Suppression of Growth Instability in Electropolymerization of Pyrrole

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The pattern formation of electropolymerized polypyrrole was studied in bulk-solution and thin-layer-solution cells with and without a magnetic field. A diffusion-limited aggregation pattern was observed in the bulk-solution cell in the absence of a magnetic field. The growth instability was found to be suppressed by thinning the solution and the application of the magnetic field.

Since the concept of fractal was introduced by Mandelbrot[1] to describe self-similar forms in nature, much attention has been paid to pattern formation of complex geometry in nonequilibrium and irreversible systems. The diffusion-limited-aggregation (DLA) model proposed by Witten and Sander,[2] which is the aggregation of random-walk particles to a 'seed', resulting in a fractal pattern, stimulated scientists to make irregular patterns in laboratories. DLA-like patterns have been found in real physical systems, e.g. electrodeposition,[3] crystal growth,[4] viscous fingers,[5] bacterial colonies,[6] etc. Matsushita et al.[3] observed a DLA-like pattern in zinc electrodeposition and estimated its fractal dimension of $D_f = 1.66$, in good agreement with that of the computer stimulation.[2] The fractal pattern was also found in the diffusion-limited electropolymerization of pyrrole[7] and 3-dodecylthiophene.[8]

The DLA pattern has an irregular structure reflecting the properties of the random-walkers and an open-ramified structure resulting from screening effect, which lets shorter branches stop growing, owing to the growth of the adjacent longer branches. The DLA thereby has large growth instability. It is known that the growth instability is suppressed by anisotropy or surface tension.[4,9] The anisotropy in crystal growth leads to a dendritic pattern, in which side branches regularly develop around a main branch. In the viscous finger, which is the phenomenon occurring when a low-viscosity liquid is forced into a high-viscosity one, the surface tension suppresses tip-splitting.[4,5]

An organic conducting polymer hardly forms a crystal but is liable to form an amorphous film on a plate.[10] The growth of the polymer has no anisotropy and it is affected by the surface tension. Moreover, the polymer forms a DLA-like fractal pattern under certain conditions as mentioned above.[7,8] It is thus considered that the pattern formation in the electropolymerization has both properties of the aggregation phenomenon and the viscous finger. In this paper we report that the growth instability in the pattern forma-

tion of the electropolymerized polypyrrole (PPy) depends on the solution thickness and a magnetic field. The former is responsible for the surface tension, and the latter induces the oriented polymerization owing to large anisotropy in the diamagnetic susceptibility of the aromatic chain.[11]

Experimental

All chemicals were of guaranteed reagent grade. We used an acetonitrile–water mixed solvent, in which the volume fraction of water is 3 or 5%. The electrolytic solution was a 0.1 M ($M = mol\,dm^{-3}$) pyrrole solution containing 5 mM sodium p-toluenesulfonate. The electrolysis was done with a two-electrode system in two kinds of electrolytic cells as shown in Fig. 1. A bulk-solution cell (Fig. 1(a)) consisted of a Petri dish ($\phi 50$ mm), a cover glass plate, and a flat glass plate placed in the dish. A thin-layer-solution cell (Fig. 1(b)) consisted of two glass plates and a Teflon®-ring sheet as a spacer, the thickness of which is 0.5 or 0.05 mm. The electrodes used here were a carbon rod ($\phi 2$ mm) as an anode and a copper ring (ϕ ca. 45 mm) as a cathode. The electropolymerization was done
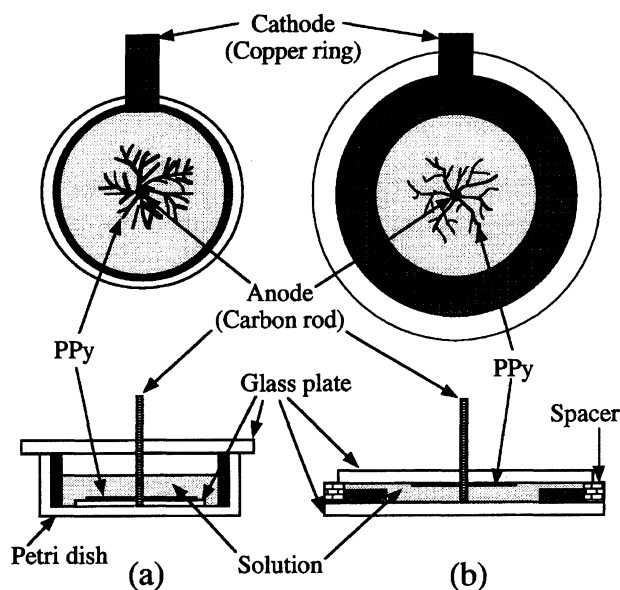

Fig. 1. Schematics of the electrolytic cells; (a) the bulk-solution cell; (b) the thin-layer-solution cell.

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at a constant voltage of 7.0 V generated by a dc voltage generator (Takeda Riken TR6141). Under such a condition a fractal growth pattern of PPy was well observed in the absence of a magnetic field.

A magnetic field was generated by a large-bore (ϕ220 mm) superconducting magnet in the High Field Laboratory of Tohoku University. The electrolytic cell was placed horizontally at the center of the magnet, and the magnetic field was applied perpendicularly to the glass plates (Fig. 2). The temperature within the magnet was controlled at 25±0.1°C using a water-circulating thermoregulator.

The growth pattern was observed using a CCD camera and recorded on a videotape. The image data were transferred to a personal computer and digitized. A fractal dimension D_f was estimated by the box-counting method[12] as follows: the pattern was covered by a square lattice with its size r, and the number of the squares including a part of the pattern $N(r)$ was counted. If the pattern is self-similar, namely fractal, $N(r)$ and r have the relation of

$$N(r) \propto r^{-D_f}.$$

The fractal dimension is evaluated from the log–log plot of $N(r)$ vs. r.

Results

Pyrrole is oxidized to form conducting PPy.[13] Under the condition of diffusion-limited polymerization PPy grows into a random fractal pattern in the two-dimensional space.[7,8] Figure 3 shows the growth pattern of PPy in the solutions (acetonitrile–water (3%) solvent) with thicknesses of (a) 9 mm, (b) 0.5 mm, and (c) 0.05 mm. In the bulk cell PPy grows along the upper surface of the glass plate at the bottom of the solution, while in the thin-layer cell it grows along the bottom surface of the upper glass plate. The growth morphology in the bulk solution (Fig. 3(a)) shows a DLA-like pattern which has large instability in the growth interface, resulting in an irregularly ramified structure. In the thin-layer cell the instability in the growth pattern gets reduced with thinning of the solution (Figs. 3(b) and 3(c)), and a tip-splitting pattern appears at 0.05 mm. Figure 4 shows the log–log plot of $N(r)$
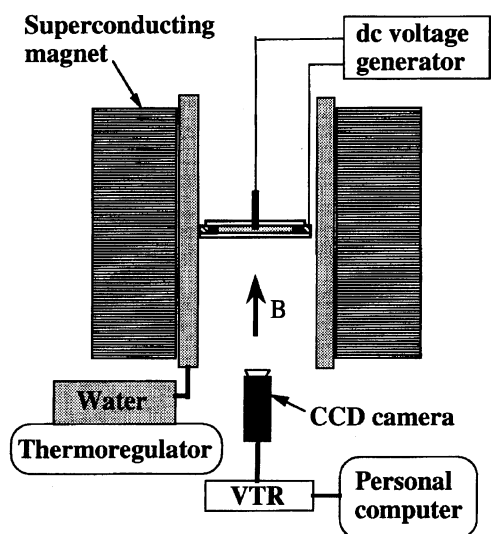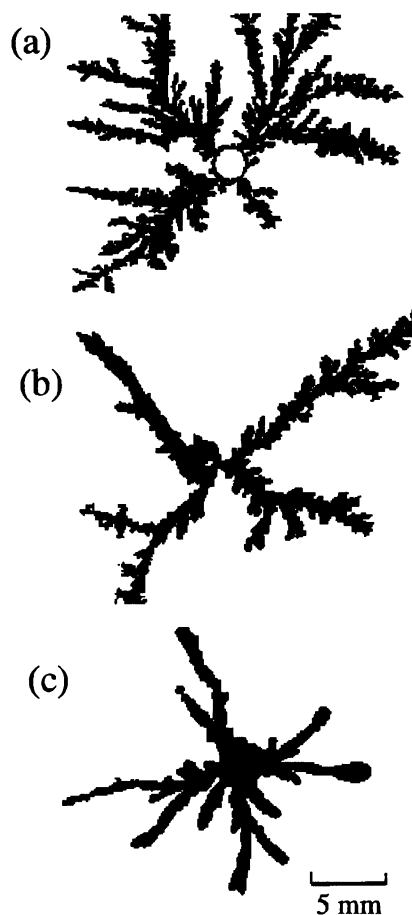

Fig. 3. Growth patterns of polypyrrole in (a) the bulk-solution cell with the thickness of 9 mm, (b) the thin-layer-solution cell with the thickness of 0.5 mm and (c) the thin-layer-solution cell with the thickness of 0.05 mm. The electrolytic solution is 0.1 M pyrrole in acetonitrile–water (3%) containing 5 mM sodium p-toluenesulfonate.

vs. r in the box-counting method for the pattern of Fig. 3(a), and the fractal dimension is estimated to be 1.63, in good agreement with that of the computer simulation of the DLA model.[2] The fractal dimension decreases with decreasing solution thickness (Table 1).

The magnetic field brings about drastic changes in the growth morphology. Figure 5 shows the growth patterns with and without magnetic field of 0.5 T in the thin-layer-solution cell (0.5 mm) with the mixed solvent of the water volume fraction of 3% (Fig. 5(a) and Fig. 5(b)) and 5% (Fig. 5(c) and Fig. 5(d)). In the case of the 3% H_2O solvent the growth pattern becomes dense and slightly spiraled in 0.5 T (Fig. 5(b)), while in the case of the 5% H_2O solvent the pattern becomes closed in 0.5 T and no fluctuation appears at the growth front (Fig. 5(d)). Figure 6(a) and Fig. 6(b) represent micrographs of the growth tips of the patterns of Fig. 5(c) and Fig. 5(d), respectively. While no clear microstructure except a needle-like main branch is seen at 0 T, the micrograph at 0.5 T has an aggregate of needle branches, most of which develop radially. This result suggests that the magnetic field causes the oriented polymerization of pyrrole.
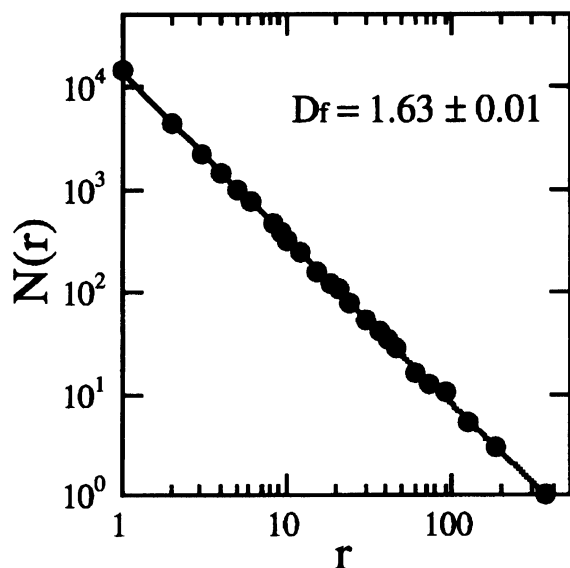

Fig. 2. Schematics of the experimental setup to observe the growth pattern of polypyrrole in magnetic fields B.

Fig. 4. Log–log plots of $N(r)$ vs. r for the estimation of the fractal dimension D_f of the growth pattern by means of the box-counting method.

Table 1. Dependence of the Fractal Dimension D_f on the Solution Thickness

Solution thickness / mm	D_f
9	1.63
0.5	1.52
0.05	1.47

Discussion

Highly ramified fractal patterns appear in some systems obeying Laplace equation, $\nabla^2\mu=0$, where μ is a growth probability field.[14] Electrodeposition of metals[3] and crystal growth[4] generate irregularly ramified patterns with large fluctuations of the growth front under diffusion-controlled conditions, which resemble the fractals produced by the DLA-model simulation.[2] In the case of the crystal growth, interface kinetics, anisotropy, and surface tension suppress the growth instability, thereby changing the growth morphology into a regularly ramified dendrite in both diffusion- and kinetic-controlled process or a single crystal in the kinetic-controlled process.[15,16] On the other hand, the viscous finger is regarded as a system described by the Laplace equation,[5] though it is not an aggregation system. It has been found that the DLA-like fingers changes into the tip-splitting pattern with increasing surface tension or a closed circular pattern at the highest limit of the surface tension if there is no anisotropy.[4]

PPy hardly forms a crystal but becomes amorphous,[10] and the electrodeposition of PPy is thus regarded as an aggregation process without the crystal anisotropy. The DLA-like growth pattern with $D_f=1.63$ in the bulk solution indicates that the growth process is diffusion-controlled (see Fig. 3(a)). Thinning the solution induces interfacial growth between the solution and the glass plate. The surface tension is probably
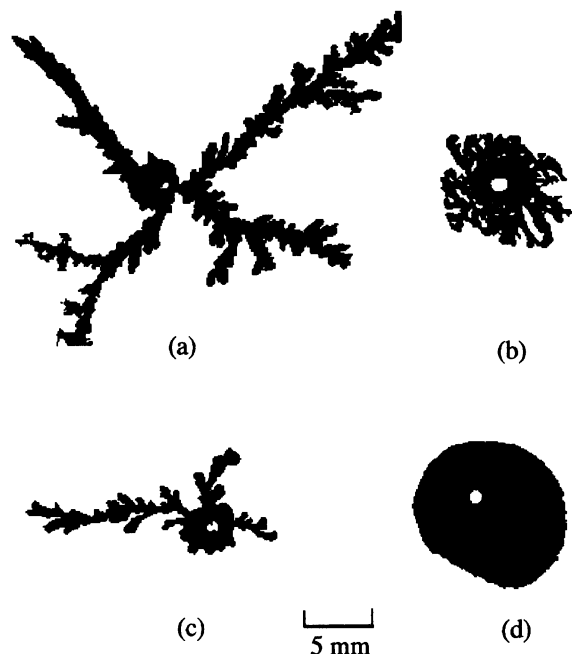

Fig. 5. Magnetic field effects on the growth pattern of polypyrrole in the thin-layer-solution cell with the thickness of 0.5 mm. The electrolytic solution in 0.1 M pyrrole in acetonitrile–water (3 or 5%) containing 5 mM sodium p-toluenesulfonate. (a) H_2O-3%, B=0 T, (b) H_2O-3%, B=0.5 T, (c) H_2O-5%, B=0 T and (d) H_2O-5%, B=0.5 T.

increased in the interfacial growth, leading to the tip-splitting pattern (see Fig. 3(c)) that appears in the diffusion-controlled growth perturbed by surface tension.

The magnetic field has two effects on the electropolymerization; the magnetohydrodynamic (MHD) effect[17,18] and the diamagnetic orientation of the polymers.[11] In these experiments the MHD effect causes a convection around the anode during the electrolysis. Such a convection increases the arrival probability of pyrrole on the upstream side, leading to the spiral growth. The convection moreover makes the diffusion layer thinner, leading to the dense growth pattern. The dense and spiral pattern in Fig. 5(b) is hence considered to reflect the MHD effect. On the other hand, PPy has a linear chain structure including aromatic rings of pyrrole, which have a large diamagnetic susceptibility perpendicular to the aromatic plane because of the diamagnetic ring current. PPy is thereby subject to diamagnetic orientation in which the aromatic rings lie parallel to the magnetic field. The oriented polymerization induces the surface kinetic process, and the growth process becomes kinetic-controlled. The kinetic-controlled growth in the absence of anisotropy generates the closed circular pattern without fluctuation at the growth front. Thus, the growth pattern in Fig. 5(d) results from the kinetic-controlled growth owing to the oriented polymerization.

Here an intriguing question has been raised as to why the magnetic field effect on the growth pattern depends on the volume fraction of water. The MHD effect is dominant in the 3% H_2O–solvent, while the effect of diamagnetic orientation is dominant in the 5% H_2O–solvent. It is speculated
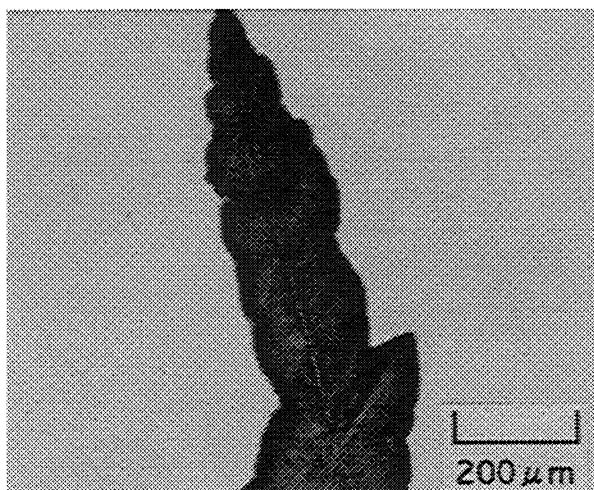
(a) 0 T

(b) 0.5 T

Fig. 6.   Micrographs of the growth tips of polypyrrole elec-
tropolymerized in (a) 0 T (Fig. 5 (c)) and (b) 0.5 T (Fig. 5
(d)).

that which effect is dominant is related to the viscosity of
the mixed solvent. The MHD effect becomes dominant in
the lower viscosity solvent, while the diamagnetic effect be-
comes dominant in the higher viscosity one. The complete
answer to this question is a future subject.

References

1)   B. B. Mandelbrot, "The Fractal Geometry of Nature,"
Freeman, San Francisco (1982).
2)   T. A. Witten and L. M. Sander, *Phys. Rev. Lett.*, **47**, 1400
(1981).
3)   M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo, and Y.
Sawada, *Phys. Rev. Lett.*, **53**, 286 (1984).
4)   E. Ben-Jacob and P. Garik, *Nature*, **343**, 523 (1990).
5)   G. Daccord, J. Nittmann, and H. E. Stanley, *Phys. Rev. Lett.*,
56, 336 (1986).
6)   H. Fujikawa and M. Matsushita, *J. Phys. Soc. Jpn.*, **58**, 3875
(1989).
7)   J. H. Kaufman, C. K. Baker, A. I. Nazzal, M. Flickner, O.
R. Melroy, and A. Kapitulnik, *Phys. Rev. Lett.*, **56**, 1932 (1986).
8)   M. Fujii and K. Yoshino, *Jpn. J. Appl. Phys.*, **27**, L457
(1988).
9)   J. Nittmann and H. E. Stanley, *Nature*, **321**, 663 (1986).
10)   G. R. Mitchell, F. J. Davis, and C. H. Legge, *Synth. Met.*,
26, 247 (1988).
11)   G. Maret and K. Dransfeld, "Strong and Ultrastrong
Magnetic Fields and Their Applications," ed by F. Herlach,
Springer-Verlag, Berlin and Heidelberg (1985), p. 143.
12)   T. Vicsek, "Fractal Growth Phenomena," World Scientific,
Singapore (1989).
13)   R. A. Bull, F. F. Fan, and A. J. Bard, *J. Electrochem. Soc.*,
129, 1009 (1982).
14)   L. Niemeyer, L. Pietronero, and H. J. Wiesmann, *Phys. Rev.
Lett.*, **52**, 1033 (1984).
15)   Y. Saito and T. Ueta, *Phys. Rev. A*, **40**, 3408 (1989).
16)   J. M. García-Ruiz and F. Otálora, *Physica A*, **178**, 415
(1991).
17)   R. Aogaki, K. Fueki, and T. Mukaibo, *Denki Kagaku*, **43**,
504 (1975).
18)   I. Mogi, M. Kamiko, and S. Okubo, *Physica B*, **211**, 319
(1995).