Fractal Growth Kinetics and Electric Potential Oscillations during Electropolymerization of Pyrrole

Ishwar Das,*,[†] Namita R. Agrawal,[‡] Sanjeev Kumar Gupta,[†] Sujeet Kumar Gupta,[†] and R. P. Rastogi[†]

Chemistry Department, DDU Gorakhpur University, Gorakhpur-273009, India, and St. Andrews College, Gorakhpur-273009, India

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Fractal growth, growth kinetics, and electrical conductivity of aggregates obtained during electropolymerization in the systems (A) pyrrole-4-toluene sulfonic acid silver salt (4-TSS)-acetonitrile, (B) pyrrole-4-TSS-$ZnSO_4$-acetonitrile, and (C) pyrrole-4-TSS-aniline-acetonitrile were investigated. In the case of system (A), effect of [4-TSS], [pyrrole], field intensity, and solvents H_2O and CH_3OH on morphology, fractal character, and growth kinetics was also studied. Fractal growth data were examined in detail. During studies on system (A), electric potential oscillations were observed and subjected to detailed study. The results indicate that fractal growth pattern and electric potential oscillations are inter-related. The mechanism of development of fractal growth, dendritic structure, and electric potential oscillations is discussed in terms of diffusion-limited aggregation and modified Diaz's mechanism, which explains the random movement of radical cations.

Introduction

Exotic phenomena far from equilibrium such as precipitation potential,[1a] electric potential oscillations, chaos,[1b] and fractal growth[1c] have evoked considerable interest during recent years. Such phenomena are also observed during electrodeposition and polymerization processes where dendritic and hyperbranched polymers are formed.[2,3] Cathode potential changes during electrodeposition of lead metal from its aqueous solution in batch and continuously stirred tank reactor (CSTR) and growth kinetic studies at constant current and potential have been studied for morphology.[4,5] Additives also play a critical role. Electropolymerization of aniline in the absence and presence of $ZnSO_4$ has been recently investigated.[6] The above phenomena have also been observed during electropolymerization of pyrrole, but detailed studies relating to dynamics of fractal growth and electric potential oscillations is lacking. Electrically conducting polymers are important on account of various applications in industries.[7−15] The conducting polymers have recently acquired notable importance in nanoscale science and technology.[16,17] Among the known conducting polymers, polypyrrole is one of the most promising materials for multifunctional applications.[18,19]

Hence, in the present investigation, fractal growth in terms of growth of fractal structure by weight and increase of length of petal with time was undertaken. During electropolymerization of pyrrole, chaotic electric potential oscillations were investigated. Role of solvents and additives was also studied. These studies indicate that fractal growth and electric potential oscillations are interrelated through random motion of cations. Results are reported in the present article.

Experimental Section

Pyrrole (AR-Merck Schuchardt), 4-toluene sulfonic acid silver salt (AR, Dr. Theodor Schuchardt & Co.), acetonitrile (AR, SD Fine Chem. Ltd.), and CH_3OH (AR, Ranbaxy Laboratories Ltd.) were used as such.

Electrochemical Synthesis and Growth Kinetics. The electrochemical synthesis of polypyrrole was carried out at room temperature using an experimental setup consisting of a Petri dish containing a solution of monomer, acetonitrile, and the oxidizing agent. Ten milliliters of the solution was taken. A cleaned platinum circular cathode was immersed into the solution, while the other platinum vertical anode was put at air/liquid interface at the center of the cathode of radius 2.5 cm. These electrodes were attached to a potentiostat (Scientific) to supply constant potential. Pyrrole concentration was varied in the range 0.05−0.25 M, whereas concentration of 4-TSS was in the range 0.025−0.125 M. Field intensity was varied in the range 1.2−6.0 V/cm. Polymerization started at the anode as soon as the potential was applied across the electrodes. Electropolymerization was carried out at moderate potential to prevent the oxidative decomposition of the solvent, electrolyte, and the polymer. Polypyrrole aggregates were collected after different intervals of time. The aggregates were washed with acetonitrile, dried in an oven at 50 °C, and weighed. Polypyrrole samples were also synthesized in the presence of zinc sulfate (0.0008 M) and aniline (0.11 M) additives. Aggregates were photographed using an Olympus microscope fitted with a camera. Results are shown in Figure 1. Experiments were also performed at different experimental conditions viz. [oxidizing agent], [pyrrole], and field intensity. Microphotographs are shown in Figure 2.

Dynamics of polymerization was studied in two ways: (i) by recording the weight of the aggregate at different time intervals and (ii) by recording the length of petal (a specific branch from the center of the circular envelope) at different time intervals with the help of a video camera attached to a TV screen and an experimental setup employed earlier. Results are shown in Figures 3 and 4.

Computation of Fractal Dimension *D*. Fractal aggregates were photographed and scanned with the help of a scanner attached to a computer. The fractal dimension *D* of scanned

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* To whom correspondence should be addressed. Tel.: 91-551-2338731. Fax: 91-551-2342880. E-mail: ishwar_das@rediffmail.com.
[†] DDU Gorakhpur University.
[‡] St. Andrews College.

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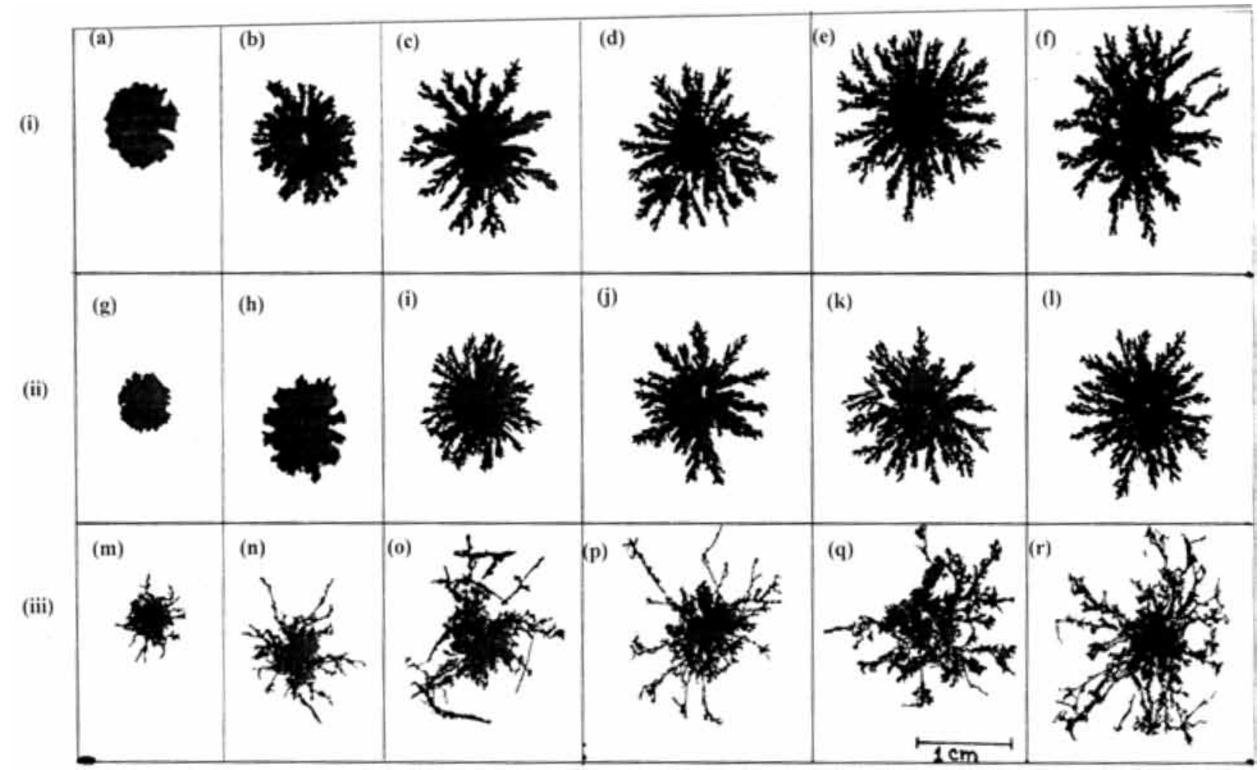


Figure 1. Microphotogrphs obtained during electropolymerization in systems (i) pyrrole-4-TSS-acetonitrile (a−f), (ii) pyrrole-4-TSS-$ZnSO_4$-acetonitrile (g−l), and (iii) pyrrole-4-TSS-aniline-acetonitrile (m−r) taken at 10, 20, 30, 40, 50, and 60 min. Conditions: [Pyrrole] = 0.10 M, [4-TSS] = 0.05 M, [$ZnSO_4$] = 0.0008 M, [Aniline] = 0.11 M, field intensity = 3.6 V/cm, separation between electrodes = 2.5 cm.

pictures was determined by the box counting method.[1d] The total number of boxes $N(r)$ are related to radius r by the relation $N(r) \approx r^D$. Fractal dimension D was obtained by plotting log $N(r)$ against log r using the method of least-squares analysis.

Electrical Conductivity Measurements. Electrical conductivity of electropolymerized aggregates was measured at room temperature using an experimental setup consisting of a 2-cm-long glass capillary (inner diameter = 0.96 mm) filled with the solid sample, the conductivity of which is to be measured. Two bright platinum electrodes (diameter = 0.337 mm) were inserted into the capillary such that these touched the sample and connected to a conductivity meter (VSI). Results are shown in Figure 5.

Oscillation in Anode Potential with Time during Electropolymerization. The voltage between anode and the reference calomel electrode was monitored during polymerization as a function of time. Potential measurements were made with the help of an x−t recorder attached to a suppressor (Digital Electronics). The experiment was conducted in a flat bottom Corning Petri dish. Two platinum electrodes at 2.5 cm apart were inserted in the solution. The circular cathode was extended below the surface of solution, while the lower end of the anode was put at the surface. Results are shown in Figure 6a. Influence of water (2%) and methanol (2%) on oscillatory characteristics of system (A) was also studied, and results are recorded in Figure 6.

Powder X-ray Diffraction Studies. Powder X-ray diffraction patterns of polypyrrole aggregates obtained using 4-TSS as oxidizing agent in the presence and absence of zinc sulfate and aniline were taken in the 2θ range 0−100°.

Results and Discussion

Irregular polymer aggregates were produced at different times of polymerization of pyrrole in the following systems: (A) pyrrole-4-TSS-acetonitrile, (B) pyrrole-4-TSS-$ZnSO_4$-acetonitrile, and (C) pyrrole-4-TSS-aniline-acetonitrile. Results are shown in Figure 1. As the time of polymerization was increased, a sharp transition in the morphology from compact to fractal was observed even in a short duration of 10 min. Such a transition may be explained on the basis of the Mullins−Sekerka theory of instability.[20] Fractal dimension ranges between 1.75 and 1.96. Results show that the fractal dimension first increases and then decreases. Aggregates at various concentrations of 4-TSS, pyrrole, and different field intensities are shown in Figure 2. Growth kinetics of polypyrrole aggregates was investigated by measuring (a) weight of aggregates and (b) length of the petal at different time intervals as explained in the Experimental Section. Weight of the polymer aggregate was measured as a function of time, and other parameters were kept fixed. Growth kinetics was also studied by varying the concentration of 4-TSS and field intensities. In case of system (A), the growth depends linearly on [4-TSS] and weight of polymer increases with increase in field intensity. The kinetics of polymerization was also studied by measuring the length of the petal from the center of the circular envelope as a function of time at different concentrations of 4-TSS and field intensity. At a higher 4-TSS concentration (0.10 M), length of the petal varied linearly with time, obeying the empirical equation $l = mt + c$ where l = length of petal, t = time, and m and c are constants while at low 4-TSS concentrations; the dependence was nonlinear. Growth rate of petals also depends on the field intensity and varies linearly at low field intensity (2.4 V/cm) but nonlinearly at higher field intensities, as shown in Figure 4.

Influence of $ZnSO_4$ and aniline on electropolymerization of pyrrole was studied. XRD data of polymer aggregates with and without $ZnSO_4$ and aniline were compared. Results indicated that on incorporation of $ZnSO_4$ and aniline different products were formed. Fractal dimensions of the aggregates in the

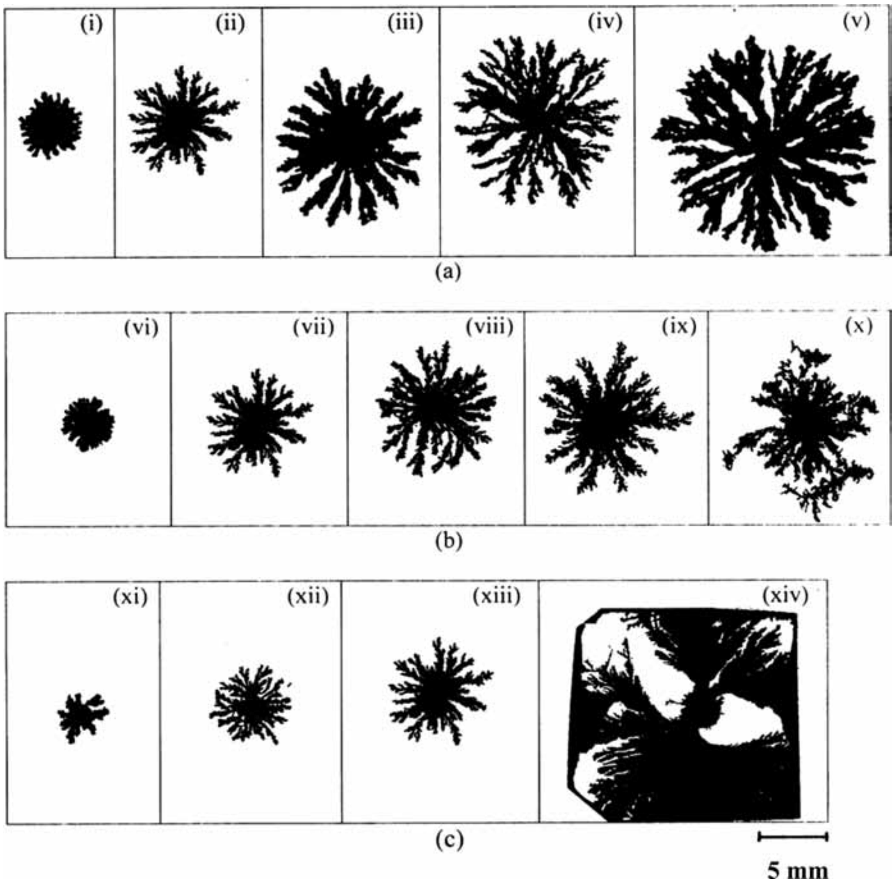


Figure 2. Microphotogrphs obtained during electropolymerization of pyrrole as a function of (a) concentration of oxidizing agent. [4-TSS] = 0.025, 0.05, 0.075, 0.10, and 0.125 M (i−v), [Pyrrole] = 0.10, field intensity = 3.6 V/cm. (b) Concentration of pyrrole. [Pyrrole] = 0.05, 0.10, 0.15, 0.20, and 0.25 M (vi−x), [4-TSS] = 0.05 M, field intensity = 3.6 V/cm. (c) Field intensity. Field intensity = 1.2, 2.4, 3.6, and 4.8 V/cm (xi−xiv), [Pyrrole] = 0.10, [4-TSS] = 0.05 M. Separation between electrodes = 2.5 cm. Duration of electropolymerization was 30 min in each case.

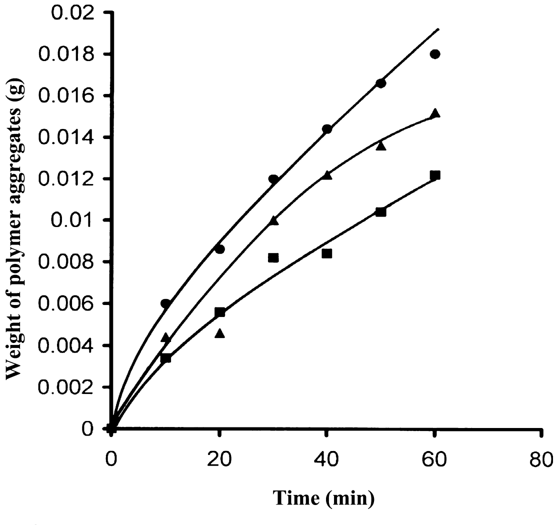


Figure 3. Dependence of weight of electropolymerized aggregates on time in (●) pyrrole-4-TSS-acetonitrile, (▲) pyrrole-4-TSS-ZnSO$_4$-acetonitrile, and (■) pyrrole-4-TSS-aniline-acetonitrile systems. Conditions: [Pyrrole] = 0.10 M, [4-TSS] = 0.05 M, [ZnSO$_4$] = 0.0008 M, [Aniline] = 0.11 M, field intensity = 3.6 V/cm, separation between electrodes = 2.5 cm.

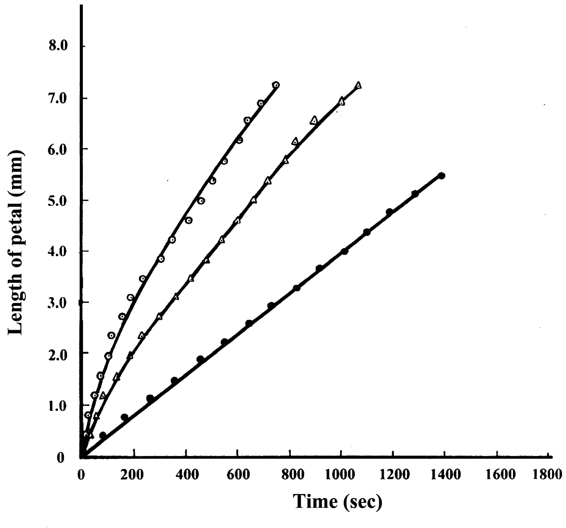


Figure 4. Length of petals of polypyrrole as a function of time at different field intensities: 2.4 V/cm (●), 3.6 V/cm (Δ), and 4.8 V/cm (○), [Pyrrole] = 0.10 M, [4-TSS] = 0.10 M, separation between electrodes = 2.5 cm.

presence of ZnSO$_4$ were collected, and we found that the fractal dimension first decreased and then increased. The trend is reversed as compared to the case when no ZnSO$_4$ was added. Influence of ZnSO$_4$ and aniline on growth kinetics was also studied. Results are shown in Figure 3. Results indicate that weight of the polymer aggregates increases with time in a nonlinear manner. In the case of polypyrrole, it increases more rapidly as compared to the case when ZnSO$_4$ and aniline were added in system (A). The addition of ZnSO$_4$ in the medium reduced the growth of polymer aggregate. It may be due to

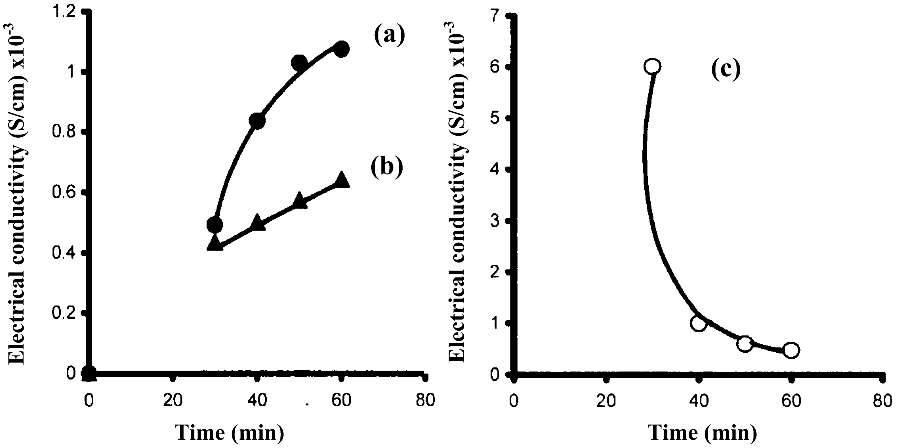
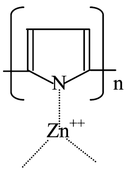


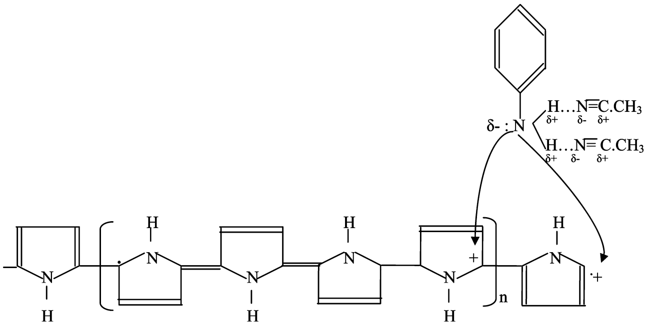
Figure 5. Electrical conductivity of aggregates at different times of electropolymerization of pyrrole in (●) pyrrole-4-TSS-acetonitrile, (▲) pyrrole-4-TSS-$ZnSO_4$-acetonitrile, and (○) pyrrole-4-TSS-aniline-acetonitrile systems. Conditions: [Pyrrole] = 0.10 M, [4-TSS] = 0.05 M, [$ZnSO_4$] = 0.0008 M, [Aniline] = 0.11 M, field intensity = 3.6 V/cm, separation between electrodes = 2.5 cm.

incorporation of Zn^{2+} ions in the polymer network, as shown in structure I, on account of which further aggregation is prevented.



structure I

Influence of aniline on polymerization behavior was studied. Aniline interacts with acetonitrile forming hydrogen bond giving intercomponent complex. Futher, addition of aniline (0.11 M) during the electropolymerization of pyrrole decreased the growth rate because of the availability of a lone pair of electrons on the nitrogen atom of aniline, which nucleophilically attacks the positive charge center of the oxidized polymer and blocks this for further reaction at α position of growing polypyrrole chain as indicated below:



To confirm the above observations, electrical conductivity of the solid polymer was also measured. The values of electrical conductivity of aggregates obtained with and without $ZnSO_4$ and aniline at room temperature for different times of polymerization were noted. In the case of system (A), the electrical conductivity of the polymer was found to increase with time of polymerization (Figure 5, curve a). It may be due to increase in the length of the polymer chain with time. However, on addition of $ZnSO_4$ the conductivity values were decreased (Figure 5, curve b) due to coordination of Zn^{2+} with nitrogen atom of polypyrrole as shown in structure I. Presence of Zn^{2+} in the polymer aggregate was also confirmed by qualitative analysis. Similarly, because of nucleophilic attack of aniline at the positive center, the oxidized polymer forms an intercomponent complex. Because of this bonding, the rate of polymerization and conductivity of polypyrrole in the presence of aniline decreased (Figure 5, curve c).

Potential changes with time during electropolymerization of pyrrole were recorded. Influence of CH_3OH and H_2O on electric potential oscillations was also studied. Results for different systems are shown in Figure 6. Corresponding morphologies are also shown in Figure 6. It was observed that amplitude of oscillation decreases in the following sequence:

pyrrole-4-TSS-acetonitrile >
pyrrole-4-TSS-CH_3OH-acetonitrile >
pyrrole-4-TSS-H_2O-acetonitrile

It is also clear from Figure 6 that amplitude of nonlinear electric oscillation is related to morphology. The higher the amplitude of chaotic oscillation, the lower the fractal dimension of the dendrite. Both solvents interact forming hydrogen bonds and giving an intercomponent complex. The experimental results show that inhibitory effect depends on the nature of the solvent.

It was observed that, during precipitation and dissolution of electrolytes, electric potential is developed depending on the relative mobility of ions.[1a] Hence, precipitation of polyelectrolyte also generates potential, but in view of the random motion of radical cations, irregular electric potential oscillations are observed. Thus, we get different types of chaotic oscillations of different amplitudes as observed in Figure 6. Normally, dendrites are obtained but compact deposits are also obtained when other solvents such as H_2O and CH_3OH are mixed with acetonitrile (Figure 6).

The mechanism of random motion of cation, development of electric potential oscillations, and diffusion-limited growth of dendritic structure of polypyrrole can be understood on the basis of Diaz's mechanism as follows:

Electropolymerization proceeds through successive electrochemical and chemical steps. It includes the oxidation of the monomer to form a radical cation. When current is passed through the system, pyrrole free radical is formed from pyrrole with the release of one electron so that free radical is attracted toward the anode. This promotes the passage of electrical current through the system. This free radical undergoes chain polym-

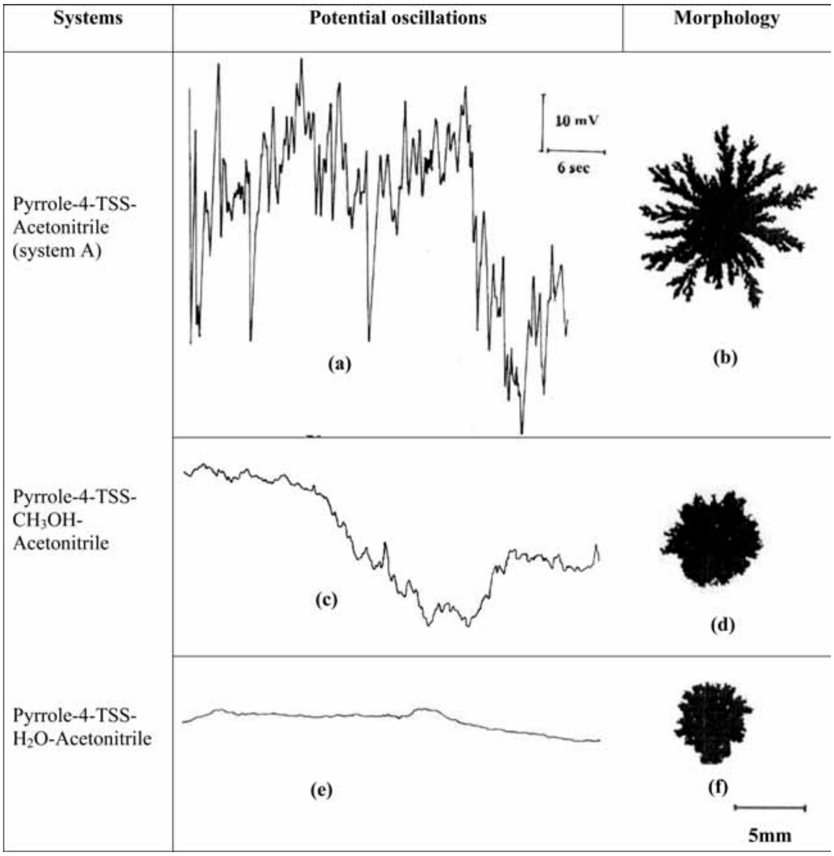
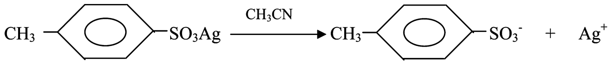


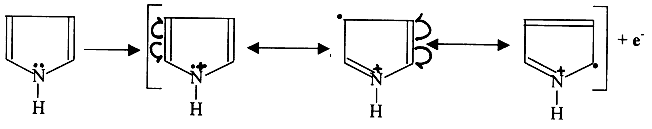
Figure 6. Anode potential changes with time during electropolymerization of pyrrole and their growth morphologies in pyrrole-4-TSS-acetonitrile (a, b), pyrrole-4-TSS-acetonitrile + 2% methanol (c, d), and pyrrole-4-TSS-acetonitrile + 2% water (e, f). Conditions: [Pyrrole] = 0.10 M, [4-TSS] = 0.10 M, field intensity = 2.4 v/cm, separation between electrodes = 2.5 cm.

erization followed by deposit of the polymer on anode and decrease in potential. When pyrrole cation is in excess, electrical potential would increase. On the other hand, when these are polymerized, the effective concentration of pyrrole ions decreased, leading to decrease in potential. When enough pyrrole ions get accumulated, the cycle is repeated again and again but in a nonperiodic manner. Thus, chaotic oscillations are observed. The structure would be more and more disordered (fractal dimension would be more) as [4-TSS] increases. One can note that greater regularity in periodicity is related with magnitude of fractal dimension.

Detailed steps of the mechanism can be formulated as follows:

In the first step, oxidation of monomers takes place at the surface of the electrode to form the cation radical. The cation radical thus obtained is further stabilized by resonance as shown below:



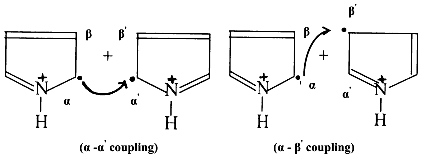


The electron thus released is associated with the Ag^+ (from 4-TSS) at the cathode:

$$Ag^+ + e^- \rightarrow Ag \text{ (deposited at cathode)}$$

The next step involves (i) radical cation−radical cation coupling, (ii) radical cation−monomer coupling, and (iii) chain propagation via oxidation of the extending polymer.[21]

It may be noted that, when the radical cation−radical cation coupling takes place, α, α′, β, and β' positions are available for coupling.



In addition to α−α′, linkage in the polypyrrole, some α−β', linkage can also take place. This can lead to greater random motion of cation radical, leading to complex fractal growth and dendritic structure. This can also lead to formation of hemispherical cusps, which can facilitate complex fractal growth and dendritic structure. Dendritic tip with a high radius of curvature is more efficient than in the linear case before a plane electrode.[22]

The above mechanism clearly shows that fractal growth (dendritic structure) and nonperiodic oscillations are closely related.

Conclusions

Since polypyrrole is a conducting polymer and chain polymerization involves random movement of radical cations, aperiodic (chaotic) electric potential oscillations are observed during polymerization. Fractal aggregates and dendritic structures are formed because of random motion of radical cations involving complex (tree type) structure due to chain branching. Fractal growth depends on several factors, such as time, [4-TSS], [pyrrole], and field intensity. Fractal growth kinetics, which provide a quantitative picture of growth mechanism, was studied.

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References and Notes

(1) (a) Rastogi, R. P. *Introduction to Non-equilibrium Physical Chemistry: Towards Complexity and Non-linear Science*; Elsevier: Amsterdam, 2008; Chapter 6, p 91; (b) Chapter 12, p 217;(c) Chapter 13, p 235. (d) Rastogi, R. P.; Das, I; Pushkarna, A.; Sharma, A.; Jaiswal, K.; Chand, S. *J. Chem. Educ.* **1992**, *69* (2), A47.

(2) McCoy, B. J. *J. Colloid Interface Sci.* **1999**, *216*, 235.

(3) Chen, A. M.; Santhakumaran, L. M.; Nair, S. K.; Amenta, P. S.; Thomas, T.; He, H.; Thomas, T. J. *Nanotechnology* **2006**, *17*, 5449.

(4) Rastogi, R. P.; Das, I.; Pushkarna, A.; Chand, S. *J. Phys. Chem.* **1993**, *97*, 4871.

(5) Kaufman, J. H.; Melroy, O. R.; Abraham, F. F.; Nazzal, A. I. *Solid State Commun.* **1986**, *60*, 757.

(6) Das, I.; Gupta, S. K.; Lall, R. S. *Indian J. Chem. Technol.* **2005**, *12*, 198.

(7) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1997**, *101*, 774.

(8) (a) Momma, T.; Nishimura, K.; Osaka, T.; Kondo, N.; Nakamura, S. *J. Electrochem. Soc.* **1994**, *141*, 2326. (b) Novak, P.; Muller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207.

(9) Sadik, O. A.; Brenda, S.; Joasil, P.; Lord, J. *J. Chem. Educ.* **1999**, *76*, 967.

(10) Alva, S.; Phadke, R. S. *Indian J. Chem.* **1994**, *33A*, 561.

(11) Hyodo, K. *Electrochim. Acta* **1994**, *39*, 265.

(12) Rudge, A.; Raistick, I.; Gottesfeld, S.; Ferraris, J. P. *Electrochim. Acta* **1994**, *39*, 273.

(13) Ehrenbeck, C.; Juttner, K. *Electrochim. Acta* **1996**, *41*, 511.

(14) Rodriguez, J.; Grande, H. J.; Otero, T. F. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 2, Chapter 10.

(15) Li, Y.; Zhang, W.; Li, G.; Ju, Y. *Polymer* **2008**, *49*, 225.

(16) Si, P.; Chi, Q.; Li, Z.; Ulstrup, J.; Moller, P. J.; Mortensen, J. *J. Am. Chem. Soc.* **2007**, *129*, 3888.

(17) Dallas, P.; Niarchos, D.; Vrbanic, D.; Boukos, N.; Pejovnic, S.; Trapalis, C.; Petridis, D. *Polymer* **2007**, *48*, 22007.

(18) Qui, Y. J.; Reynolds, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1315.

(19) Madaeni, S. S. *Indian J. Chem. Technol.* **2006**, *13*, 65.

(20) Mullins, W. M.; Sekerka, R. F. *J. Appl. Phys.* **1963**, *34*, 323.

(21) Genies, E. M.; Bidan, G.; Diaz, A. F. *J. Electroanal. Chem.* **1983**, *149*, 101.

(22) Fukami, K.; Nakanishi, S.; Yamasaki, H.; Tada, T.; Sonodo, K.; Kamikawa, N.; Tsuji, N.; Sakaguchi, H.; Nakato, Y. *J. Phys. Chem. C* **2007**, *111*, 1150.

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