Electropolymerization of 9-vinylanthracene: kinetic study using thin-layer spectroelectrochemistry

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An *in situ* spectroelectrochemical technique has been employed to investigate the electropolymerization of 9-vinylanthracene. The propagation reaction as monitored from excimer emission of poly(9-vinylanthracene) followed pseudo-first-order kinetics. The dependence of the polymer yield and the propagation reaction rate constant on the monomer and initiator concentrations has been studied to elucidate the kinetics of the electropolymerization process. The energy of activation of the propagation reaction was 7.85 kcal mol^{-1}.

(Keywords: electropolymerization; spectroelectrochemistry; kinetics; 9-vinylanthracene; excimer emission)

INTRODUCTION

Many aromatic heterocyclic molecules, upon electrochemical oxidation, lead to the formation of electrically conducting polymer films at the electrode surface[1]. Increasing interest in conducting polymers and polymer-modified electrodes has made it necessary to study various aspects of the electropolymerization process, including the kinetics of the reaction. Attempts have been made in the past to investigate the free-radical, anionic and cationic polymerizations of 1- and 9-vinylanthracene monomers[2,3]. Electroinitiated polymerization of aryl vinyl polymers was also performed by Smith *et al.*[4] in the presence of $ZnCl_2$ and with the application of high voltage. Recently we reported that 1-vinylpyrene[5] and 9-vinylanthracene[6] can be polymerized at a conducting SnO_2 electrode with the application of anodic potentials ($\gtrsim 0.6$ V and 1.1 V *versus* SSCE, respectively). These polymers with aryl molecules as pendant groups can act as probes since these groups often exhibit emission that is distinctively different from the monomer fluorescence emission. Such a difference in a physical property enables one to monitor the electropolymerization process directly.

The study of electrogenerated reactants using optically transparent electrodes has been the topic of many recent research efforts[7,8]. A typical spectroelectrochemical experiment involves the study of a thin layer of solution confined near the transparent electrodes using various techniques, such as transmission, reflectance, luminescence and scattering spectroscopies[9]. The combination of electrochemistry and spectroscopy could be an effective approach in probing the electropolymerization process. We have recently demonstrated the use of fluorescence emission spectroscopy in monitoring the electropolymerization of 9-vinylanthracene[6]. The principle of such a technique is described in *Figure 1*. Spectroelectrochemical experiments that give some preliminary insight into the kinetics of the electrochemically initiated polymerization of 9-vinylanthracene at an SnO_2 electrode are described here.

EXPERIMENTAL

Materials

9-Vinylanthracene (Aldrich), acetonitrile (Aldrich, gold label) and tetrabutylammonium perchlorate (TBAP) (Alfa) were used as supplied. The n-SnO_2 working electrodes (WE) were cut from an antimony-doped NESA glass obtained from PPG industries (also available from Metavac Inc.), and were cleaned as described earlier[10].

Instrumentation

Electrochemical and spectroelectrochemical measurements were done with a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, a PAR model 175 universal programmer and a Kipp and Zonnen X–Y recorder. Electrochemical experiments were performed in a standard three-compartment cell with a Pt wire as a counterelectrode (CE) and a saturated sodium chloride calomel electrode (SSCE) as a reference electrode (RE). The potentiostat had a provision to compensate for the iR drop and this was employed during the electrochemical measurements. For spectroelectrochemical measurements a Teflon (polytetrafluoroethylene) block was machined to accommodate a 0.5×4 cm SnO_2 plate (WE), a Pt wire (CE) and an Ag wire (RE) and was inserted into the $1 \times 1 \times 4.6$ cm cuvette. The gap between the SnO_2 and the front wall of the cuvette allowed the presence of a very thin layer ($\leqslant 0.04$ cm thick) of the sample. The total volume of the sample in the cell was 0.75 ml. The whole assembly could then be inserted into the sample chamber

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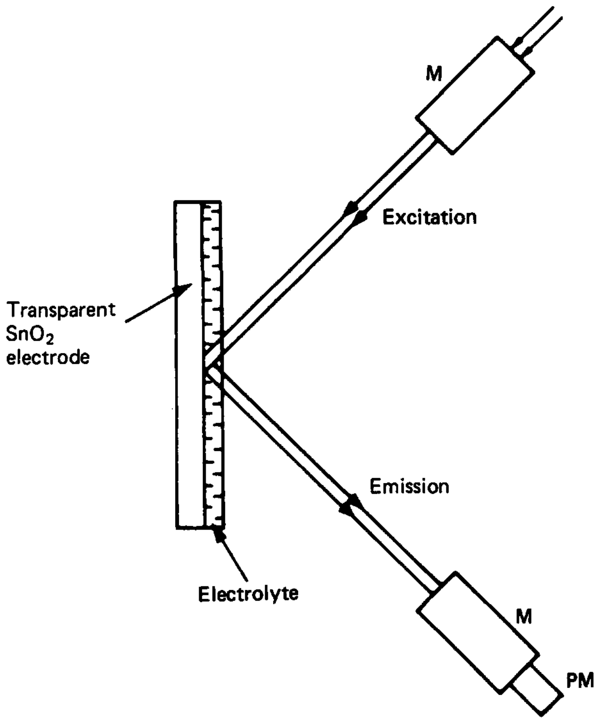

Figure 1 Schematic diagram of the spectroelectrochemical technique employed to probe the electropolymerization process

of the fluorimeter such that the excitation beam was at 45° to the SnO_2 electrode. The coulometer (PAR model 179) allowed simultaneous measurement of the charge passed through the circuit, from which the number of moles of initiator generated in 0.75 ml of the sample was determined. The initiator concentrations were then converted into moles per litre for the determination of k_p, the propagation rate constant. Fluorescence measurements were carried out in front-face geometry. An SLM single-photon-counting fluorescence spectrometer was used to monitor the fluorescence emission. Water from a thermostatted bath was passed through the cell holder to vary the temperature. Absorption spectra were recorded with a Cary 219 spectrophotometer. Unless otherwise specifically mentioned, all experiments were performed at room temperature (295 K).

ANALYSIS

It is known that electropolymerization of olefins occurs through radical cations[1]. A plausible kinetic scheme for the electropolymerization of 9-vinylanthracene could, therefore, be written as:

Initiation

$$M_1 - e^- \rightarrow M_1^{+\cdot} \qquad (1a)$$

Propagation

$$M_1^{+\cdot} + M_1 \xrightarrow{k_{p,1}} M_2^{+\cdot} \qquad (1b)$$

$$M_n^{+\cdot} + M_1 \xrightarrow{k_{p,n}} M_{n+1}^{+\cdot} \qquad n = 2, 3, \ldots \qquad (1c)$$

where M_1 is the monomer (9-vinylanthracene), $M_n^{+\cdot}$ is a growing polymeric radical cation having n monomeric units linked together covalently and $M_{n+1}^{+\cdot}$ is a growing polymeric radical cation having $(n+1)$ monomeric units. Several side reactions including chain transfer reactions (to solvent, etc.)[11] could be incorporated in equations (1), but in the present work these are relatively unimportant and so are omitted from equations (1a–c). Also, Waltman and Bargon[1] have suggested an alternative kinetic scheme incorporating (a) the generation of $M_n^{+\cdot}$ from a 'dead' polymer molecule M_n ($n = 1, 2, \ldots$) followed by (b) a combination of two radical cations $M_n^{+\cdot}$ and $M_1^{+\cdot}$ to give M_{n+1}^{2+}, which further gives M_{n+1} and $2H^+$. Our experimental results do not appear to agree with this hypothesis, as will be discussed later. Equations (1a–c) are therefore being suggested as a plausible kinetic scheme. The detailed kinetic scheme given in equations (1a–c) can be rewritten *schematically* as:

Initiation

$$M_1 - e^- \xrightarrow{k_I} P_1 \qquad (2a)$$

Propagation

$$P_n + M_1 \xrightarrow{k_p} P_{n+1} \qquad n = 1, 2, \ldots \qquad (2b)$$

where P_n and P_{n+1} are growing radical cations having n and $(n+1)$ monomeric units linked together covalently. In equation (2), k_I and k_P are the rate constants of the initiation and propagation steps, respectively. In writing this equation, Flory's equal-reactivity hypothesis[11,12] has been invoked. This states that the reactivity of a growing polymeric species is independent of its chain length, n. This hypothesis, which is well documented experimentally[11,12], leads to considerable simplifications of the mass-balance equations and is used extensively in the design and analysis of polymerization systems.

Two sets of experiments have been performed in this study using the same experimental set-up. In the first set of experiments (Experiment 1), a potential (1.1 V) is applied *continuously* to the SnO_2 electrode. The initiator $M_1^{+\cdot}$ is thus formed continuously at the electrode surface, according to the scheme of equations (1a–c). It is assumed that each electron transfer generates one initiator species (diffusion from the bulk to the solution is assumed to be very rapid[1]). Once generated, the radical cations add on monomer molecules sequentially to give longer polymeric radical cations, $M_n^{+\cdot}$. Thus, monomer molecules are being depleted from the solution both by the initiation mechanism as well as by propagation. In the absence of any other side reaction, the polymer present at any time would consist of an entire range of molecular weights, since the radical cations formed earlier have propagated for a longer period of time, while the ones generated later have propagated for a shorter time, and so have added fewer monomer molecules. The polymer formed gets deposited as a thin (and visible) film at the electrode surface. This process continues till the monomer in the solution gets completely exhausted. Experiment 1 is not being mathematically modelled in the present paper.

In the second set of experiments (Experiment 2), there are two stages. In stage 1, one applies a potential at the SnO_2 electrode for a short period of time only, similar to what is done in Experiment 1. After this, the initiation process is stopped by removing the applied potential to begin stage 2. One defines $t = 0$ as the time when the applied potential is removed, i.e. at the beginning of stage 2. The total charge passed through the circuit during stage 1 of this experiment is measured with a coulometer. This gives the amount of radical cations present at the electrode surface during stage 2. If the kinetic scheme of equations (1a–c) were indeed correct, then these radical cations would continue to propagate to give longer molecules even after the applied potential is removed and polymerization would continue till the monomer in the solution is completely exhausted. This is indeed what is observed experimentally, as discussed later, and so it is inferred that equations (1a–c) are at least a plausible picture of what is really taking place.

In Experiment 2, since the only reaction taking place in stage 2 is propagation (assuming that the side reactions are not dominant), the rate of monomer consumption during this stage can be written as[11,12]:

$$d[M_1]/dt = -k_P[M_1]\sum_{n=1}^{\infty}[P_n] \equiv -k_P[M_1][I]_0 \qquad (3)$$

where $[M_1]$ and $[I]_0$ are the monomer and initiator concentrations. The summation $\sum_{n=1}^{\infty}[P_n]$ is the total concentration of the radical cations (irrespective of the molecular weight) at any time, t. The latter is identical to their concentration, $[I]_0$, at the beginning of stage 2, since no depletion or generation of radical cations takes place in this stage. $[I]_0$ is thus related to the total charge applied in the short time period (i.e. stage 1), and is known experimentally. Integration of equation (3) gives the monomer concentration $[M_1]$ at any time, t, in stage 2 as:

$$\ln([M_1]/[M_1]_0) = -k_P[I]_0 t \qquad (4)$$

Here, $[M_1]_0$ is the monomer concentration at the beginning of stage 2, and is approximately the same as in the original solution since very little monomer is consumed in the short stage 1 polymerization just preceding stage 2. Since the fluorescence (intensity) I^f is proportional to the concentration of monomeric units on the polymer formed, one can write the fluorescence intensity at infinite time as:

$$I^f_\infty \propto [M_1]_0 \qquad (5)$$

Similarly, since all the monomer molecules in the solution show up as polymer, the fluorescence intensity at any time t in stage 2 is given by:

$$I^f \propto ([M_1]_0 - [M_1]) \qquad (6)$$

Equations (4)–(6) can be combined to give:

$$\ln[(I^f_\infty - I^f)/I^f_\infty] = -k_P[I]_0 t \equiv -k'_P t \qquad (7)$$

Plots of $\ln[(I^f_\infty - I^f)/I^f_\infty]$ vs. time during stage 2 should then be linear and the slope should give experimental values of k'_P (and hence k_P, since $[I]_0$ is available experimentally).

In the above derivation, it is implicitly assumed that there are no significant mass transfer limitations present in the experiment, and that the *local* concentration of the monomer at the electrode surface is the same as that in the entire solution. If diffusional characteristic times are of the same order as the reaction times, a slightly more complex mathematical analysis will be necessary, and the integrated form of the final equation will have a different form from that of equation (7). Since our results do conform to equation (7), it is assumed that our assumptions are valid. Waltman and Bargon[1] also confirm the lack of importance of diffusional limitations. In any case, experiments with varying rates of mixing to speed up diffusional rates could be designed, if necessary, to provide further confirmation of this fact.

RESULTS AND DISCUSSION

Electrochemical and spectroelectrochemical characterization of the polymerization process

It has been shown earlier[6] that electrochemical oxidation can initiate the polymerization of 9-vinylanthracene. (A typical cyclic voltammogram of 9-vinylanthracene is shown in *Figure 2a*.) The polymerization can be achieved either by continuous cycling between 0 and 1.2 V vs. SSCE or by application of a constant potential of ~1.1 V. As shown earlier[5], the molecular weight of such an electrochemically obtained polymer is ~13 000. The emission maxima of the monomer in solution are at 420 and 428 nm, while the polymer exhibits a broad maxima around 500 nm. Since these two emissions are distinctively different, one can conveniently monitor the monomer with emissions at 420 nm or the polymer with its excimer emission at 520 nm. Two anthracene units attached to the C–C chain overlap partially to induce an excimer emission. Hence the observed excimer emission intensity is directly

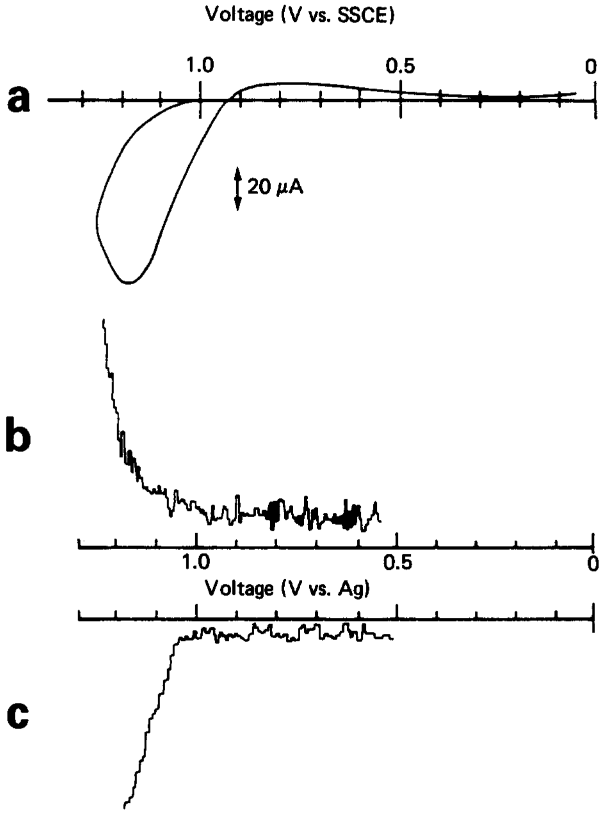

Figure 2 (a) Cyclic voltammogram of 0.1 M 9-vinylanthracene in acetonitrile. (b) Fluorescence emission monitored at 520 nm and (c) fluorescence emission at 420 nm monitored during anodic cycling (WE, SnO_2; electrolyte, 0.1 M TBAP; scan rate, $10\,mV\,s^{-1}$)

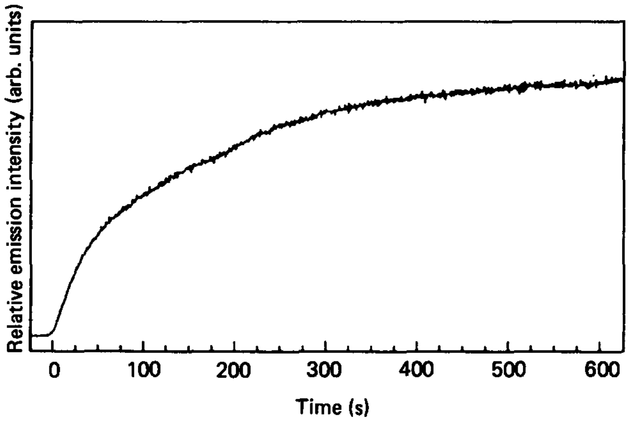

Figure 3 Plot of fluorescence emission intensity at 520 nm *versus* time in Experiment 1 (1.1 V vs. Ag was applied *continuously*)

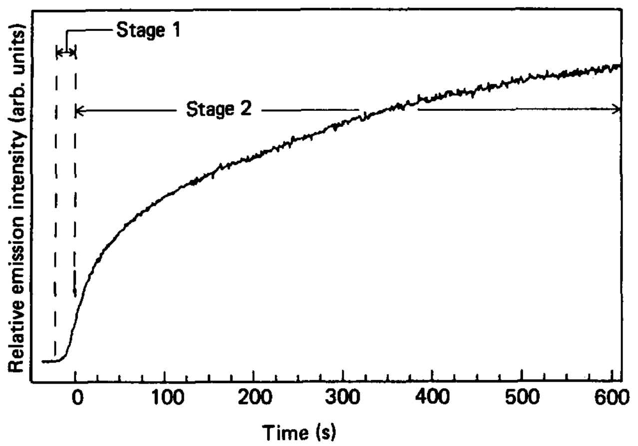

Figure 4 Increase in the relative fluorescence emission intensity at 520 nm representing the polymerization in Experiment 2. Time $t=0$ represents the point at which the applied potential was disconnected (0.1 M TBAP and 0.2 M 9-vinyl anthracene in CH_3CN at 295 K; charge passed through the circuit (in stage 1) was 1.2×10^{-2} C)

proportional to the concentration of the monomer units in the polymer chain.

A typical spectroelectrochemical plot of the fluorescence emission observed during the electrochemical cycling is shown in *Figure 2*. A sudden increase in the excimer emission at 520 nm and a decrease in the monomer emission at 420 nm (*Figures 2b* and *2c*, respectively) occurred at a potential where the oxidation of 9-vinylanthracene was observed in the cyclic voltammogram. In order to assess the kinetics of electropolymerization, a constant potential of ~1.1 V *versus* Ag was applied to initiate the polymerization, and the excimer emission at 520 nm was monitored to follow the propagation reaction.

Polymerization in Experiment 1

As described in the previous section, polymerization was achieved with the continuous application of potential (1.1 V). This led to the continuous formation of $M_1^{+}\cdot$ and higher oligomers until all the monomer was exhausted in the polymerization process (as confirmed by lack of further polymerization by shaking or by applying higher voltage). The fluorescence emission plateau was taken as the measure of the maximum polymer yield for the corresponding monomer concentration. A typical plot of the fluorescence emission observed during the continuous application of potential of 1.1 V is shown in *Figure 3*. Upon conducting stage 1 polymerization for a long period of time, both initiation and propagation reactions occurred simultaneously and it is difficult to get the individual rate constants from such studies. As such, the emphasis in this study was on Experiment 2.

Polymerization in Experiment 2

Since the application of potential was for only a short period of time (<10 s) in this set of experiments, one could obtain experimentally the propagation rate constant k_P (equation (2)) by monitoring the increase in the fluorescence emission at 520 nm in the absence of further initiation. A typical plot of fluorescence emission *versus* time is shown in *Figure 4*. This increase in fluorescence emission, which represents the propagation reaction, was exponential and can be fitted to pseudo-first-order kinetics (*Figure 5*) as described by equations (3)–(7). Once the fluorescence intensity has attained a plateau, further application of anodic potential did not yield any polymerization, thus indicating that the monomer is exhausted in the solution (and giving credence to the validity of equations (1)). It may be mentioned that obtaining kinetic data in the absence of initiation has precedence in other polymerizations too, e.g. the rotating sector method used in free-radical polymerizations[13].

Kinetics

Table 1 gives experimental values of k'_P and the relative yield of the polymer obtained from stage 2 polymerization of vinylanthracene solutions, with different values of $[I]_0$. It is observed that the polymer yield in Experiment 2 (when the plateau is attained, see *Figure 4*) is the same as that obtained when the potential is applied continuously (Experiment 1). This indicates the validity of the kinetic scheme of equation (2). Deviations of the relative yield in some experiments in *Table 1* are attributed to experimental error.

It may be emphasized that Waltman and Bargon[1] have suggested the following kinetic scheme for elec-

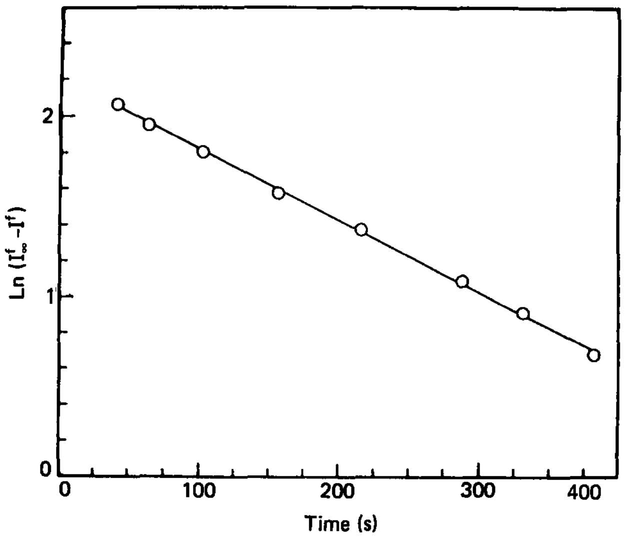

Figure 5 Plot of $\log(I^f_\infty - I^f)$ *versus* time representing the pseudo-first-order fit of the fluorescence emission growth in *Figure 4*

Table 1 Relative yield of polymer and k'_P for different $[I]_0$

Expt. No.	$[I]_0$ (10^{-4} mol l^{-1})	Relative yield (%)	k'_P (s^{-1})	$k_P = k'_P/[I]_0$ (l mol^{-1} s^{-1})
2	1.07[a]	100	0.0037	34.6
2	1.20[a]	89	0.0038	31.6
2	1.74[a]	91	0.0056	32.2
2	2.26[a]	100	0.0070	31.0
1	6.75[b]	100	–	–

[a] 0.2 M vinylanthracene in acetonitrile at 295 K; 1.1 V vs. Ag was applied for different times to achieve different $[I]_0$ (Experiment 2)

[b] 1.1 V vs. Ag was continuously applied (Experiment 1) till polymerization was complete. Fluorescence intensity at complete polymerization assumed to represent 100% relative yield

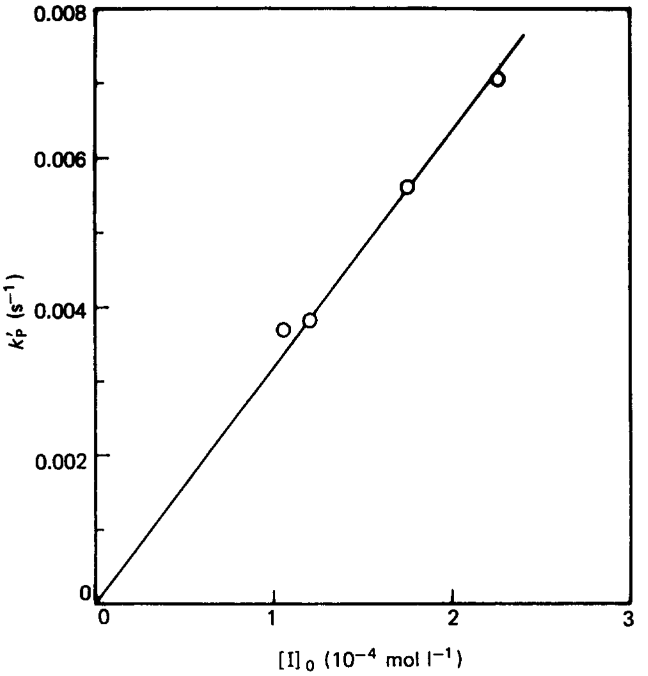

Figure 6 Plot of observed pseudo-first-order propagation rate constant, k'_P, *versus* the initiator concentration, $[I_0]$, giving $k_P = 32$ l mol^{-1} s^{-1}

tropolymerization of several monomers:

$$M_n - e^- \longrightarrow M_n^{+}\cdot \qquad (8a)$$

$$M_n^{+}\cdot + M_1^{+}\cdot \xrightarrow{k_P^*} M_{n+1}^{2+} \longrightarrow M_{n+1} + 2H^+ \qquad n = 1, 2\ldots \qquad (8b)$$

where $M_n^{+}\cdot$ represents a polymeric radical cation having n monomeric units covalently linked together (as in equations (1)), and M_n is a 'dead' polymer molecule having n monomeric units. If this kinetic scheme did indeed correctly describe the polymerization of vinylanthracene, then at the end of the short stage 1 polymerization preceding stage 2, one would have only a small concentration of radical cations and these would deplete very rapidly on the removal of the applied potential. Continuation of polymerization in the absence of the applied potential till the monomer is completely exhausted, as shown by the results of stage 2 in *Table 1*, cannot be explained at all by the mechanism of equation (8).

Table 1 also shows that the rate constants k'_P increase as the value of $[I]_0$ is increased. The plot of k'_P *versus* $[I]_0$ is a straight line with intercept at the origin (*Figure 6*). The value of k_P obtained from this plot is 32 l mol^{-1} s^{-1}.

Table 2 shows the relative yields of the polymer and values of k'_P obtained from Experiment 2 and with different initial monomer concentrations. The relative yield increases linearly with $[M_1]_0$ and further confirms that the polymerization in stage 2 proceeds till all the monomer present in the solution is exhausted. This also indicates the superiority of the kinetic mechanism in equations (2) over that of equations (8). The values of k'_P in *Table 2* are again similar to those in *Table 1* under similar conditions and indicate some experimental scatter, as indicated earlier.

It may be added here that, based on the several observations discussed above, equation (2) is a more feasible kinetic scheme for the present system than equation (8). A word of caution must be added, however. Our experiments are not designed to obtain *exact* mechanistic details of the polymerization. For example, it

Table 2 Relative yield of polymer and k'_P at different initial monomer concentrations

$[M_1]_0$ (mol l^{-1})	$[I]_0$ (10^{-4} mol l^{-1})	k'_P (s^{-1})	Relative yield[a] (arbitrary units)
0.15	1.07	0.0046	9
0.20	1.33	0.0054	12
0.30	1.07	0.0060	17

[a] Relative yields represent the heights of the plateau, I_∞, in the fluorescence intensity curves

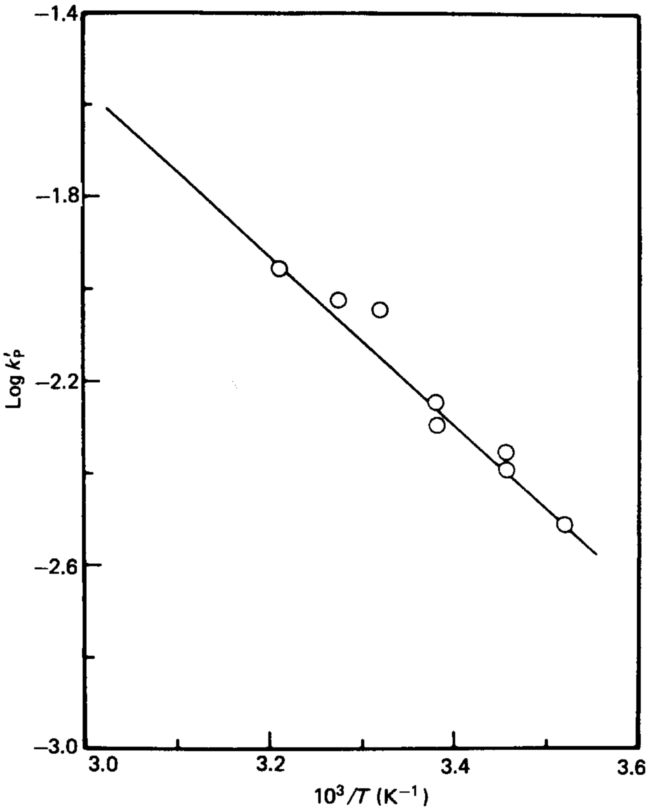

Figure 7 Arrhenius plot of log k'_P *versus* $1/T$ (0.2 M 9-vinylanthracene and 0.1 M TBAP in acetonitrile; charge passed through the circuit was $\sim 10^{-2}$ C to initiate the polymerization (stage 1))

is possible that two monomeric radical cations, $P_1^{+}\cdot$, may dimerize to give a doubly charged species which may propagate at either end. Our analysis for Experiment 2 is still valid, but k_P then is the rate of monomer molecules adding to such species.

Effect of temperature on the propagation reaction

Since the effect of $[I]_0$ is not discernible in our system, the dependence of k'_P on temperature also indicates the effect of temperature on k_P. *Figure 7* is an Arrhenius plot based on this information. The following equation represents our data fairly well:

$$k'_P = k_P[I]_0 = A \exp(-E_a/RT) \qquad (9)$$

The activation energy of the propagation reaction in the present experiment was 7.85 kcal mol^{-1} and was similar to the value of 7.88 kcal mol^{-1} for the chemically initiated polymerization of 2-vinylpyridine[13]. This is an interesting coincidence indeed.

CONCLUSIONS

The kinetic features of electropolymerization of 9-vinylanthracene have been elucidated using an *in situ* spectroelectrochemical technique. The excimer emission of vinyl aryl polymers could serve as an excellent probe to investigate the propagation reaction in the electropolymerization process. It will be interesting to see whether one could employ such aryl molecules as probes to monitor the electropolymerization of non-fluorescent substrates.

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