

Electric Field-Assisted Grafting of 4-Vinylpyridine on an Activated Cation Exchange Membrane

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Synopsis

The influence of forced diffusion by a d.c. electric field on the graft polymerization of ionic 4-vinylpyridine onto a host membrane was determined. The host was a commercial cation exchange membrane. Initiation was by a redox couple of titanous ions at the exchange sites of the membrane and *t*-butylhydroperoxide in the bulk solution along with the monomer. Undesirable effects of electrode reactions were avoided by isolation of the electrode compartments with permselective membranes. Measurements were at monomer concentrations of 0.05, 0.1, and 0.2*M* and d.c. current densities of 0.08 and 0.16 mA/cm². Applying the field accelerated the graft rate and provided greater control of the amount and distribution of the polymer than when free diffusion alone directed the reaction. This suggests possible value of forced diffusion by an electric field to tailor-make membranes to special properties such as in the case of ampholytic mosaic membranes.

INTRODUCTION

During the last decade, increasing attention has been given to the effects of external electric fields on polymerization processes and the products of such reactions. Both direct and indirect electrode reaction mechanisms and also field-assisted phenomena have been studied. Free-radical, anionic, and cationic propagation mechanisms have been observed.¹⁻³ A particularly interesting observation was the apparent grafting of methyl methacrylate onto cellulose films immersed in an electrolytic cell containing the monomer.⁴

In these prior electrochemical applications, the polymerization propagation reactions are generally bulk phenomena. Even in the case of the direct reaction of monomer at an electrode, the primary effect is usually one of initiation followed by propagation of the initiated species in the bulk serum. In no reported instance does initiation and propagation occur simultaneously at an interface other than an electrode. Nor is there any reported example of an external field being used to influence a graft polymerization reaction occurring elsewhere in the system independently of some electrode phenomenon.

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Redox initiation is widely used to graft vinyl monomers on natural and synthetic polymers of suitable degree of ion exchange capacity.^{5,6} The ionic groups of the host polymer function as restrictive sites for one of the components of the redox couple. A frequently used redox combination is a polyvalent cationic reducing agent paired with one of several oxidizing agents. When they react, a free radical is generated which in turn initiates a monomer molecule and the chain reaction begins. If sufficient monomer can diffuse to the reaction zone, then an efficient polymer add-on results.

These authors previously investigated the electrolytic deposition of ionic colloidal materials on paper substrates.⁷ It was discovered that such materials could also be deposited at nonmetallic interfaces such as ion-exchange membranes. If preformed polymers can be transported to a nonmetallic interface and then deposited, it should similarly be possible to transport to a reactive interface an ionic vinyl monomer. Furthermore, if the reaction is diffusion controlled, as are many heterogeneous grafting reactions,⁸⁻¹¹ forced diffusion should increase the graft reaction rate.

The objective of the present work was to determine the influence of forced diffusion by an external electric field on the graft polymerization rate of an ionic vinyl monomer. As host, a commercial cationic ion exchange membrane was used. The practical importance of the study is its evaluation of a process variable which can control selectively the graft rate and the structure of the resulting membrane.

EXPERIMENTAL

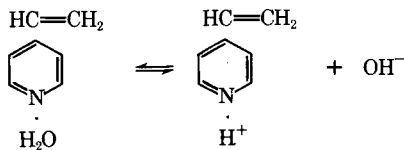
Materials

Monomer

The prerequisites for the monomer were: (1) electrolytic but of low specificity for the cation exchange sites on the host membrane, (2) high transmembrane electrical transport number, (3) easily grafted by redox initiation mechanism, (4) soluble in water at ordinary temperatures, and (5) no interaction of its functional groups with the polymerization initiators.

The monomer chosen was 4-vinylpyridine. This monomer was supplied by Eastman Kodak Company and was purified prior to use by vacuum distilling at 60–65 mm Hg and 94–96°C. Distilled monomer was stored in glass and kept refrigerated at 12°C. If the distilled monomer developed the slightest trace of color, it was redistilled.

4-Vinylpyridine is a weak organic base and dissociates when dissolved in water according to



with a dissociation constant determined by conductometric methods to be 10^{-9} to 10^{-10} equivalents/l. at 24°C .

Membranes

A commercial cation exchange membrane of poly(ethylene-*g*-styrene-*g*-sulfonic acid) was used as the host onto which the vinyl monomer was grafted. It was supplied by the American Machine and Foundry Company under designation C-60. Such a membrane is produced by successively grafting styrene and sulfonic acid groups onto polyethylene film. The membrane was conditioned for use by hydrating it in deionized water for one week, equilibrating it overnight with 5% hydrochloric acid, and then washing it with deionized water. This procedure was followed to fully swell the membrane and ensure that it was completely in the hydrogen counterion form prior to use.

The spacer membrane, Figure 1, was an anion exchange membrane of poly(ethylene-*g*-styrene-*g*-quarternary amine). This membrane was supplied by the American Machine and Foundry Company under the designation A-100. It differs from the C-60 membrane in that quarternary amine groups are substituted on the styrene-modified polyethylene film. The membrane was preconditioned by soaking it for one week in deionized water, equilibrating it overnight in 0.1*N* potassium hydroxide, and then subsequently washing it with deionized water. Thus, the membrane was always initially in the hydroxyl counterion form. Reported properties of both membranes as received are listed in Table I.

An oxidation-reduction couple of titanium (ous) ions and *t*-butyl hydroperoxide was used as the source of free radicals. The titanous ions were adsorbed by ion exchange with the host C-60 membrane. This was done by equilibrating with titanous chloride solution under a constant set of conditions. The titanous chloride was supplied as a 20% solution by Fisher Scientific Co. and was used without further purification.

The *t*-butylhydroperoxide oxidizing agent was supplied as a 70% aqueous solution by the Lucidol Division, Pennsalt Corporation. It was also used

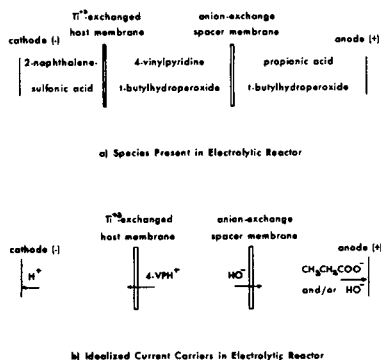


Fig. 1. Species and current carriers present in reactor.

TABLE I
Membrane Properties

	Cation exchanger C-60	Anion exchanger A-100
Selectivity (0.5 <i>N</i> KCl/1.0 <i>N</i> KCl), %	80	90
Ionexchange capacity, meq/dry gram	1.5	1.5
Gel water, % dry basis	40	20
Wet thickness, mils	12	7
Resistance, ohm-cm ²	5	8

without further purification. This compound was selected both for its high reactivity with polyvalent cationic reducing agents and its very slow first-order thermal decomposition rate at 40°C.

It has been reported that 4-vinylpyridine undergoes a "matrix polymerization" catalyzed by polyacids and simple organic and mineral acids.¹²⁻¹⁴ Despite the nature of the host membrane used in this study, all indications were that, with this selection of initiator couple, the reaction followed standard free-radical polymerization mechanisms.

Reactor and Procedures

Reactor Design

A primary feature in the design of the electrolytic reactor was to permit a graft polymerization reaction to occur within the host membrane with the monomer approaching unidirectionally. Figure 1 gives the location of functional species and elements in the reactor.

The system contained the redox couple to initiate the graft polymerization reaction, namely, titanium (ous) ions bound to the host membrane and *t*-butylhydroperoxide in the monomer serum.

The anode and cathode of platinum gauze were in separate cells filled respectively with propionic acid and 2-naphthalenesulfonic acid to provide ionic conductivity. In this way, undesirable effects of reactions at electrodes on the graft reaction were avoided.

The details of the various electrode reactions were not studied. It is assumed that the cathode reaction consisted of the reduction of hydrogen ions to produce nascent hydrogen and hydrogen gas. The passage of current at the anode is proposed to be accounted for either by the Kolbe reaction route involving the propionate anion or possibly by the oxidation of hydroxyl ions to generate molecular oxygen.

Between the electrode compartments are the host membrane and reactants. The anion exchange membrane A-100 served as a spacer material between the center monomer compartment and the anode cells. It was selected because of its nonreactivity with the monomer and its low transport of cations from the anode cell. *t*-Butylhydroperoxide was added to the anode cell at an equivalent concentration to that in the monomer cell in order to prevent its diffusion loss through the spacer membrane.

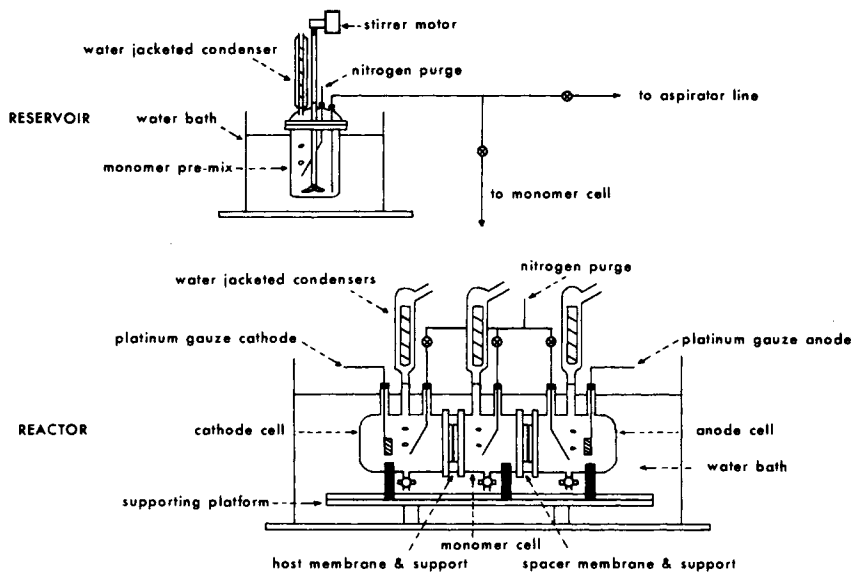


Fig. 2. Diagram of the electrolytic reaction apparatus.

Current carriers at the various phase boundaries are pictured in Figure 1b. The 2-naphthalenesulfonic acid, 4-vinylpyridine, and propionic acid provided ionic conductance in their respective cells.

Both hydroxyl ions generated in the center or monomer cell from the dissociation of 4-vinylpyridine and hydrogen ions from the dissociation of propionic acid in the anode cell are available as current carriers across the spacer membrane. Since the latter is an anion exchanger with a positively charged immobilized backbone, the hydroxyl ion from the monomer cell presumably accounts for most of the ionic flux.

At the host membrane, the major available current carriers are 4-vinylpyridinium cations from the monomer cell and 2-naphthalenesulfonate anions in the cathode. As mentioned, this membrane is a cation exchanger with negatively charged sulfonic acid groups which repulse the 2-naphthalenesulfonate anions. Thus, the main current carrier across the host membrane is the reactive vinyl monomer cation.

A Hewlett-Packard Model 6186B power supply provided the constant current source. The overall reactor potential drop relative to the grounded cathode for each field-assisted experiment was followed by a reduced proportional signal forwarded to a Leeds & Northrup Model XL 680 potentiometric recorder. Platinum wire probes were inserted through the membrane supports to place a probe on each side of each membrane to monitor local gradients throughout the reactor in addition to the total potential drop. Gradients below 100 volts were measured with a Keithley Model 610 C electrometer. A diagram of the actual reactor is shown in Figure 2.

Preparation of Solutions and Host Membrane Activation

A 4 $\frac{3}{8}$ -in.-diameter cation exchange membrane disc in the hydrogen counterion form was equilibrated with a solution prepared from 2.0 ml 20% titanous chloride dissolved in 500 ml water. This procedure gave 1 mole of exchanged titanous ions per 8 equivalents of monovalent alkali exchange sites in the membrane.

The anode and cathode cell solutions were prepared by adding the appropriate amounts of 2-naphthalenesulfonic acid and propionic acid to degassed, thermally equilibrated glass bottles which were then capped and kept at the reaction temperature until used.

In the case of the monomer solution, the appropriate quantity of distilled, refrigerated 4-vinylpyridine was added to the continuously degassed external reservoir (Fig. 2). Just prior to transferring the monomer solution to the reactor, the required quantity of *t*-butylhydroperoxide was added to both the monomer solution and the anode cell solution.

Assemblage and Starting Reaction

The spacer membrane in the hydroxyl counterion form was placed in its polyethylene support and inserted between the center and anode cells. The titanous-exchanged activated host membrane was also placed in an identical polyethylene support and placed between the center and cathode cells. The degassed anode and cathode cell solutions were added to their respective cells. The assembled reactor, with filled end cells, was then placed in the water bath maintained at 40°C. The monomer solution was then transferred by gravitational flow from the external reservoir to the monomer cell and the graft polymerization reaction commenced. This latter step required approximately 30 sec, and the total elapsed time from when the titanous-exchanged host membrane was removed from its final water rinse to the onset of the graft reaction was invariably between 10 and 11 min.

Termination and Determining Polymer Add-On

At the conclusion of the reaction period, the external electric field was first shut off (if the experiment was field assisted) and the entire reactor was withdrawn from the constant-temperature bath. The individual cells were drained and samples taken if desired. Then, the grafted membrane was removed from its support and immersed in water while the rest of the reactor was being dissembled.

The grafted membrane was equilibrated with 500 ml 5% hydrochloric acid for 2 hr, washed with 500 ml water, and dried to constant weight at 110°C. The weight of polymer add-on was expressed as the final weight minus the average initial weight of the membrane in the hydrogen counterion form. It was found that this procedure effectively eliminated titanium ions exchanged with the host membrane to initiate the graft reaction.

TABLE II
Variables Studied

Monomer concentration, moles/l.	Constant current density, mA/cm ²
0.05	0 and 0.08
0.1	0, 0.08, and 0.16
0.2	0 and 0.16

The reproducibility of the add-on analysis is indicated by the observed standard deviation of 1.18% for the host membrane. Four identical experiments were performed at a monomer concentration of 0.2M 4-vinylpyridine, constant current density of 0.16 milliamperes/cm², and elapsed reaction time of 12 hr. These grafted membranes showed a standard deviation of 2.43% from the arithmetic mean value.

Variables Studied

The experimental program was designed to study the polymeric graft add-on of the host membrane as a function of monomer concentration and the magnitude of an external constant current d.c. field according to the schedule in Table II.

Preliminary screening experiments demonstrated that many factors influenced the primary graft polymerization reaction. The following variables were held constant throughout the bulk of this experimental program: reaction temperature, 40.0 ± 0.1°C; anode cell components, propionic acid at 0.02M and *t*-butylhydroperoxide at 1.0 ml 70% TBHP per 1500 ml; monomer cell, *t*-butyl hydroperoxide at 1.0 ml 70% TBHP per 1500 ml; cathode cell, 2-naphthalenesulfonic acid at 0.005M; spacer membrane, initially in the hydroxyl counterion form; host membrane, initially placed in hydrogen counterion form and then substituted with 1 mole titanous ions per 8 equivalents alkali exchange capacity.

RESULTS

Polymer Add-On

The results for free diffusion and field-assisted experiments at a monomer concentration of 0.05M, 0.1M, and 0.2M are plotted in Figure 3. From the inception of the reaction, the kinetic behavior in all cases followed a similar pattern of a monotonical decrease in rate with elapsed time. No induction effects were noted with the time schedule of sampling employed. The data show that a considerable increase in the graft reaction rate was caused by the external field at all monomer concentrations.

To illustrate the magnitude of the effects solely attributable to the external field, values from the plotted kinetic data expressed relative to the free diffusion level at the same time are shown in Figure 4. From this plot, it is observed that the relative field effect was most prominent during

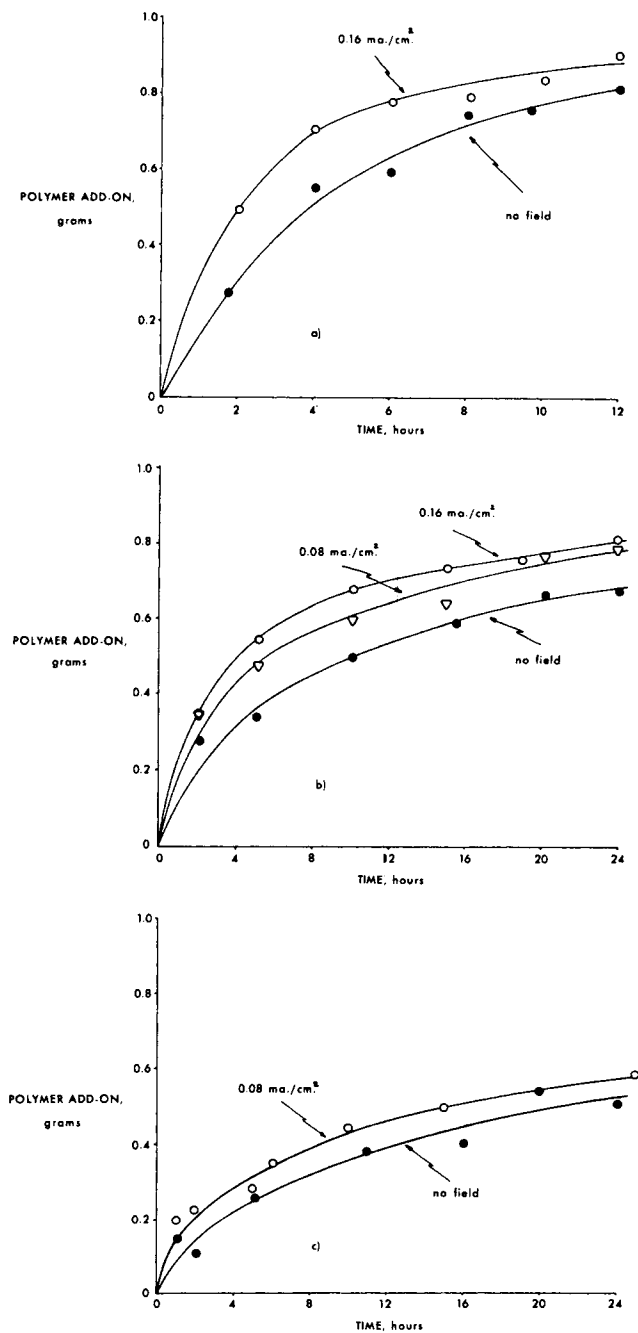


Fig. 3. Polymer add-on to host membrane as function monomer concentration and current density. (a) 0.2 m 4-vinylpyridine, (b) 0.1 m 4-vinylpyridine, (c) 0.05 m 4-vinylpyridine.

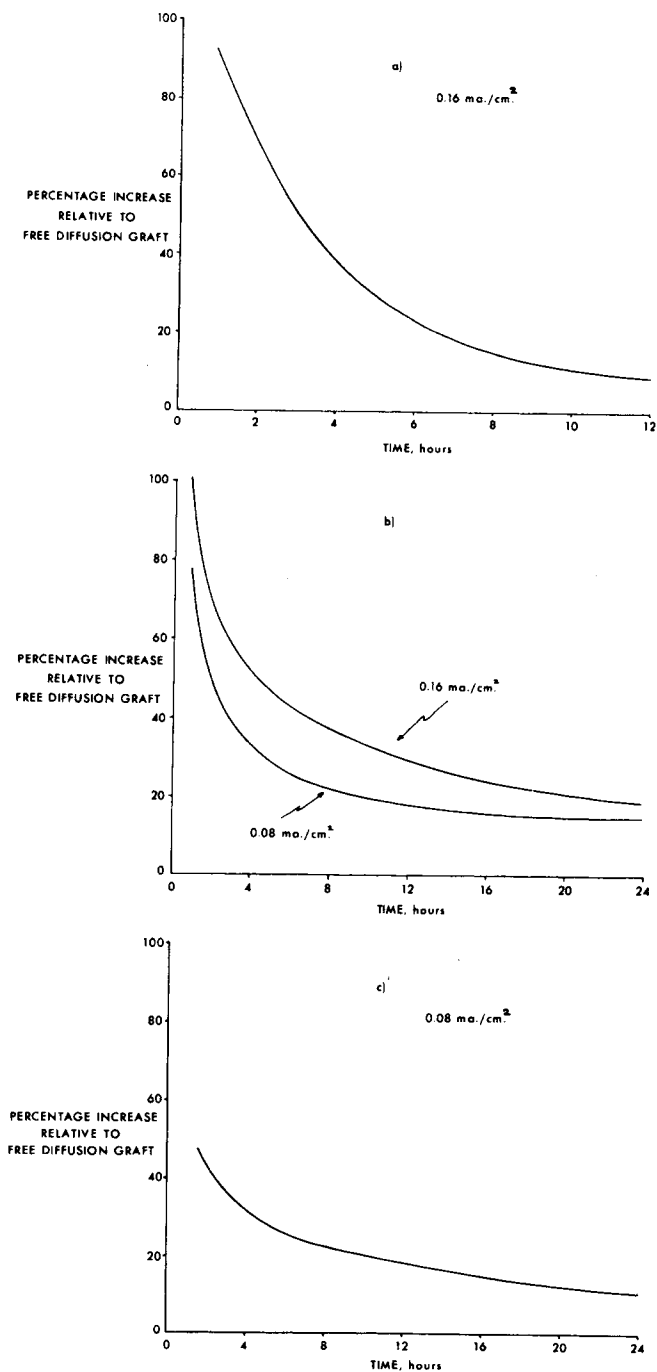


Fig. 4. Rate enhancement due to external field. (a) 0.2 m 4-vinylpyridine, (b) 0.1 m 4-vinylpyridine, (c) 0.05 m 4-vinylpyridine.

the initial reaction period. For example, at 0.2M monomer concentration, a 90% graft add-on enhancement over free diffusion after 1 hr decreased to 9% after 12 hr. During the initial stage, the free diffusion rate was at its highest level, and during this same period the external field had its greatest influence.

Applied Field Behavior

Potential drops measured successively relative to the cathode potential are recorded in Figure 5a for the case of 0.2M monomer concentration. The drop across the cathode chamber, marked "cathode side of host membrane," was low and relatively constant with time. From the cathode to the monomer cell side of the host membrane, the potential drop decreased from 4 to 6 hr and then leveled off. This is shown in more detail in Figure 5b, which gives the drop across the membrane alone. Proceeding further to the monomer cell side of the spacer membrane which separates the monomer from the anode compartment, the major potential drop occurs. The drop rises after 3 to 4 hours to a maximum at 5 hr whereupon it decreases sharply for the duration of the reaction period. Further drops to the anode side or totally across the reactor to the anode proper were of low relative magnitude and essentially constant throughout the entire reaction period. The overall behavior across the cell was duplicated at 0.1M monomer concentration except for the maxima occurring at a later time, 8 hr and 12 hr at current densities of 0.16 mA/cm² and 0.08 mA/cm², respectively. The differences in initial values corresponded to the difference in current density. Measurements at 0.05M monomer and 0.08 mA/cm² did not reach a maximum although they did show a continuous increase with time over 24 hr of 160 to 244 volts.

These observations indicated marked changes in the electromigration behavior between the cathode and anode compartments, more specifically of the host membrane and the monomer cell. Various experiments were conducted to determine the cause of these effects since they indicated changes in the nature of the grafted membrane.

There were no marked changes in the pH of the different reactor compartments with or without applied field. Changes over 12 hr in the case of the 0.2M monomer reactions were of the order of 1 pH unit, falling from about 9.5 to 8 in the monomer cell, and rising from 2.5 to about 3.5 in the cathode cell and from 4 to 5 in the anode cell. Variations were similar at the other monomer concentrations.

The Grafted Membrane

Morphology. Prior to removal from the reactor, the grafted membrane buckled toward the monomer cell side increasingly as the polymer add-on level increased. When the membrane was removed from the reactor at the conclusion of an experiment and subsequently washed with water, it retained this expanded state. However, when acidified to the acid chloride form, it immediately took on a curled configuration with the grafted side

out. The severity of the curl was also always proportional to the add-on level.

Attempts were made to examine directly the structure of the grafted membranes by scanning electron microscopy. Standard sample prepara-

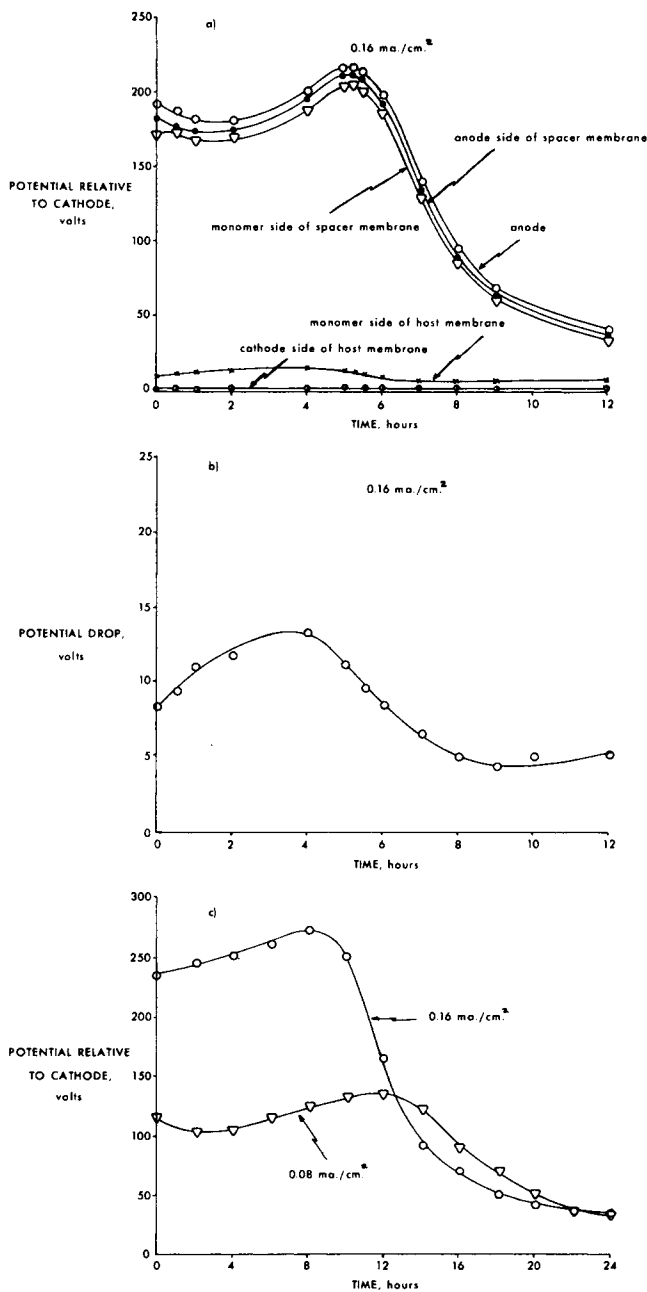


Fig. 5. Potential gradients across reactor vs. time. (a) potential drop at various points at 0.2 m 4-vinylpyridine, (b) potential drop across host membrane at 0.2 m 4-vinylpyridine 0.16 ma/cm², (c) potential drop across reactor at 0.1 m 4-vinylpyridine.

tion techniques were used. Unfortunately, no distinguishing structural features could be discerned even at magnifications up to $10,000\times$, nor were any distinguishing features of the initial ungrafted host membrane noted. Apparently the grafted membrane was relatively uniform in both structure and the electron emissive properties which generate SEM images. More extended studies using, for example, low temperature fracture techniques were not undertaken.

When formed from monomer concentrations of $0.1M$ and $0.2M$, the membranes became visually more transparent with reaction time, and the graft surface was very uniform. At $0.05M$, however, the graft was often blotchy, which possibly related to visual inhomogeneities originally in the host membrane surface. The fact that this was not noted on grafts at higher monomer concentrations suggests an influence of concentration on the morphology of the add-on surface.

Chain uncoiling and expansion as a function of the degree of neutralization is common for polymers of weak acids or bases. This phenomena, coupled with concentration gradients, may be responsible for the curling behavior of the grafted membranes when acidified. The polymer chains as polymerized are in the form of the weak base poly(4-vinylpyridine); there is little dissociation and only a low degree of intra- and intermolecular electrostatic repulsion between the 4-vinylpyridine segments. However, once acidified, the increased electrostatic repulsive forces may cause the membrane to relieve internal stress by assuming highly curled configurations.

Ion Permeability. The potential drop behavior in the reaction cell, Figure 5, showed changes with time occurring in the electrolytic behavior of the graft membrane and the adjacent monomer cell. Since the graft might influence the overall electrolytic membrane behavior, a study was undertaken of its resistance to ion carriers. Measurements were made of the transport of 2-naphthalenesulfonic acid and the 4-vinylpyridine monomer through the membrane. At no time was it possible to detect titanium in the reactor compartments showing that it never functioned as an ion carrier nor was involved in any ion exchange equilibria with the adjacent phases under the reaction conditions employed.

The diffusion of the 2-naphthalenesulfonate anion through the host membrane and into the monomer cell was followed by UV adsorption measurements at $320\text{ m}\mu$. No trace could be detected in the monomer cell for the duration of the reaction without the applied field, and only small quantities in experiments at 0.08 mA/cm^2 . However, at 0.16 mA/cm^2 , an abrupt change occurred in the vicinity of 6 hr, Figure 6. From this time on, the 2-naphthalenesulfonate anion carried 20% of the total current at the $0.1M$ monomer concentration and 40% at $0.2M$. The time of about 6 hr corresponded closely to that of the falloff in potential across the monomer cell and the cathode. Accumulation of 2-naphthalenesulfonic acid in the monomer cell decreased the potential proportionately (Fig. 5). At the inception of change in ion permeability, the grafted add-on amounted to

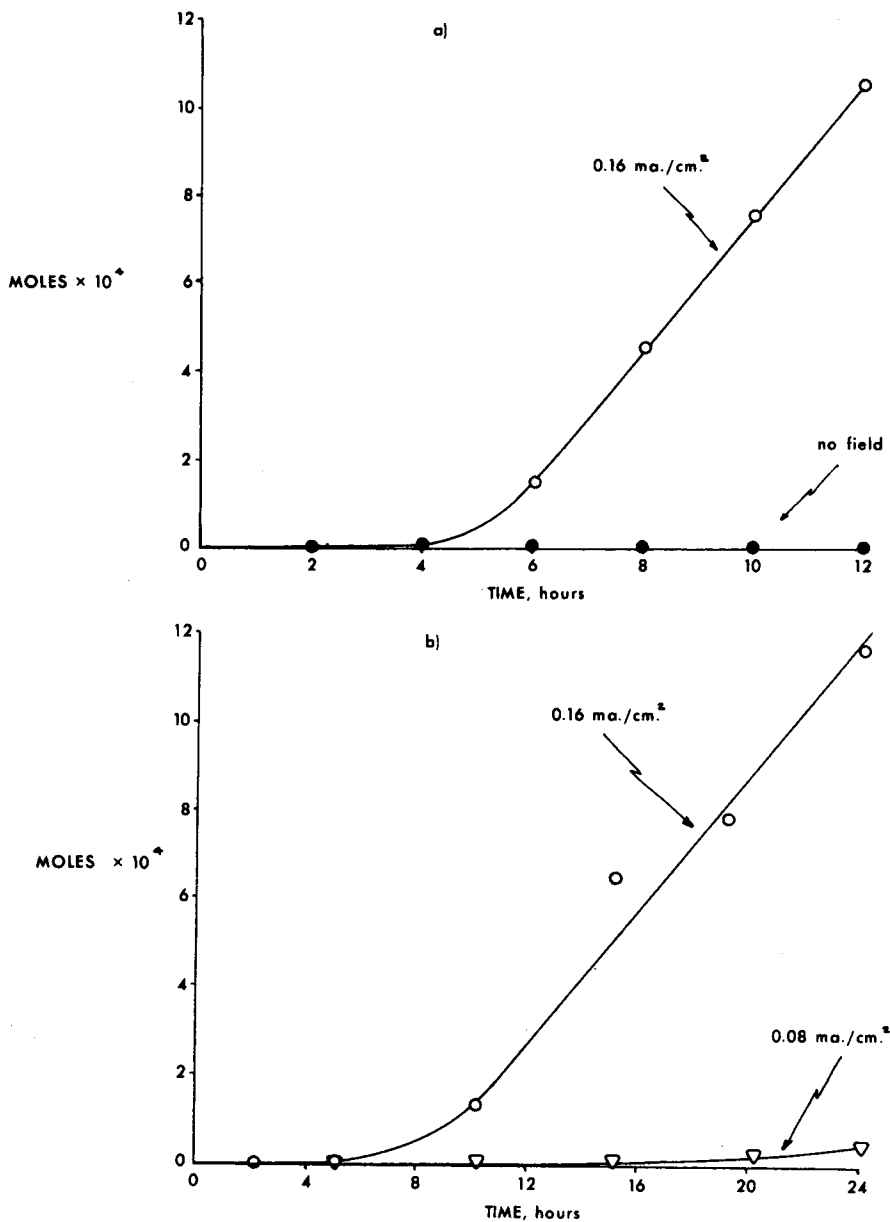


Fig. 6. Diffusion of 2-naphthalenesulfonic acid through host membrane. (a) 0.2 m 4-vinylpyridine, (b) 0.1 m 4-vinylpyridine.

55% on a weight basis. These data indicate an alteration of the grafted host membrane from its initial strongly, cationic exchange character to a mixed amphoteric character as the graft level increased. This could easily result from grafting the host membrane in depth.

It was not possible to follow the diffusion of unreacted monomer penetrating through the host membrane into the cathode cell because of the con-

flecting UV absorption of 2-naphthalenesulfonic acid and the 4-vinylpyridine. However, by using water in the cathode cell, at the expense of a decrease in conductivity, it was possible to conduct measurements, Figure 7. Under these conditions, at 0.1M monomer concentration the unreacted

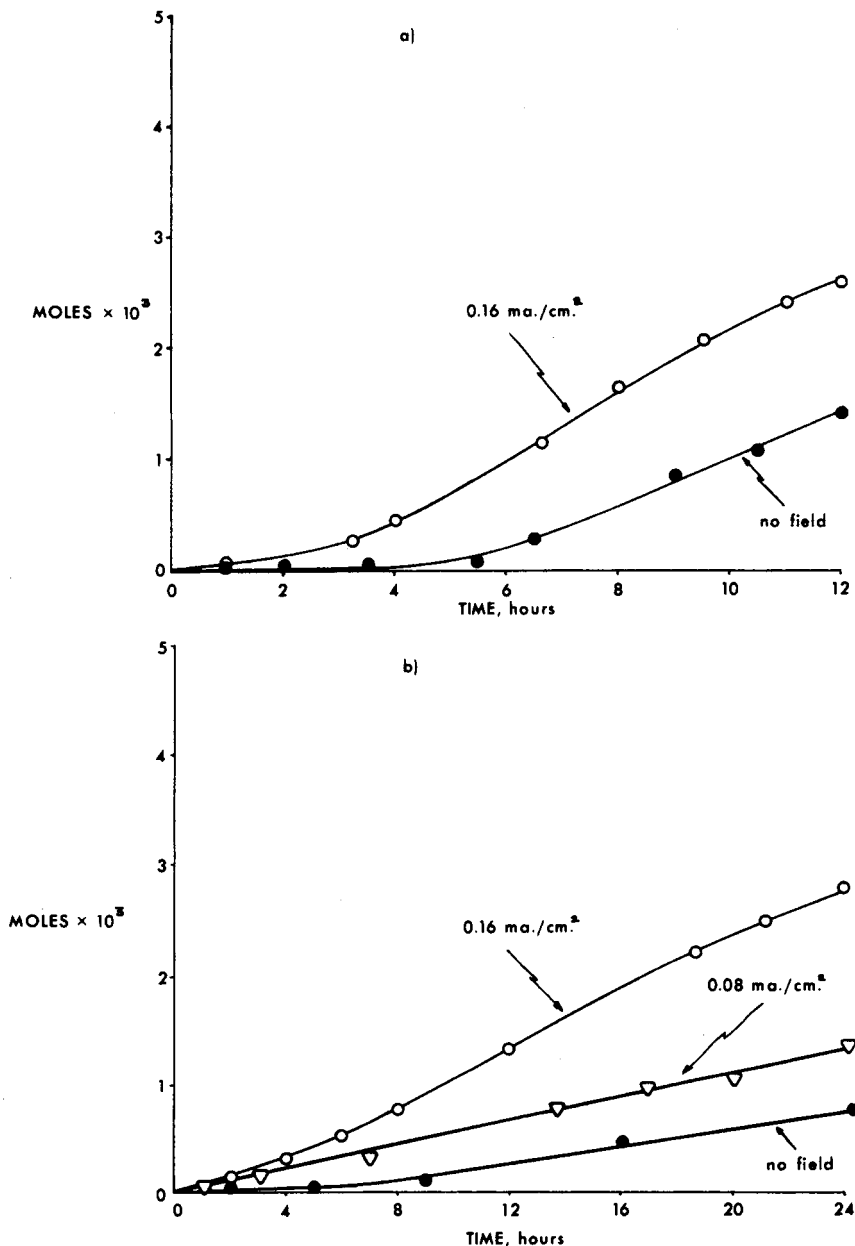


Fig. 7. Diffusion of unreacted 4-vinylpyridine through host membrane (with water in cathode cell). (a) 0.2 M 4-vinylpyridine, (b) 0.1 M 4-vinylpyridine.

monomer carried 31% and 30% of the total current at 0.08 and 0.16 mA/cm², respectively. However, at 0.2*M* monomer concentration, the unreacted monomer accounted for 71% of the current through the host membrane phase at 0.16 mA/cm². The diffusion of unreacted monomer increased with time of reaction to a near-constant rate roughly proportional to current density. The initial flux of monomer diffusing through without reacting was small compared to the add-on rate. Since monomer was diffusing through without reacting at an increasing rate, there may have been a decrease in the concentration of reactive species within the host phase. The field logically forced the monomer into the activated membrane at a faster rate than free diffusion under no external field.

Potential measurements across the cells were conducted with water alone in the cathode cell. The potential drop across the monomer cell and host membrane increased monotonically presumably due to the gradual reduction of monomer concentration and to the increasing resistivity of the grafted host membrane.

In summary, a consistent picture developed from conductivity and ion migration of changing ion permeation properties of the host membrane as grafting proceeded. The possibility of synthesizing membranes of controlled ion permeability by controlling the applied field is thereby apparent.

DISCUSSION OF RESULTS

The experimental results clearly demonstrate that an external d.c. field was capable of controlling the migration of the reactive monomer into the host membrane at a rate exceeding that of free diffusion. There was no visual or kinetic evidence to suggest that homopolymer had formed in the bulk fluid of the monomer cell and was simply electrodeposited on the membrane. The add-on rate of the graft decreased with elapsed time which would not be true for homopolymer deposition at constant current density. Visually, the homopolymer of 4-vinylpyridine is not soluble at the experimental pH in the monomer cell, yet none could be observed.

The graft add-on rate with free diffusion conditions followed a time-dependent function in which the initial rate and the terminal asymptotic limit were a function of the external monomer concentration. These initial rates are given in Table III. The add-on rate was proportional to the external field, when applied, but the general features of free diffusion behavior were preserved. The flux of unreacted monomer penetrating through the membrane was also proportional to field strength suggesting that the field increases the graft rate because it increases the rate at which the monomer enters the host membrane phase, i.e., forced diffusion superimposed on a polymerization reaction.

It might be expected that, at a given current density, the external field ought to exert more influence on the graft reaction rate at lower monomer concentrations. However, as reported earlier, the apparent transport

TABLE III
Initial Graft Rates Under Free Diffusion

Monomer concentration, moles/l.	Initial add-on rate, (moles/hr) $\times 10^3$
0.05	0.7
0.1	1.1
0.2	1.5

number of the 4-vinylpyridinium cation varied in proportion to the external monomer concentration. Factors influencing strong electrolyte transport numbers through cation-exchange membranes are membrane semipermeability, back diffusion from the receiving cell, and concentration polarization in the donating cell.¹⁵⁻¹⁷ In this research, the concentration of current carriers in the receiving cell was deliberately kept low to minimize back diffusion. Concentration polarization also was not likely a prominent factor since at the concentration, 0.1M, where two field levels were examined, observed transport numbers were independent of current density. Hence, the observed proportional dependence of monomer transport number with external monomer concentration must be due to membrane semipermeability behavior and/or the inherent transport behavior of the ionic vinyl monomer as a function of concentration.

External film diffusion, while probably involved, is not believed to have been the dominant rate-controlling factor in the process. Alone, it cannot explain the increase with time of the monomer flux penetrating the membrane under constant field conditions. Controlling resistances within the membrane must be involved. Unfortunately, the kinetic system is very complex, and the present data are too limited for the definitive choice of a rate-controlling mechanism. Not only does the monomer concentration vary across the thickness of the membrane but the transport properties change with the amount of add-on. For these reasons, it is doubtful that a steady-state approach to the free-radical concentration is justified. In bulk systems, a steady-state free-radical concentration leads to a time-independent rate of polymerization. If this assumption is not made, the amount of monomer reacting to form polymer can be shown to be proportional to the logarithm of time. Extension of such a simple model to the graft system under an applied field is unrealistic, although Figure 8 indicates it has some merit for representing the data.

SUMMARY

The present work showed that, by applying an external d.c. electric field, an ion-permeable membrane can be grafted under controlled conditions with an ionic monomer polymerized by free radicals initiated on the membrane. The monomer used was 4-vinylpyridine. Initiation was by the redox couple of titanium (ous)-t-butylhydroperoxide with the titanium

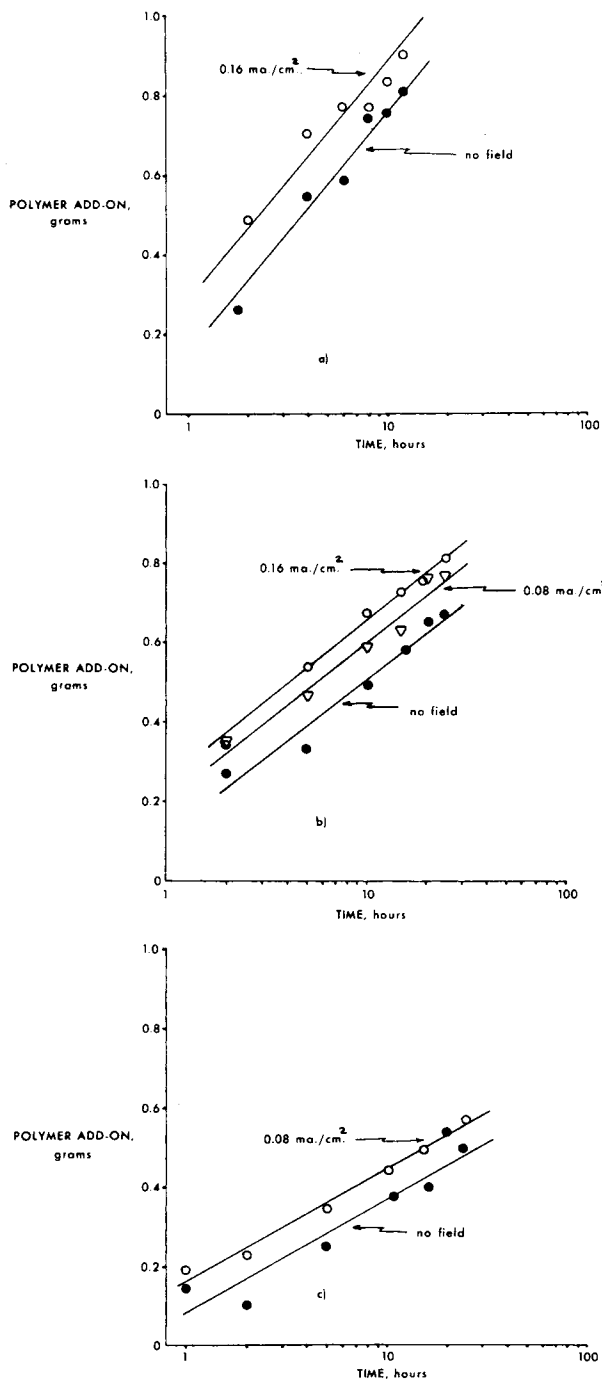


Fig. 8. Semi-log plot of polymer add-on vs. time. (a) 0.2 m 4-vinylpyridine, (b) 0.1 m 4-vinylpyridine, (c) 0.05 m 4-vinylpyridine.

ion initially adsorbed on a cationic host membrane and the oxidant in bulk solution with the monomer. Applying a field accelerated the graft rate and provided greater control of the amount and distribution of polymer than when free diffusion alone directed the monomer to the reaction sites. The possibility of using this technique for tailoring membranes to particular properties is apparent, possibly being another route to design of ampholytic mosaic membranes.

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