

## Macromolecular Diffusion and the Autoadhesion of Polybutadiene

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**ABSTRACT:** A determination of the self-diffusion constant of polybutadiene was obtained from small-angle neutron scattering experiments. By ensuring that intimate contact was achieved between plied sheets of the polybutadiene, measurements were made of the diffusion of macromolecules across the interface as reflected by the development of adhesive forces at this interface. It was found that the increase in adhesion occurred over a much longer time scale than would be predicted from the measured values of the self-diffusion constant. This behavior of polybutadiene was contrasted with that of other elastomers. An interpretation of these results in terms of the presence of branched polymer chains in the material is discussed.

**Introduction**

The autoadhesion (tack) of elastomers is a property of much practical importance<sup>1,2</sup> that has as well stimulated intense scientific interest.<sup>3-8</sup> This paper describes a study of the autoadhesion of polybutadiene (PB). Measurements of the self-diffusion constant, determined from small-angle neutron scattering data, are reported. It is shown that the development of autoadhesive bonding between plied PB sheets is drastically slower than would be predicted from the measured value for the diffusion constant and simple notions of the reptative motions of polymer chains.

**Experimental Section**

The polybutadienes used in this study were synthesized by using *n*-butyllithium or, in the case of the in vacuo polymerization of deuterated PB, *tert*-butyllithium as the catalyst.

The EPDM rubber used in this work was Epsyn 55 obtained from the Copolymer Rubber and Chemical Corp. The natural rubber used was Hartex 20.

Self-diffusion constants were obtained by a method similar to that suggested by Bartels, Graessley, and Crist.<sup>9</sup> Polybutadiene sheets of 0.25-mm thickness were prepared by compression molding. The samples were supported on one side by Mylar film to facilitate handling. Sheets of each isotope of the PB were then carefully brought into contact in such a fashion as to prevent air occlusions and to ensure intimate contact between the surfaces. After about a 1-week period of time ( $6.6 \times 10^5$  s), the laminate was exposed to electron beam irradiation to a level sufficient to effect about 2 cross-links per weight-average molecule (i.e., 5.4 Mrad for a polymerization index of 1660). This cross-linking prevents any further interdiffusion of the plied rubber sheets since an infinite network has been formed. The Mylar backing was now removed from the sample and three 52 mm diameter circular specimens were cut out and stacked together in order to increase the intensity of the neutron scattering.

The small-angle neutron scattering measurements were conducted at Oak Ridge National Laboratory. A sample-to-detector distance of 11.5 m was employed, allowing intensity measurements to be made at reduced scattering angles  $h (=4\pi/\lambda) \sin(\theta/2)$ , where  $\lambda = 4.75 \text{ \AA}$  and  $\theta$  is the scattering angle) as small as  $0.005 \text{ \AA}^{-1}$ . Additionally, scattering data were collected on a sample containing equal volumes of the two PB isotopes mixed in solution. This specimen served to simulate complete interdiffusion of the polybutadiene layers. Also, two respective sheets were irradiated to the 5.4-Mrad dosage prior to plying them together, in order to allow measurement of any scattering originating from the pure PB components.

Tack testing was done in the T-peel geometry at a crosshead velocity of 0.85 mm/s (nominal strain rate  $2 \text{ s}^{-1}$ ). The specimens were prepared by compression molding at room temperature overnight or at 100 °C for 10 min against Mylar. The Mylar was subsequently removed by immersing the sample in liquid N<sub>2</sub> so as to effect delamination without significant disruption of the rubber surface. The samples were warmed to room temperature in vacuo and then plied together in a fashion similar to that employed for the self-diffusion experiments.

The surface topography was measured by using a Federal Surfanalyzer System 2000, which measures the deflection of a

stylus as it traverses the surface of the specimen.

**Results**

**Establishment of Molecular Contact.** In order that the interface, separating the plied rubber sheets, be eliminated by macromolecular interdiffusion from both sides, intimate contact between the two surfaces must be achieved. Displayed in Figure 1 is the surface profile of a PB specimen molded against Mylar film. It can be observed that the resulting asperities are exceedingly small (ca. 400 nm), such that for a typically thick rubber sheet ( $\sim 2 \text{ mm}$ ), compressive strains equal to  $\sim 10^{-4}$  must be imposed in order to deform these asperities and form a flat surface. The loading conditions employed (12 kPa for 300 s) for the preparation of tack specimens were, in fact, determined to be sufficient to achieve compressive strains of ca.  $10^{-1}$ . To the extent that this applied load is borne by asperities, the local deformations would exceed even this magnitude.

Although the above considerations imply that the attainment of complete molecular contact will not be prevented by roughness at the surfaces, a more direct demonstration that this is indeed the case is provided by simply measuring the force required to separate the rubber sheets as a function of the loading conditions used to ply them together. Data of this type are displayed in Figure 2. Five minutes at 12-kPa pressure was employed in the experiments discussed below, and it can be observed that autoadhesion between the plied sheets would not be augmented by a more severe compressive loading. It can be concluded therefore that intimate contact is indeed established between the surfaces of the rubber sheets so that tack should not be limited by this contact area.

**Macromolecular Interdiffusion.** Displayed in Figure 3 are Guinier plots<sup>10</sup> of the scattering data measured for samples containing equal volumes of deuterated PB and protonated PB (PI = 1570,  $M_w/M_n = 1.1$ ). It can be seen that the scattered intensity is reduced, corresponding to a shorter path length of the incident neutron beam through mixed isotopic species, as the temperature at which interdiffusion was allowed to occur is reduced from 55 to 23 °C. The product of the respective volume fractions of the two isotopic species averaged over the total sample path length is given by<sup>9</sup>

$$\frac{I(t) - I(0)}{I(\infty) - I(0)} = \frac{\langle \phi(1 - \phi) \rangle_t}{\langle \phi(1 - \phi) \rangle_\infty} \quad (1)$$

where the above zero-angle intensities represent the intercepts of the linear least-squares fits to the scattering data as displayed in Figure 3; i.e.

$$I(t) = \lim_{h \rightarrow 0} [\ln(I(t, h^2))] \quad (2)$$

For a blend containing equal volumes of the two species

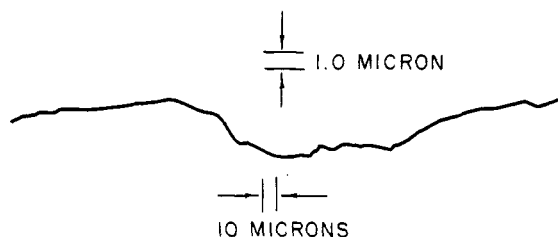


Figure 1. Surface profile of polybutadiene sheet molded against Mylar film.

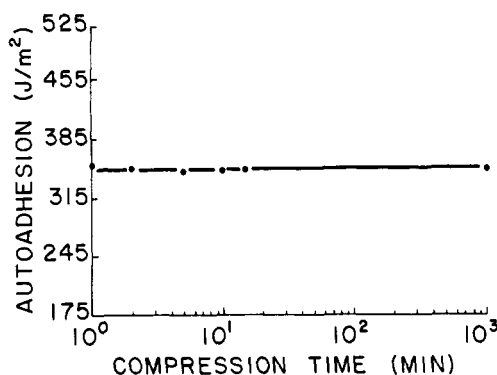


Figure 2. Autoadhesion of plied PB sheets measured as a function of the duration of compressive loading at 12-kPa pressure. In all cases, the total contact time before testing was  $10^3$  min.

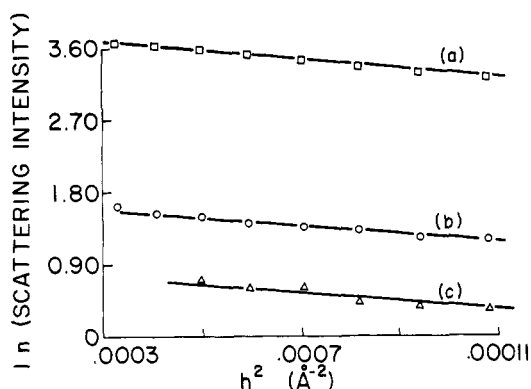


Figure 3. Scattering data displayed in the form of Guinier plots after correction for the scattering from samples radiation cross-linked before the two isotopic species of PB were brought into contact: (a) deuterated PB and protonated PB samples mixed in solution, (b) interdiffusion of the plied sheets occurred over  $6.6 \times 10^5$  s at  $55^\circ\text{C}$ , (c) same as b, but the temperature was  $23^\circ\text{C}$ .

of PB, the denominator in the right-hand side of eq 1 is equal to 0.25. Accordingly, the average product of the respective volume fractions of the two PB isotopes after a time period,  $t$ , of interdiffusion can be determined from the SANS intensities (after correction by a factor of 3 to account for the stacking used to enhance the measured signal).

For the case of a constant diffusion coefficient with an initial distribution corresponding to these plied PB sheets

$$C(x) = C_0 \quad x < 0, \text{ at } t = 0$$

$$C(x) = 0 \quad x > 0, \text{ at } t = 0$$

(where  $C(x)$  represents the concentration of one of the isotopic species as a function of position along the normal to the face of the sheets, with the initial interface located at the origin), the concentration profile is described by<sup>11</sup>

$$C(x,t) = (c_0/\pi^{1/2}) \int_{x/(4Dt)^{1/2}}^{\infty} e^{-u^2} du \quad (3)$$

Table I  
Results for SANS Determination of Self-Diffusion Coefficient of Polybutadiene<sup>a</sup>

temp, °C	$\phi(1-\phi)$	$D$ , cm <sup>2</sup> /s
23	0.015	$3.4 \times 10^{-13}$
55	0.032	$1.5 \times 10^{-12}$

<sup>a</sup>PI = 1570;  $M_w/M_n = 1.1$ .

The product of the respective volume fractions averaged over the sample thickness can then be computed by assuming a magnitude for the diffusion constant,  $D$ , and calculating the concentration profiles using eq 3. In this manner the self-diffusion constants listed in Table I were determined for the polybutadiene. In view of the uncertainties associated with plying together of the PB sheets and maintaining a uniform thickness throughout the cross-sectional area, the errors inherent in these tabulated results are not well established. The values given can be regarded only as order-of-magnitude estimates. Nevertheless, they are in essential agreement with published data for other low- $T_g$  elastomers determined from the self-absorption of  $\beta$  radiation.<sup>12</sup>

**Interface Destruction.** When the respective sheets of PB are brought into contact, the interdigitation process commences. After a time period sufficient to allow macromolecular diffusion over distances greater than the coil size, the interfacial region will assume the microscopic configuration of the bulk; that is, the laminate will become a homogeneous sheet. From the slope of the curves in Figure 3, the radius of gyration,  $R_g$ , of the PB can be determined to be<sup>10</sup>

$$R_g = \frac{1}{3}(\text{slope})^{1/2} = 134 \pm 6 \text{ \AA} \quad (4)$$

Accordingly, at  $23^\circ\text{C}$  the time required for macromolecular diffusion over an average squared distance equal to this value is

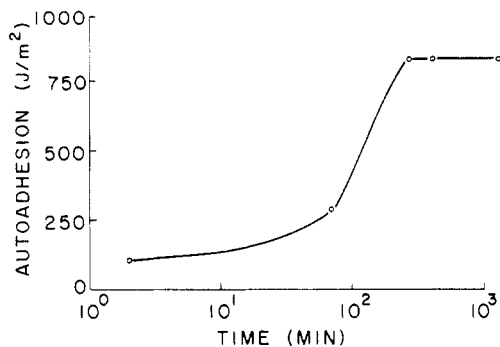
$$\tau = \langle R_g^2 \rangle / 2D \approx 3 \text{ s} \quad (5)$$

This implies that once molecular contact has been established between the plied PB sheets, interdiffusion will be essentially instantaneous. The measured force of adhesion should then equal the bulk cohesive strength; that is, the interface in effect no longer exists.

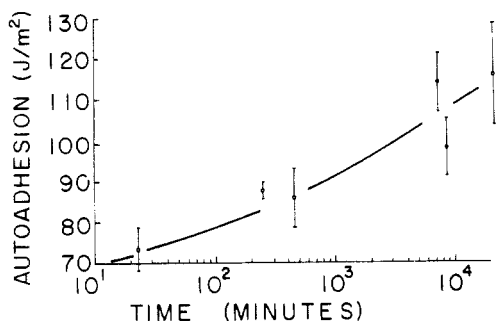
In order to test this prediction, the peel adhesion of PB sheets was measured as a function of the duration of their contact period. The compressive loading used to establish contact is as described above (12 kPa for 5 min). After removal of this load, the specimens were peeled apart after various time periods. In order to facilitate handling of the test samples, a higher molecular weight PB was employed (PI = 2000,  $M_w/M_n = 1.9$ ) than for the neutron scattering experiments. The self-diffusion coefficient according to reptation theory<sup>13</sup> scales with the inverse second power of chain length, while the radius of gyration for a flexible macromolecule is proportional to the half power of molecular weight. Therefore, the time scale for destruction of the interface (i.e., complete interdiffusion) will be a factor of

$$\left( \frac{2200}{1570} \frac{1.9}{1.1} \right)^3 \approx 14$$

higher than the aforementioned 3 s (eq 5), but will still be fast relative to the time scale of the autoadhesion experiment. This leads to a prediction that the force required to peel apart the PB sheets should be invariant to the time



**Figure 4.** Autoadhesion measured for PB sheets plied together for 300 s at 12-kPa pressure and then left in contact for the indicated time period. The initial sheets were molded at room temperature.

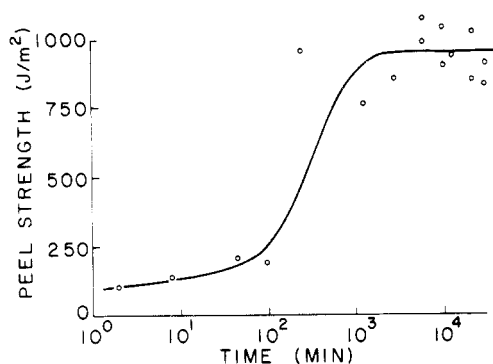


**Figure 5.** Same as Figure 4 but in this case the PB sheets were molded at 100 °C for 10 min.

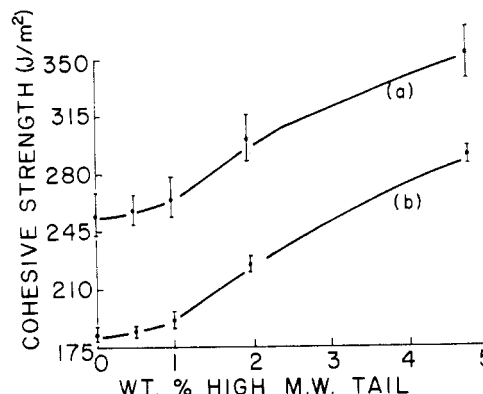
period over which they are left in contact.

**Autoadhesion Results.** Displayed in Figure 4 are the autoadhesion of PB, measured as a function of the time period over which the sheets were left in contact. The bond strength is observed to be continuing to increase through about a 2-h time period, which is 2 orders of magnitude longer than the time associated with complete interdigitation (as determined by using eq 5 and the scaling law estimates of  $D$  and  $R_g$  from the values obtained by SANS for the lower molecular weight PB). Moreover, it should be noted that the locus of failure in these samples was at the interface until the limiting value of autoadhesion was achieved. Apparently, although the interdigitation process has transpired following the plying together of the PB sheets (the SANS experiment shows this directly), the interfacial region remains, however, weaker than the bulk material for a much longer time period than expected.

The autoadhesion experiment directly involves prepared surfaces, so the possibility exists that the observed behavior is an artifact resulting from this surface preparation. In fact, as can be seen in Figure 5, when the tack specimen is prepared not by room-temperature molding, but rather by molding at 100 °C for 10 min, the development of surface bonding is drastically slowed. This probably is due to oxidation of the PB surface. Note that cross-linking of the surface molecules alone would not affect the autoadhesive behavior that much, since it would then only be required that polymer chains one or two monolayers back from the surface diffuse across this interface. This would delay bond development, but not by the orders of magnitude degree of retardation displayed in Figure 5. A more serious consequence of extensive oxidative cross-linking of the surface layers would be a reduction in the driving force for interdiffusion due to chemical differences between the oxidized and original chains. In order to be assured that the data of Figure 4 are not an artifact of the surface preparation, an alternative experiment was performed



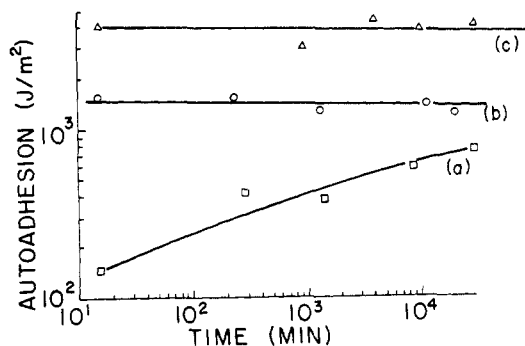
**Figure 6.** Healing of fractured PB sheets. The kinetics of the process is in agreement with the autoadhesion data of Figure 4.



**Figure 7.** Cohesive strength (measured in a 180° peel geometry) of uncured PB elastomer of  $M_w = 115000$  (PI = 1600), measured as a function of the added concentration of PB of  $M_w = 702000$ . Nominal strain rate and test temperature, respectively, were (a) 33 s<sup>-1</sup> and 23 °C, (b) 3.3 s<sup>-1</sup> and 0 °C.

which, while not duplicating the autoadhesion experiment, does involve the same molecular processes. Polybutadiene sheets were sliced apart and immediately rejoined. The strength of the bonding between the fractured surfaces was then measured as a function of the time allowed for healing. It can be seen in Figure 6 that even though variability in the cut surface produces some scatter in the data, the healing process proceeds according to the same time scale as the autoadhesion experiments. Again it is found that macromolecular self-diffusion as inferred from strength measurements transpires at a much slower rate than the direct determination of the self-diffusion coefficient would suggest. The anomaly is not due to any peculiarity of the material at the surface, but rather the suggestion is that the scattering data and the peel resistance have a different sensitivity to the macrostructural details of the polybutadiene samples.

**Cohesive Strength of Polybutadiene.** The diffusion coefficient varies reciprocally with the second power of the weight-average molecular weight.<sup>13</sup> The cohesive strength of a material measured in the peel geometry is, on the other hand, essentially a reflection of its extensional viscosity averaged over a range of elongation rates.<sup>14</sup> The relationship between extensional flow behavior at large strains and a polymer's macrostructure and macrostructural homogeneity is complex.<sup>15,16</sup> The presence in the material of a small concentration of very long chains could influence the cohesive strength to a larger extent than they might alter the measured value of the self-diffusion constant. Displayed in Figure 7 is the cohesive strength of a PB elastomer (PI = 1600) measured as a function of concentration of high molecular weight PB (PI = 7400) added to simulate, for example, the presence of a high molecular



**Figure 8.** Autoadhesion measured for (a) ethylene-propylene rubber, (b) 90% hydrogenated vinyl PB, (c) natural rubber as a function of the contact time before peeling (loading conditions were as described for Figure 4).

weight tail in the distribution of chain lengths. It can be seen that even low levels of long, linear chains increase the strength markedly. This cannot, however, account for the data of Figure 4. The development of adhesive strength requires more than 3 orders of magnitude longer time than the prediction of eq 5. This would require the presence of linear chains of greater than  $10^6$  molecular weight, which cannot be the case.

A more realistic possibility is that there exists sufficient branching of some of the chains to give an increase in the ultimate level of autoadhesion achieved. The branching would suppress reptative motions, and thus the interdigitation process would be severely hindered.<sup>17</sup> To investigate this further, the autoadhesion study was extended to other elastomers. Data on ethylene-propylene rubber (EP), natural rubber (NR), and a hydrogenated high vinyl PB (HVPB) were obtained and are shown in Figure 8. Two remarks can be made. First, the NR and HVPB rapidly develop a level of autoadhesion that does not increase with time and is essentially equal to the rubber's bulk strength (as evidenced by the cohesive tearing which occurs when the test specimens are peeled apart). This attests to the completeness of surface contact achieved by the procedure used to ply together the rubber sheets for autoadhesive testing. Secondly, the EP elastomer exhibits behavior very similar to that of the PB. Note that its bulk cohesive strength was measured to be  $1260 \text{ J/m}^2$ , roughly twice the level of autoadhesion. In the case of NR, even lower molecular weight chains, which bridge the interface most rapidly, can impart high strength due to their capacity for strain-induced crystallization. The vinyl PB used as the precursor for the HVPB, moreover, is believed to consist essentially of linear macromolecules. Their hydrogenation would not affect this. Although it is not explicitly known, it is conceivable that the delayed development of autoadhesion in the case of the EP reflects the presence of branched material.

### Summary

PB is one of numerous synthetic elastomers which lack the ability to strongly adhere to themselves. Although this has been variously attributed to poor green strength,<sup>18,19</sup> poor compliance and wetting,<sup>4,7,19</sup> or slow interdiffusion,<sup>3,7,20</sup> it is clear that none of the above hypotheses can account for the experimental data presented herein. It should also be pointed out that lack of a correspondence between tack and the magnitude of the self-diffusion constant has previously been observed for SBR and butyl rubbers<sup>12</sup> and can be inferred from recently published data on the relative tack of SBR.<sup>21</sup> Analogous studies of the buildup of interfacial strength through interdiffusion in plastics ("polymer welding") have been reported.<sup>22-24</sup> The difficulty

therein lies in relating the strength of the bond to the extent of interdigitation at time scales less than the  $\tau$  expressed in eq 5. For long times (relative to this "tube renewal" time) the obvious assumption is made that the strength of the adhesive bond just equals the bulk cohesive strength.

From data such as those exhibited in Figures 4 and 8, the indication is that elastomers conventionally regarded as possessing good tack (e.g., NR) in fact develop autoadhesion levels that rapidly reach the stock's cohesive strength and are therefore essentially invariant to contact time. On the other hand, rubbers considered to be deficient in tack (e.g., PB, EP) develop increasing autoadhesion with time, but on a time scale longer than the typical tack test. It is tempting to conclude that "high-tack" elastomers are simply those which can exhibit high cohesive strength without the presence of long branches on the polymer chains. This concept might be applicable in the case of natural rubber, which exhibits strain-induced crystallization, and also account for the observance of poor tack in some rubbers, but it is not a tenable explanation for the tack behavior of all elastomers in general. To cite one example, the vinyl PB used as the precursor for the HVPB consists of linear molecules, but nevertheless has poor tack prior to hydrogenation.<sup>25</sup>

It is clear that autoadhesion is a complex phenomenon that remains to be completely understood, notwithstanding the innumerable research studies on this subject conducted over the past 40 years. Current efforts in our laboratory are being directed toward investigating the effect of an elastomer's macrostructure on tack, and on the kinetics of the development of this bonding.

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## 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  $28.4 \times 10^{-3}$  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,<sup>1</sup> 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,<sup>2-6</sup> 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.<sup>7</sup> 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<sup>3</sup> 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.<sup>8</sup> Zinc acetate (E. Merck pro-analysis), 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<sup>3</sup>), 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<sub>3</sub> and CDCl<sub>3</sub> as solvents, respectively. The viscosity average molecular weights ( $\bar{M}_v$ ) of the polymer were determined in benzene by using the following relation:<sup>9</sup>

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

### 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