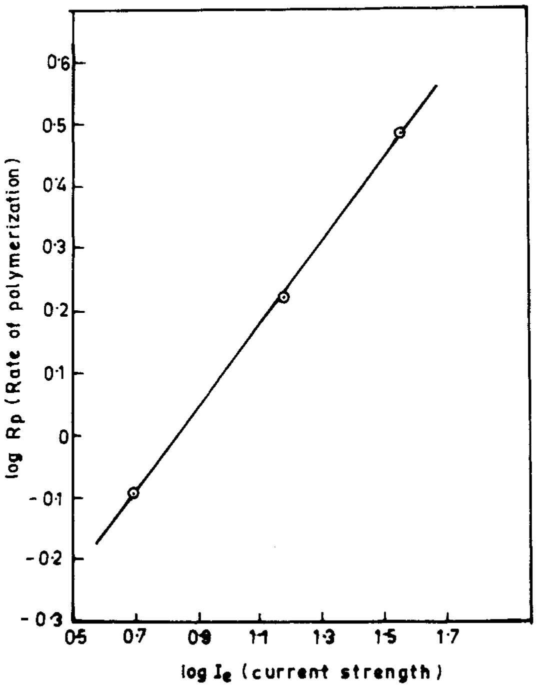

Figure 6. Determination of current exponent in the rate equation $R_p = k(I_e)^n + C$.

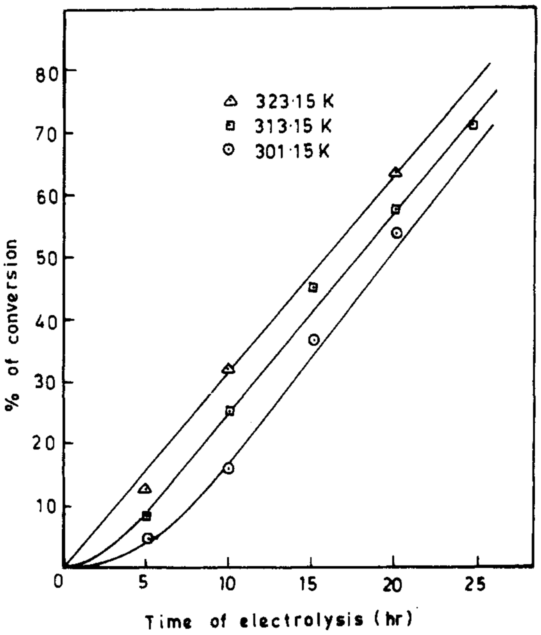

Figure 7. Polymer formation as a function of the time of electrolysis and temperature: feed composition (mole ratio), formamide:toluene:NVC:$FeCl_3$ 20:1.86:0.04:0.12; current, 35 mA.

The rate of polymer formation as a function of the monomer concentration in the nonpolar phase is shown in Figure 8. It is noted that at the lower concentration range, the polymer yield is proportional to the monomer concentration, but at higher concentrations, it is insensitive to the monomer concentration.

Postelectrolysis polymerization studies as shown in Table II clearly show the dependence of polymer yield on the total charge passed through the electrolytic cell and also a postelectrolysis polymerization effect.

When water was used as the solvent for the polar phase, it produced the unexpected effect of inhibiting the polymerization process whereas substituting the nonpolar phase by a solution of NVC in either benzene or xylene decreased the polymer yield, the decrease with benzene

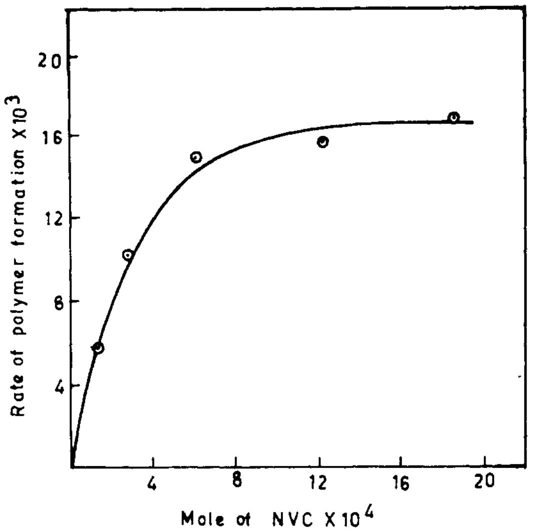

Figure 8. Rate of polymer formation as a function of the quantity of monomer added: feed composition (mole ratio), formamide:toluene:$FeCl_3$ 20:1.86:0.12; time of electrolysis, 10 h; temperature, 313.15 K; current, 15 mA.

Table II
Postelectrolysis Polymerization Effect on the Polymerization of *N*-Vinylcarbazole in Mixed Biphasic Media[a]

time of current flow, h	time allowed for polymerizn in absence of current flow, h	conversion, %
10	0	12.46
10	15	27.85
5	0	5.32
5	20	23.40

[a] Feed composition (mole ratio), formamide:toluene:NVC:$FeCl_3$ 20:1.86:0.04:0.1174; temperature, 313.15 K; current, 15 mA.

solution being much more than with xylene solution. These results are summarized in Table III.

Figure 9 gives the percentage of conversion with the total charge transfer through the solution based on two different sets of experiments described earlier, i.e., (a) by varying the current while fixing the time of electrolysis constant and (b) by varying the time period of electrolysis at fixed values of the currents. Although the points in Figure 9 show some scattering, a distinct trend showing a correlation between the percentage of conversion and total charge transfer is seen. The trend is more or less similar to that observed in Figure 3.

Introduction of hydroquinone, a radical quencher, did not produce any inhibiting effect on the electropolymerization process, but pyridine, an inhibitor for cationic polymerization processes, had a drastic inhibiting effect on the polymer formation.

Molecular weights of the polymer under certain trial determinations showed that $\bar{M}_v$ was in the range (10–15) × 10^3.

Discussion

The foregoing results show that it is possible to carry out the electropolymerization of NVC in a biphasic system following the novel technique as outlined earlier. One of the significant aspects of these studies was that when the two phases were allowed to separate after the electrolysis, the nonpolar phase carried virtually the whole of the polymer with it while the polar phase the whole of the electrolyte.

The fact that, in a split-cell experiment, the locus of polymerization was found to be the anode is suggestive of a cationic or radical mechanism. However, the possibility of a radical mechanism is eliminated as it cannot explain the absence of any inhibiting effect by hydroquinone or due to the presence of air in the system. Moreover, the inhibiting effect of pyridine, a cation quencher, and the development of color in the nonpolar phase during electrolysis clearly suggest that some cationic mechanism for polymerization was operating in the system. This is in contrast to the radical mechanism observed earlier in the case of electropolymerization of styrene under biphasic electrolysis.

Table III
Effect of Various Biphasic Systems on the Electropolymerization of NVC[a]

biphasic system	polar solv:monomer:nonpolar solv[b]	R_p, %/h	10^3(polymerizn efficiency), mol of NVC polymerized/faraday
formamide + NVC + toluene	20:0.04:1.86	1.064	1.18
formamide + NVC + xylene	20:0.04:1.62	0.754	8.38
formamide + NVC + benzene	20:0.04:2.24	0.116	1.29
water + NVC + toluene	44.4:0.04:1.86	nil.	nil.

[a] Moles of $FeCl_3$, 1.767 × 10^{-3}; temperature, 313.15 K; current, 15 mA; time of electrolysis, 5 h. [b] Mole ratio.

Considering all these aspects, and taking into account the fact that no polymerization occurs in the absence of any electrolytic current or the electrolyte, the following mechanism may be suggested for the electropolymerization. The main anodic reaction in the polar phase may be visualized as follows:

$$2FeCl_3 \rightleftharpoons FeCl_4^- + FeCl_2^+ \tag{3}$$

$$FeCl_4^- - e^- \rightarrow FeCl_4\cdot \tag{4}$$

$FeCl_4\cdot$ thus formed moves to the interface of the polar and nonpolar phases and there it acts as an electron acceptor, the donor being the monomer molecule. The monomer radical cation and $FeCl_4^-$ thus formed are held together by Coulombic forces (similar to ion-pair formation) and the resulting species thereafter helps the propagation of the polymerization reaction. The mechanism can be further illustrated as follows, i.e.:

$$FeCl_4\cdot + NVC \rightarrow \underset{A}{FeCl_4^-\cdots NVC^{+}\cdot} \tag{5}$$

$$FeCl_4^-\cdots NVC^{+}\cdot + nM \rightarrow FeCl_4^-\cdots n(M+1)^{+}\cdot \tag{6}$$

$$2[FeCl_4^-\cdots n(M+1)^{+}\cdot] \rightarrow 2FeCl_4^- + 2H^{+}(\text{solvated}) + \text{dead polymer} \tag{7}$$

As the species A occurs only at the interface, the $FeCl_4^-$ part being solvated by the polar phase and the $NVC^{+}\cdot$ part held by the nonpolar phase (see Figure 10), it is further suggested that monomer molecules available very close to the reaction center can only take part in the polymerization process.

The mechanism postulated above can satisfactorily explain the experimental findings such as the postelectrolysis polymerization and insensitivity of the polymer yield to the current at higher values of the same. In the latter case, the saturation value of $[FeCl_4\cdot]$ at the interface determines the rate of polymerization rather than its rate of formation

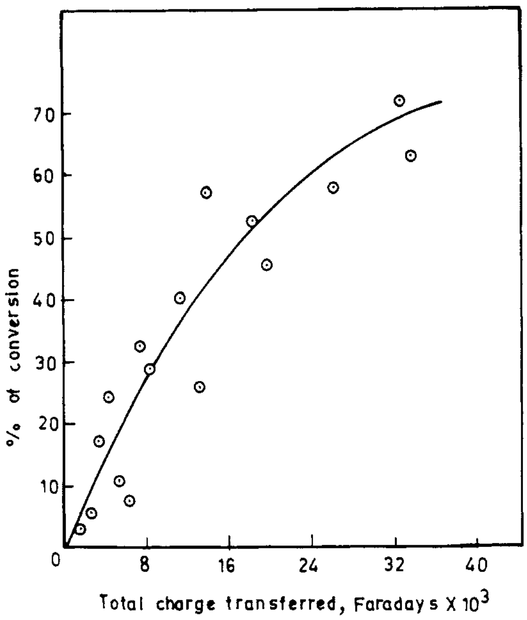

Figure 9. Polymer formation as a function of the total charge transferred into the system: feed composition (mole ratio), formamide:toluene:NVC:$FeCl_3$ 20:1.86:0.04:0.12; temperature, 313.15 K.

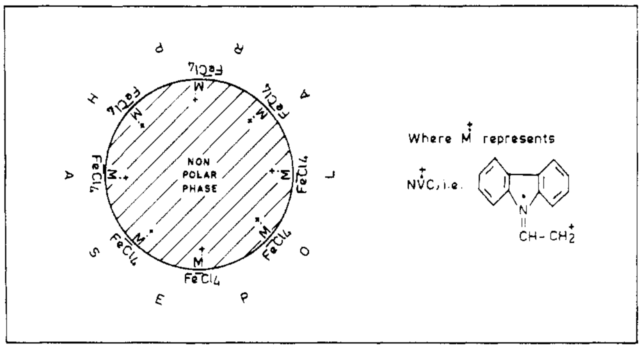

Figure 10. Formation of radical cation–anion pairs at the interface.

through the anodic reaction. This leads to the accumulation of $FeCl_4\cdot$ in the polar phase and its partial destruction by an alternative path:

$$FeCl_4\cdot \rightleftharpoons FeCl_3 + Cl\cdot \quad (8)$$

$$Cl\cdot + Cl\cdot \rightarrow Cl_2 \quad (9)$$

This view is further supported by the current exponent study where the exponent n has a fractional (0.687) value.

The variation of rate of polymerization with the increase in the concentration of the electrolyte which exhibits a peculiar trend (Figure 4) can also be partly explained with the help of the mechanism postulated above. As the electrolyte concentration is increased, it is expected that the concentration of $FeCl_4\cdot$ formed due to the anodic reaction (4) will also increase and this will facilitate the formation of species A at the interface and subsequent polymerization. However, the gradual and stepwise decrease of the rate of polymerization at higher values of the electrolyte concentration is rather difficult to explain. This could be due to the fact that the increase in concentration of $FeCl_3$ might lead to the formation of charge-transfer complexes between the monomer and $FeCl_3$ molecules at the interface and this reaction competes with the formation of the species A at the interface involving the monomer and $FeCl_4\cdot$ which only can lead to the initiation of polymerization reaction.

The increase in polymer yield with the time of electrolysis is rather easy to explain as with the progress of electrolysis the continued formation of $FeCl_4\cdot$ would lead to its increased concentration as well as that of A, and moreover there will also be a postpolymerization effect. The induction period noticed at the initial stage of the electrolysis is possibily due to the presence of water molecules as impurity in the polar phase. The electrolysis of such water molecules would partly hinder the formation of $FeCl_4\cdot$. As expected, such an induction period is less visible at higher current because of quicker decomposition of water molecules by electrolysis.

The effect of temperature on the electropolymerization reaction studied at relatively high electrolytic current is well understood, as under this condition, diffusion of $FeCl_4^-$ to the electrode will be a limiting factor, and the increase of temperature would generally promote such diffusion facilitating the formation of $FeCl_4\cdot$.

The mechanism also enables us to explain the effect of the monomer concentration on the rate of polymer formation. At constant electrolytic current, while the surface concentration of the initiating species remains the same, that of the monomer, however, would increase in the nonpolar phase with the increase of monomer concentration in the system. This would explain the increase in the rate of polymer formation with the increase in the monomer concentration at lower values of the same as seen in Figure 8. However, ultimately with the further rise in the monomer concentration, there will be an overcrowding of monomer molecules in the vicinity of the reaction center and therefore the rate of polymer formation will tend to assume a constant value.

The enhancement of polymerization due to stirring is easily explained as it firstly increases the diffusion of $FeCl_4^-$ to the electrode and secondly increases the surface area by causing intimate mixing of the two phases. It is rather curious that when water is used as the polar solvent, no electropolymerization occurs. One possible explanation may be that, water being more basic than formamide, the reaction sequences in this medium may be somewhat different and may not permit electrode reaction 4 to occur to a significant extent:

$$FeCl_3 + nH_2O \rightarrow FeCl^{2+}(aq) + 2Cl^-(aq) \quad (10)$$

$$Cl^-(aq) - e^- \rightarrow Cl\cdot \quad (11)$$

$$2Cl\cdot \rightarrow Cl_2 \quad (12)$$

The effect of the replacement of toluene by either benzene or xylene in the nonpolar phase is rather difficult to explain. It is expected that a polymerization proceeding by a cationic mechanism would be more favored by a solvent with higher dielectric constant. In this case, however, all these solvents have dielectric constants very close to each other ($\epsilon_{benzene} = 2.3$, $\epsilon_{toluene} = 2.4$, $\epsilon_{xylene} = 2.4$ at 293.15 K); the difference observed in rate of polymerization is most probably not due to this factor. Possibly other factors such as the viscosity differences or differences in the nucleophilic character of these molecules have some roles to play.

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Registry No. NVC, 1484-13-5.

References and Notes

(1) B. Nayak and R. C. Bhakta, *J. Appl. Electrochem.*, 13, 105 (1983).

Macromolecules **1985,** *18,* 1319–1324 **1319**

(2) J. W. Breitenbach and Ch. Srna, *Pure Appl. Chem.*, **4**, 245 (1962).
(3) D. C. Phillips, D. H. Davies, and J. D. B. Smith, *Macromolecules*, **5**, 674 (1972).
(4) D. C. Phillips, D. H. Davies, and J. D. B. Smith, *Makromol. Chem.*, **169**, 177 (1973).
(5) Y. Kikuchi and H. Fukuda, *Nippon Kagaku Kaishi*, **1**, 200 (1974).
(6) E. B. Mano and B. A. L. Calafate, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 829 (1983).
(7) U. N. Das and B. Nayak, *Indian J. Chem.*, **8**, 659 (1970).
(8) A. I. Vogel, "A Textbook of Practical Organic Chemistry", Longmans, New York, 1971, pp 173, 172.
(9) A. Ledwith, P. M. Bowyer, and D. C. Scherrington, *Polymer*, **12**, 509 (1971).
(10) S. Tazuke and T. Yamane, *J. Polym. Sci., Part B*, **9**, 331 (1971).

Effects of Chain Length Dependence of Termination Rate Constant on the Kinetics of Free-Radical Polymerization. 1. Evaluation of an Analytical Expression Relating the Apparent Rate Constant of Termination to the Number-Average Degree of Polymerization

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ABSTRACT: The nonclassical kinetics of low-conversion, free-radical polymerization have been studied. The models adopted assume a termination rate constant for radicals of size m and n given by $k_{t(n,m)} = k_{t0}(nm)^{-a}$. Using the expression for radical population and the rate of production of polymer, a relationship between apparent rate constant of termination $\bar{k}_t$ and average degree of polymerization, $\bar{X}_n$, is found to be $\bar{k}_t = (\text{constant})(\bar{X}_n)^{-2a}$. This relationship is in good agreement with the experimental data obtained in the polymerization of styrene and methyl methacrylate.

Introduction

Deviations of polymerization kinetics from simple systems of rules of free-radical polymerization have mostly been discussed in terms of primary radical termination,[1,2] portion of disproportionation in the termination,[3] variation in the efficiency of initiation,[4] etc. On the other hand, several workers[5-17] remarked that the rate of termination between polymer radicals is not always independent of their chain length; e.g., in a recent series of papers[10-15] it has been pointed out that the termination rate constant in free-radical polymerization, k_t, is a decreasing function of the size of reacting radicals (k_t is a decreasing function of the chain length and the linear expansion coefficient). The polymerization kinetics may also be influenced by the chain length dependence of termination rates between polymer radicals. Conventional methods for the kinetic study of radical polymerization are shown to lead to erroneous conclusions if the effect of the chain length dependence of termination rate constants is not taken into account.[16,18,19]

These studies clearly show that a command of the complete solution of a "nonclassical" kinetic scheme, i.e., a kinetic scheme which involves a chain length dependent termination rate constant, would be a very useful idea. To much greater accuracy, the above-mentioned effects could be analyzed. In addition, all further predictions of this scheme could be easily put to test by comparison with the appropriate basic experimental data.

The complete solution to a nonclassical kinetic scheme requires not only an appropriate analytical function relating the chain length of two reacting radical chains to the termination rate constant, but also a procedure which provides the solution of the system of equations resulting from the introduction of this analytical function so that finally the desired relationships between the various characteristic quantities of the kinetics are obtained.

A number of models exist which give a functional dependence of termination rate constant, k_t, on the chain length of two reacting radical chains.[9-11,17,20] These models can be simplified to the relationship

$$k_{t(n,m)} = k_{t0}(nm)^{-a} \qquad (1)$$

where $k_{t(n,m)}$ is the specific rate constant of termination between two radicals of size n and m and k_{t0} is a constant. In this work an attempt to solve the nonclassical kinetic scheme was made by using eq 1. A relationship between the apparent rate constant of termination and the average degree of polymerization was found. In a subsequent communication the analytical relationships between other characteristic quantities of the kinetic scheme will be presented.

Kinetic Analysis

The mechanism of polymerization to be considered consists of chemical initiation by first-order decomposition of initiator to produce radical with chain length unity, first-order propagation with respect to monomer, and chain transfer to produce a dead polymer. Second-order terminations by disproportionation and/or combination are taken into account. The kinetic mechanism may be represented as

initiation $\quad \mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^\circ$

$$\mathrm{R}^\circ + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1{}^\circ$$

propagation $\quad \mathrm{P}_n{}^\circ + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}{}^\circ$

chain transfer $\quad \mathrm{P}_n{}^\circ + \mathrm{Y} \xrightarrow{k_{tr,y}} \mathrm{P}_n + \mathrm{Y}^\circ$

termination

by disproportionation $\quad \mathrm{P}_n{}^\circ + \mathrm{P}_m{}^\circ \xrightarrow{k_{td(n,m)}} \mathrm{P}_n + \mathrm{P}_m$

by combination $\quad \mathrm{P}_n{}^\circ + \mathrm{P}_m{}^\circ \xrightarrow{k_{tc(n,m)}} \mathrm{P}_{n+m}$

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