

Electrochemical growth of poly(3-dodecylthiophene) and its interpretation as a fractal

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 6109

(<http://iopscience.iop.org/0953-8984/2/28/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.103

The article was downloaded on 11/05/2010 at 06:01

Please note that [terms and conditions apply](#).

Electrochemical growth of poly(3-dodecylthiophene) and its interpretation as a fractal

Masaharu Fujii[†], Kiyomitsu Arai[†] and Katsumi Yoshino[‡]

[†] Department of Electrical Engineering, Faculty of Engineering, Ehime University, Bunkyo 3, Matsuyama, Ehime 790, Japan

[‡] Department of Electronic Engineering, Faculty of Engineering, Osaka University, Yamada-Oka 2-1, Suita, Osaka 565, Japan

Received 18 September 1989, in final form 11 April 1990

Abstract. Poly(3-dodecylthiophene) with a fractal pattern has been prepared by an electrochemical method on the surface of a solution. The fractal dimension has been calculated by four methods. At an applied voltage of about 10 V, the fractal dimension indicates a maximum value of 1.79. The growth rate in the radial direction has a maximum value at about 7.5 V and the conductivity in the iodine doped state is a maximum for the sample prepared at a voltage of about 15 V in accordance with the voltage dependence of fractal dimension. Although the conducting polymer is usually doped by the counter-ion, BF_4^- , in polymerisation an undoped region has been observed in the branches of the conducting polymer at high voltage. The time dependence of the fractal dimension has been calculated and the rise time has been found to depend on the applied voltage. By short circuiting the electrode after the polymerisation, the undoped region in the branch has proceeded concentrically from the tip of the growth to the needle electrode.

1. Introduction

Conducting polymers with highly extended conjugated molecular structure have attracted much interest from both fundamental and practical viewpoints, since they demonstrate various interesting properties [1, 2]. Many new conducting polymers have been synthesised and various types of applications of conducting polymers have also been proposed [3, 4].

The electrochemical polymerisation method has been proved to be a useful one for preparing uniform and flexible conducting polymer films which are easily doped and undoped electrochemically. The characteristics of these conducting polymers are influenced by the polymerisation conditions which depend on the kind of conducting polymer [5, 6].

Recently, poly(3-alkylthiophene) has been reported to be soluble in some solvents [7–9] and to be fusible at relatively low temperatures [10, 11]. When poly(3-alkylthiophene) was electrochemically prepared in certain conditions with the parallel electrode configuration, it grew on the anode as a film and at the same time, different, tree-like conducting polymer grew from the edge of the anode to the cathode. This pattern was similar to that of electrical tree deterioration in an insulating polymer. We, therefore,

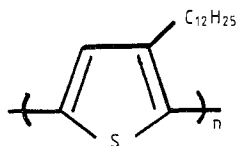


Figure 1. The molecular structure of poly(3-dodecylthiophene).

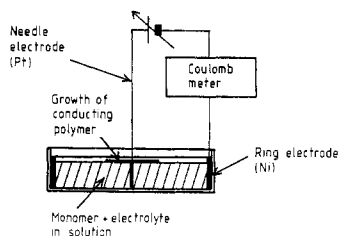


Figure 2. Experimental configuration

investigated this polymerisation process with point-to-circle electrode configurations. The pattern obtained is the same as that of a Lichtenberg figure [12], an electrodeposited zinc metal leaf [13–15], a viscous finger [16], or a diffusion-limited aggregation (DLA) of particles [17] all of which are characterised by a fractal dimension. Therefore, these growing patterns in the polymerisation process are analysed by fractal geometry [18]. A conducting polymer is synthesised from two components under some potential. One is a neutral monomer and the other is an anion. The analysis method applied to zinc and copper depositions [19–22], therefore, apparently cannot be simply applied to conducting polymers. The patterns found in conducting polymers in the present work are described as fractal.

In this paper, we report the growth process and physical properties of poly(3-dodecylthiophene), and discuss the growth mechanism using the analysis of the fractal dimension calculated by several methods.

2. Experimental details

Poly(3-dodecylthiophene) shown in figure 1 was prepared in an electrolyte solution (0.2M LiBF₄ in benzonitrile with 0.1 M 3-dodecylthiophene) under argon atmosphere. The experimental configuration is shown in figure 2. A platinum needle (0.5 mm in diameter) and a nickel ring (7 cm in diameter, height 1 cm, thickness 0.2 mm) were set concentrically in a cell as the anode and cathode, respectively. Electrolyte solution was poured into the cell to a depth of about 3 mm. Total charges for the synthesis were measured with a Coulomb meter (Hokuto denko, HF-201). The conductivities of the iodine-doped polymers were also measured by the four-probe technique. The conducting polymer prepared was then put in a vacuum. The doping was carried out by exposing the sample in vacuum to I₂ vapour until an equilibrium state was established. Though the iodine content was not determined, all samples were doped under the same conditions. The experiment was observed with a scanning electron microscope (JEOL, JSM-T20).

Several photographs of prepared polymers were taken at successive stages of growth and were digitised with an image scanner. The digitised structures were then transferred onto a computer (NEC PC-9801VM) for analysis to determine the fractal dimension and were displayed on the CRT. The fractal dimensions were computed using four methods [23, 24].

(i) Cover method. The figure is covered with a number of squares with side r in units of one pixel. In order to obtain the least number of squares, $N(r)$, the origin of the

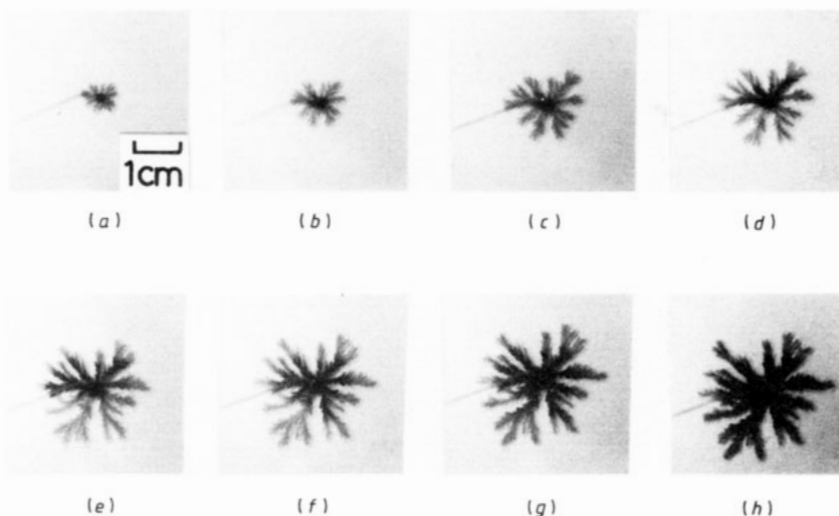


Figure 3. Growing process of poly(3-dodecylthiophene) at 15 V. Time and total charge; (a) 1 min 10 s, 0.033 C; (b) 2 min 00 s, 0.063 C; (c) 3 min 00 s, 0.111 C; (d) 3 min 40 s, 0.157 C; (e) 5 min 02 s, 0.220 C; (f) 6 min 00 s, 0.255 C; (g) 8 min 00 s, 0.300 C; and (h) 11 min 00 s, 0.353 C.

coordinates is shifted up and down, and right and left every one fifth pixels of the side and 25 times in all. A double logarithmic plot of $N(r)$ versus r has slope $-D$ in a fractal figure and D is called the fractal dimension.

(ii) Density–density correlation function method. This correlation function, $C(r)$, is computed using the density function which corresponds to the pixels in the range occupied by the figure on the CRT, where r is the distance measured in pixel units. When this correlation function obeys a power law, $C(r) \sim r^{-A}$, the fractal dimension is obtained from the relation, $D = d - A$, where d is the Euclidean dimension and A is the absolute value of the slope.

(iii) Radius of gyration (Hausdorff method using a circle box). The number of pixels of the figure, $N(r)$, is counted and the radius of the figure, r , is measured at each stage. In the fractal figure the relation, $N(r) \sim r^D$, is valid.

(iv) Charge during the polymerisation. The total polymerisation charge, $Q(t)$, is proportional to the polymer mass. If the thickness of the structure is constant, then the fractal dimension is obtained from the relation, $Q(t) \sim t^D$, where t is time.

In addition, the average of the branch angles was measured.

3. Results and discussion

Figure 3 shows the growth process of poly(3-dodecylthiophene). The polymer floated on the surface of the solution and grew to the counter electrode with branching. At first, the conducting polymer started to grow on the surface of the needle electrode. At the same time, polymer sheets grew, spread and branched out on the surface of the solution. We have previously reported that a tree-like polymerisation pattern was also observed in polypyrrole [25], however, in the case of polypyrrole, it grew in the solution or along

the bottom of the cell contrary to poly(3-dodecylthiophene). The difference of the growth pattern and of the position where the conducting polymer was formed depend not only on the chemical reaction process but also on physical properties such as specific weights of the monomer, polymer, electrolyte and solvent etc. The concentration of monomer and electrolyte also influence the growing pattern.

Although the mechanism of electrochemical polymerisation is not clarified in detail, the dynamics of the polymeric growth is explained as follows. In the initial stage of polymerisation, an electron is removed from the 3-dodecylthiophene monomer to the electrode. The resultant radical cation encounters another radical monomer or oligomer, and then loses two alpha hydrogens. This process is repeated. At the same time, the poly(3-dodecylthiophene) chains are oxidised by the counterion, BF_4^- , which acts as a dopant. The polymer, therefore, has a good conductivity and acts as a new electrode. The polymerisation reaction may depend on the rate of diffusion of monomer and counter-ion to the region of the electrode, the electrical potential at the tip of the grown conducting polymer, and the conductivity of the polymer etc.

The patterns formed on the surface depended on the applied voltage. It should be noted that at higher applied voltage, the colour of the polymer branches changed from blue to brown in the growth process (black regions in figure 3(c)–(h)). The blue conducting polymer is in the doped state during the polymerisation reaction. This colour change suggests that undoping has occurred in some branches. Although the undoped state is a higher insulating state, the growth of polymer does not stop. In general, to continue electrochemical polymerisation, the front of the polymer must be kept at a certain voltage. Details of this phenomenon are currently being studied.

Fractal dimensions of these figures were calculated using four methods. Figures 4(a)–(d) show double logarithmic plots at an applied voltage of 15 V; (a) cover method: the number of squares to cover the pattern, $N(r)$ versus the length of the side, r ; (b) density–density correlation function method: density–density correlation function, $C(r)$, versus distance, r ; (c) Hausdorff method: the number of pixels of the pattern, $N(r)$, in a circle with radius, r , and (d) charge during the polymerisation: total polymerisation charge, $Q(r)$, versus time. It should be noted that each characteristic obeys a power law. The pattern, therefore, has fractal structure. The growth patterns for other applied voltages are also found to be fractal. However the calculated fractal dimension is found to depend on the applied voltage. Figure 5 indicates voltage dependences of the fractal dimension evaluated by various methods. The fractal dimension evaluated by (i) the density–density correlation function method gives a value of 1.80 ± 0.01 for an applied voltage of 10–15 V. On the other hand, that by (ii) the cover method is 1.69 ± 0.01 . The maximum difference in the dimension by these two methods is 0.11 at 15 V, but the difference in dimension between methods (i) and (ii) is within about 0.1 over 5–15 V. Therefore, in this study the fractal dimension is defined by the average of dimensions obtained by methods (i) and (ii). Although the number of photographs is not enough to evaluate fractal dimension by the Hausdorff method, a Hausdorff plot yields a straight line as shown in figure 4(c). However, the observed voltage dependence of the dimension obtained by the Hausdorff method is a little different from that obtained by the other three methods as evident in figure 5. Although the Hausdorff fractal dimension has the highest value at 15 V, the difference in the dimensions might be within the error of the calculation because of the limited number of data.

We plotted the total charge against time in figure 4(d). The total polymerisation charge is proportional to the polymer mass. Since the total charge during polymerisation also obeys a power law, one can calculate the fractal dimension (method (iv)). However,

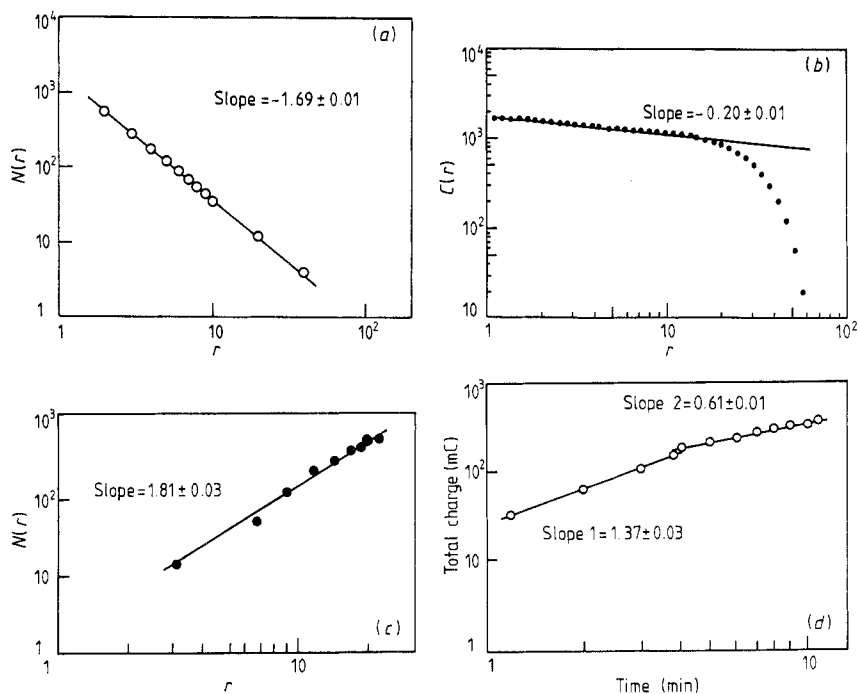


Figure 4. Determination of the fractal dimension; (a) cover method; (b) density–density correlation method; (c) Hausdorff method, and (d) charge during the polymerisation. $22.5 \text{ pixel cm}^{-1}$. Maximum radius of pattern at 15 V is 1.8 cm.

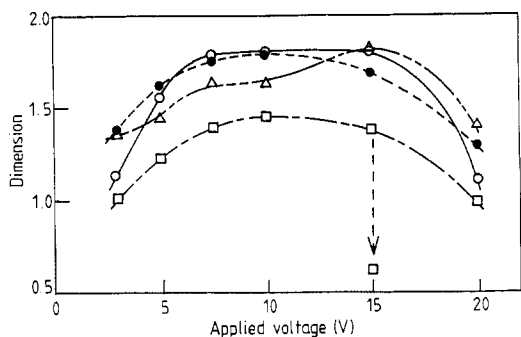


Figure 5. Dependence of the fractal dimension on the applied voltage; cover method (●); density–density correlation method (○); Hausdorff method (△), and total charge (□). Maximum radius of pattern at various voltages; (i) 1.2 cm, 3 V, (ii) 2.5 cm, 5 V, (iii) 1.9 cm, 7.5 V, (iv) 2.3 cm, 10 V, (v) 1.8 cm, 15 V, and (vi) 1.1 cm, 20 V.

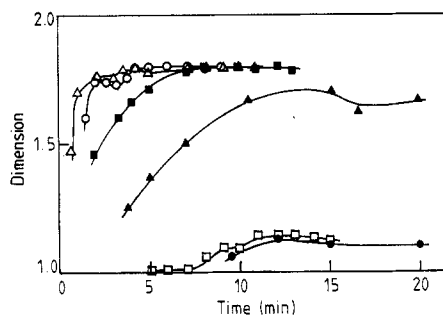


Figure 6. The time dependence of the fractal dimension. Applied voltage 3 V (●), 5 V (▲), 7.5 V (■), 10 V (○), 15 V (△), and 20 V (□).

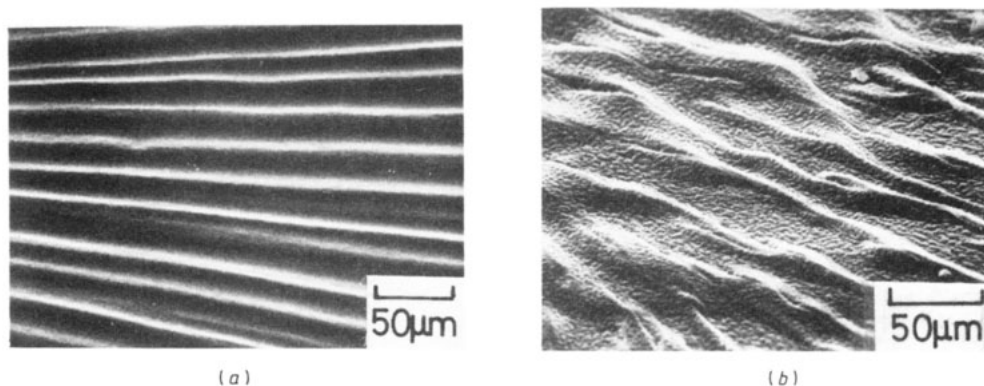


Figure 7. SEM photographs of the branch of poly(3-dodecylthiophene) at applied voltage (a) 3 V, and (b) 7.5 V.

two straight lines were necessary to fit the experimental data at 15 V as shown in figure 4(d). The first slope (1.37 ± 0.03) was taken to calculate the dimension since the undoped state appeared at about 5 min. The obtained values are about 0.4 less than the fractal dimensions obtained using the above methods. If the irregularity of polymer surfaces (as shown in figure 7) [24] and the oligomers prior to aggregation were taken into consideration, then the dimension can be evaluated to have a larger value, closer to the value obtained by the other methods. The second slope is straight in spite of the undoped state. The dimension from this line, slope = 0.61 ± 0.01 , is also plotted in figure 5. It should be noted that this voltage dependence of the dimension calculated from charges corresponds to that from the radial growth rate in figure 9, although the reason for the linearity of the second curve cannot be explained at this stage.

The voltage dependence of the fractal dimension calculated by the various methods show the same tendencies, indicating a peak value at 10–15 V. Since the conditions of the polymerisation reaction change with applied voltage, the shape of the conducting polymer changes with applied voltage so that its fractal dimension changes. In this experiment, the fractal dimension increases with increasing applied voltage and has a maximum value at about 10 V as shown in figure 5. At smaller voltages, only some part of the conducting polymer will satisfy the conditions for polymerisation, and current flows into those growth points since the potential is highest in this vicinity. Increasing the applied voltage, the number of growth points increases and the fractal dimension rises. At some voltage, polymerisation could occur at any place where monomers and counter-ions meet. This condition is similar to that of the DLA model [17]. Since migration or drifting together by diffusion becomes a dominant factor for polymerisation and the potential of the tips deviates from the optimum value [5, 6] at higher voltages, the fractal dimension changes. However, it should be noted that similar values of the fractal dimension as a function of applied voltage were obtained in zinc electrodeposition by Kahanda *et al* [14, 15].

Figure 8 shows the dependence of the branch width and the average of the branch angles on the applied voltage. The grown pattern has many small branches. However, the widths of the branches that grew from the central needle electrode to the tips of the pattern were nearly constant. Therefore, the width of these branches was measured as the branch width. When the applied voltage increased, the branch width decreased and

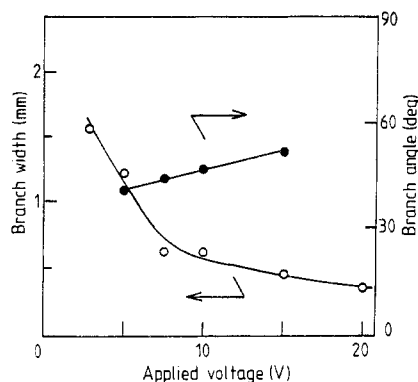


Figure 8. The applied voltage dependence of the branch width and the average of branch angles.

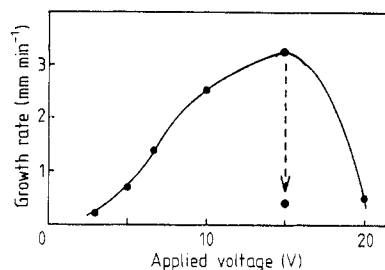


Figure 9. The applied voltage dependence of growth rate of a branch of poly(3-dodecylthiophene).

the average branch angles increased, although the former should be a constant according to the DLA model. It should be mentioned that the branch could be developed in all directions with increasing applied voltage so that a complicated figure might be formed. However, some instabilities such as the Mullins–Sekerka theory [26, 27] must be taken into consideration to understand the branching problem.

Figure 9 shows the dependence of the growth rate in a radial direction on the applied voltage. The radial velocity of the tip of the conducting polymer furthest from the needle electrode is measured as the growth rate. The velocity is nearly constant up to half of the cell radius. The growth rate increases with increasing applied voltage and reaches the maximum value of 3.2 mm min^{-1} at 15 V. However, it should be noted that, at about 5 min after polymerisation was started, the colour changed suddenly in some parts of the branches as shown in figure 3, and then the growth rate began to decrease as shown by a dashed line in figure 9. The change in the growth rate corresponds to that of the dimension calculated by the polymerisation charge in figure 5 (the second slope in figure 4(d)). Above 15 V the colour of the solution changed to yellow near the anode, so that the growth rate decreased. In this region, the applied voltage deviated from the optimum value of polymerisation. It was thought that another chemical reaction might have occurred. The analysis of the yellow solution is now under way. It should be noted that the average branch angle was $46 \pm 5 \text{ deg}$, which coincides with the value computed from the DLA model [28]. This means that the experimental conditions in this study are similar to those of the DLA model.

Figure 6 shows the time dependence of the fractal dimension calculated by method (ii). The fractal dimension increases with time, tending to saturate. This means that the pattern gradually becomes complicated and at some time branches out while preserving complexity. The rise time of the fractal dimension was dependent on the applied voltage. The rise time was shortened with increasing applied voltage. After indicating the minimum value at 15 V, the rise time became long at 20 V. This suggests that the pattern is formed as follows. In the first step, the linear structure with some branches appears near the anode, and then the figure spreads. After some time, which depends on the applied voltage, the conducting polymer develops along the surface in all directions. The time analysis of the fractal dimension may make it possible to understand the dynamics of the pattern formation. This approach is now being pursued.

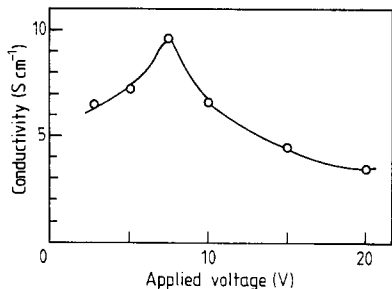


Figure 10. The applied voltage dependence of the conductivity of iodine doped poly(3-dodecylthiophene).

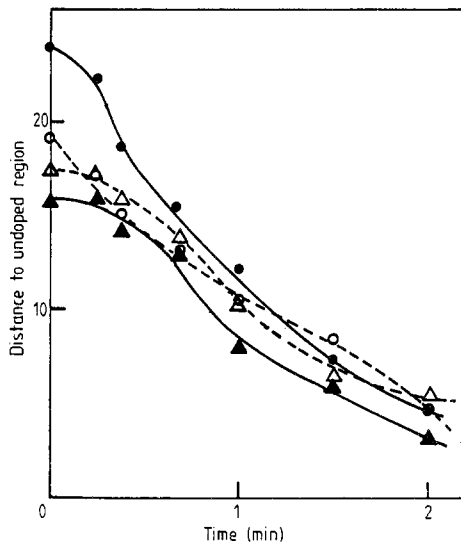


Figure 11. The change of distance from the needle electrode to the undoped region with time in four branches.

Morphological changes as well as the changes of structure mentioned above were also observed. Figure 7 shows the SEM photographs of branches at applied voltages (a) 3 V and (b) 7.5 V. At 3–5 V, the smooth surface of the branch has waves perpendicular to the growth direction (a). At 7.5–15 V, wrinkles are seen (b), and at 20 V the surface becomes smooth but is wrinkled. The differences of surface structure might be influenced by the internal structure (morphology). In particular the conductivity of the conducting polymer in the doped state is influenced by the internal structure [5, 6]. Therefore, the conductivity of the obtained polymer with a characteristic fractal pattern was also measured. Figure 10 shows the applied voltage dependence of conductivity of the iodine-doped polymer. Although BF_4^- acts as dopant in polymerisation, iodine is used as dopant in measuring conductivity. The conductivity increases with increasing applied voltage up to 7.5 V and decreases above 7.5 V. This change in the fractal pattern conductivity corresponds to that observed in the polymer surface. It should be mentioned that the internal structure changes at 7.5 V. The growth of the fractal conducting polymer is dependent on the voltage at the tips. However, the voltage at the tip is determined not only by the applied voltage but also by the conductivity of the branch. Therefore, the growth rate and the fractal dimension are influenced by the conductivity.

Since the thin pattern of the conducting polymer spread from the central needle electrode, the undoping process of the conducting polymer was easily observed. When the electrodes were short-circuited for undoping after the preparation of the conducting polymer at 10 V, the undoping was initiated from the tip of the polymer and proceeded to the needle electrode. Figure 11 shows the change of distance from the needle electrode to the undoped region with time. This indicates that the undoped region proceeds concentrically to the central needle electrode. When the applied voltage source is short-circuited, the discharge of current from the conducting polymer is followed not only in the electrolyte solution but also in the conducting polymer and thus the potential

distribution has the same slope. Therefore, the undoping starts from the tip of the polymer and proceeds to the needle electrode. Since this undoping velocity (about $1.2 \times 10^{-2} \text{ cm s}^{-1}$) is of the same order as that for polythiophene reported previously [29, 30], the diffusion of ions must be a dominant factor in the process.

4. Conclusion

Poly(3-dodecylthiophene) with a fractal pattern has been prepared on the surface of the solution by the electrochemical method with the point-to-circle electrode configuration.

The fractal dimension has been calculated by: (i) the cover method; (ii) the density–density correlation function method; (iii) the Hausdorff method; and (iv) total charge during the polymerisation. The values calculated by methods (i), (ii) and (iii) were nearly the same. However, the value obtained by method (iv) is about 0.4 less than the others. The difference could be attributed to the pattern's irregularity in thickness and the oligomers prior to aggregation.

The fractal dimension against applied voltage has been plotted and the fractal dimension has a maximum value at 10 V. The growth rate and the conductivity of the conducting polymer also have a maximum value at about 7.5 V and 15 V, respectively.

The time dependence of the fractal dimension has been also investigated and the rise time has been found to depend on the applied voltage.

By short-circuiting, undoping was shown to be initiated from the tips of the grown fractal and proceeded concentrically to the needle electrode at a rate of about $1.2 \times 10^{-2} \text{ cm s}^{-1}$.

References

- [1] Su W P, Schrieffer J R and Heeger A J 1979 *Phys. Rev. Lett.* **42** 1698
- [2] Scott J C, Pfluger P, Krounbi M T and Street G B 1983 *Phys. Rev. B* **28** 2140
- [3] Nigrey P J, MacInners D Jr, Nairns D P and MacDiarmid A G 1981 *J. Electrochem. Soc.* **128** 1651
- [4] Kaneto K, Yoshino K and Inuishi Y 1983 *Japan. J. Appl. Phys.* **25** L157
- [5] Satoh M, Kaneto K and Yoshino K 1986 *Synth. Met.* **14** 289
- [6] Satoh M, Yamasaki H, Aoki S and Yoshino K 1987 *Polymer Commun.* **28** 144
- [7] Sato M, Tanaka S and Kaeriyama K 1986 *J. Chem. Soc., Chem. Commun.* 873
- [8] Elsenbaumer D L, Jen K Y and Oboodi R 1986 *Synth. Met.* **15** 169
- [9] Sugimoto R, Takeda S, Gu H B and Yoshino K 1986 *Chem. Express* **1** 635
- [10] Yoshino K, Nakajima S and Sugimoto R 1987 *Japan. J. Appl. Phys.* **26** L1038
- [11] Yoshino K, Nakajima S, Fujii M and Sugimoto R 1987 *Polymer Commun.* **28** 309
- [12] Niemeyer L, Pietrinero L and Wiesmann A J 1984 *Phys. Rev. Lett.* **52** 1033
- [13] Matsushita M, Sano M, Hayakawa Y, Honjo H and Sawada Y 1984 *Phys. Rev. Lett.* **53** 286
- [14] Kahanda G L M K S and Tomkiewicz M 1988 *Phys. Rev. B* **38** 957
- [15] Kahanda G L M K S and Tomkiewicz M 1989 *J. Electrochem. Soc.* **136** 1497
- [16] Nittman J, Daccord G and Stantry H E 1984 *Nature* **314** 141
- [17] Witten, T A Jr and Sander L M 1981 *Phys. Rev. Lett.* **47** 1400
- [18] Mandelbrot B B 1982 *The Fractal Geometry of Nature* (San Francisco: Freeman)
- [19] Sawada Y, Dougherty A and Gollub J P 1986 *Phys. Rev. Lett.* **56** 1260
- [20] Grier D, Ben-Jacob E, Clarke R and Sander L M 1986 *Phys. Rev. Lett.* **56** 1264
- [21] Grier D, Kessler D S and Sander L M 1987 *Phys. Rev. Lett.* **59** 2315
- [22] Garik P, Barkey D, Ben-Jacob E, Bochner E, Broxholm N, Miller B, Orr B and Zamir R 1989 *Phys. Rev. Lett.* **62** 2703
- [23] Nittman J, Daccord G and Stanley H E 1986 *Fractal in Physics* ed Pietronero L and Tosatti E (Amsterdam: North-Holland) p 193

- [24] Villert B and Nechtschein M 1987 *Solid State Commun.* **64** 4
- [25] Fujii M and Yoshino K 1988 *Japan. J. Appl. Phys.* **27** L457
- [26] Mullins W W and Sekerka R F 1963 *J. Appl. Phys.* **34** 323
- [27] Mullins W W and Sekerka R F 1964 *J. Appl. Phys.* **35** 444
- [28] Kaufman J H, Melroy O R, Abraham F F, Nazzari A I and Kapitulnik A 1987 *Synth. Met.* **18** 19
- [29] Kaneto K, Ura S and Yoshino K 1984 *Japan. J. Appl. Phys.* **23** L189
- [30] Kaneto K, Agawa H and Yoshino K 1987 *J. Appl. Phys.* **61** 1197