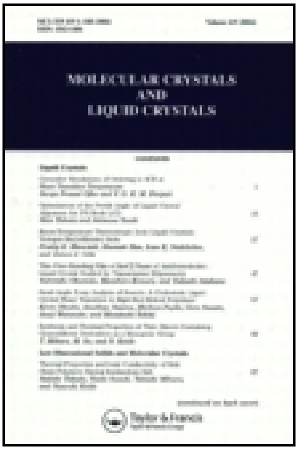

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Specific Conductivity Dependence on Diameter of Submicro-Sized Polythiophene Fibrils

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Specific Conductivity Dependence on Diameter of Submicro-Sized Polythiophene Fibrils

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Deposition mechanism and a diameter dependence of the conductivity of polythiophene derivative fibrils polymerized in pores of a membrane filter having submicrometer-sized pores aperture were discussed. Deposition process of the fibrils was able to be divided in the following three stages from SEM observation and polymerization current measurements. The first stage is the generation of deposition growth nucleus on the pore-inside wall and the filter surface, the second is growth of thickness of a thin-layer-deposit, and the third is the accumulation of a spherical deposit. And, when the pore size became big, the second stage shortened remarkably, and thickness of the thin-layer-deposit became thinner, and the spherical deposition began earlier. From the simulated conductivity of the fibrils with each diameter, at the smaller pore aperture than a specific value, the thickness of the thin-layer-deposit having high-conductivity increases. When the pore aperture becomes smaller, the thin-layer-deposition is remarkably easy to occur.

Keywords: polythiophene; conductive polymer ; electropolymerization; submicrometer-sized polymer fibril; electric conductivity; LEDs

INTRODUCTION

Minute shape processing is an important to make devices with organic electronics materials. If conductive polymer fibrils having a nanometer-sized diameter is formed, it gets possible to make light sources of light emitting diodes (LEDs) very small. Application is anticipated as light sources of scanning near-field optical microscopes (SNOMs) [1] and light source arrays for the high density optical disk. As one method to realize LEDs having minute light source less than a wavelength of the emitting light, 100-nm LEDs making by the fibrils of polythiophene derivatives polymerized in pores of a membrane filter with submicrometer-sized apertures have been attempted to prepared [2]. Already, a diameter dependence[3] of conductivity and deposition mechanism[4] for polymer fibrils has been examined. In that case, polythiophene has to be polymerized only in pores of a membrane filter, and it is required not to let the filter surface top deposit polymer as the additional surface layer. However, actually, when it is tested, polymer has deposited it on filter surface as soon as deposition to pore-inside wall begins. Deposition mechanism of polymer needs to be understood to form such minute shape. When it is compared in case of film, the conductivity of such minute fibril type polymer is higher remarkably. This is related to growth of the tubes to the fibrils along pore-inside wall. In the fibril surface, orientation of polymer chain increases[3]. Specific correlation may appear between thickness of the layer of orientated polymer and the pore apertures of template. In this studies, to make clear deposition phenomenon of polythiophene to the inside of minute pores. The formation process of polythiophene fibrils in size of sub-micrometer was discussed on the basis of SEM observation and polymerization current profiles. Furthermore, specific effect of the minute pores to formation of the highly conductive fibrils by simulating diameter dependence of conductivity was examined.

EXPERIMENT

Polycarbonate membrane filters (Millipore and Toyo) with thickness 10 mm, pore aperture 0.05-8.0 μm were hot-pressed at 240 degrees on an ITO/ glass electrode. Using an electrochemical analyzer (BAS100B/W), polythiophene fibrils were polymerized from acetonitrile solution of 0.37 M 3-alkylthiophene (methyl-, ethyl-, and butyl-) and 0.1M lithium perchlorate. A platinum plate and an Ag/Ag^+ electrode were used as counter and reference electrodes, respectively, and the polymerization potential was set up as with 1.5V *vs.* Ag/Ag^+. A change by time of polymerization current was measured too. Surface and a section of membrane filters polymerized with the time, between 1 and 900 sec were observed with a field effect scanning electron microscope (FE-SEM; Hitachi S-4100). The conductivity of the fibrils in pores was measured with a two-point technique using crossed two Au wire (0.3 mm) electrodes. Because the the conductivity depended on the pressure that applied on a cross-section of the Au wires, the pressure kept it in a fixed value with 260 kPa. The conductivity was revised at the ratio of total pore area for filter surface area. A change of conductivity by fibril diameters, polymerization time, polymerization potential, and monomer species was considered too. And, the conductivity of the fibrils was also discussed from pore size dependence of thickness of the thin-layer-deposit. As a possible dependence, the followings were assumed. ***A*** : Even if pore size changes, thickness of the thin-layer-deposit doesn't change. ***B*** : As the pore size becomes small, the thickness increases. ***C*** : When the pore size becomes smaller than a specific value, the thickness becomes increase. An approximation calculated conductivity of each fibrils (σ_{Fibil}) by Eq. (1)

$$\sigma_{Fibil} = \sigma_L\{(t_S + t_L)^2 - t_S{}^2\} / (t_S + t_L)^2 + \sigma_S t_S{}^2 / (t_S + t_L)^2 , \qquad (1)$$

where t_L and t_S are thickness of the thin-layer-deposit and the spherical deposit with the conductivities σ_L and σ_S, respectively. Effect of the pore size to the conductivity of the fibrils was considered.

RESULT AND DISCUSSION

Sectional SEM images of filters deposited P3MT with polymerization time of 2, 5, 30, and 40 sec in pores of 1.2 μm in aperture was shown at Fig. 1. With polymerization time of 2 sec, very thin P3MT deposit appeared on an inside wall of pores. At 5 sec, the deposit smoothly grew up in thin-layer. When polymerization time became 20 sec, spherical P3MT deposit appeared in the pores and on the filter surface. Between 40 and 60 sec, P3MT grew up to the more large spherical deposit. Then, the pores were almost filled up at 80 sec. P3MT didn't deposit on the surface of an ITO at the pore bottom, but it began to deposit along the inside wall. It was suggested that the inside wall became a growth site of P3MT just after the polymerization was started. Even at very short polymerization time, the formation of additional surface layer by P3MT was identified on the membrane filter. The deposition to the filter surface showed that growth nucleus is formed there too.

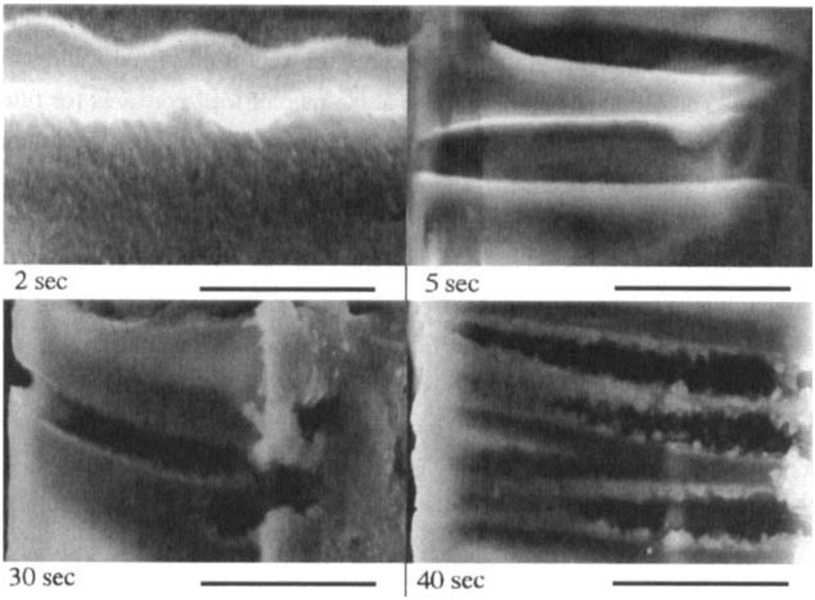

FIGURE 1 SEM images of vertical sections for P3MT-deposited membrane filters with pores of 1.2 μm in aperture. Scale bars indicate 1.0 μm (2 sec) and 5.0 μm (5, 30, and 40 sec).

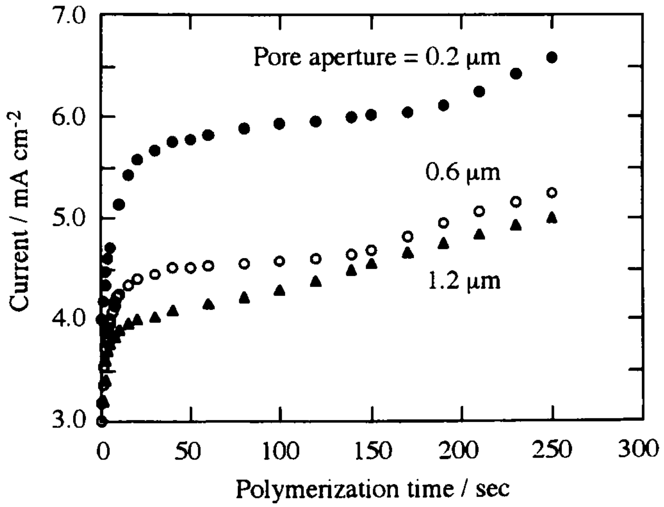

FIGURE 2 Current profiles for polymerization of P3MT in 0.4 and 0.6 μm pores.

Fig. 2 shows current profiles during P3MT-polymerization in the pores of aperture 0.2, 0.6, and 8.0 μm. In 0.2 μm, the current profile was clearly divided into 3 parts; a initial steep rise, a constant current part, and a gradual increasing part. Each part of the current profiles was assigned to the following three stages of the fibril formation on the bases of SEM observations. The first stage is generation of deposition growth nucleus on the pore-inside wall and the filter surface, the second is smooth growth of a thin-layer-deposit, and the third is accumulation of a spherical deposit. When the pore size became big, the second stage shortened remarkably and thickness of the thin-layer-deposit became thinner, and the spherical deposition began earlier. It is important in growth of the thin-layer-deposition that the pore aperture is smaller.

As showed with solid plots in Fig. 3, when the pore size beceme smaller than 0.35 μm, the conductivity of P3MT fibril increased suddenly. This specific size dependence of conductivity suggested that the fibrils consist of a spherical deposition part and a thin-layer-deposition part, and those ratio receives influence by the pore size. Using assumed thickness and conductivities of the thin-layer-deposit as well as the spherical deposition layer, the conductivity of the fibrils with each diameter was simulated and compared with the measured. When the above-mentioned dependences ***A*** and ***B*** were adopted in the simulation, any thickness and conductivity of thin-layer-deposition were impossible to bring calculation values close to the measured. On the other hand, using the dependence ***C***, the calculation value was able to be brought close to the measured. When thickness of the thin-layer-deposit is between 0.007 and 0.025 μm, and its conductivity is 1600 S/cm, the curve that seemed to be shown with Fig. 3 was provided. Accordingly, when the pore size becomes smaller than a specific value, the thickness of the thin-layer-deposit having the high conductivity increases. It was suggested that the higher conductivity polymer fibrils could be formed with the thin-layer-deposit entirely by using the pores less than 0.05 μm in aperture. Probably, this specific value depends on molecule structure of the deposited polymer. The detailed reason of existence of the specific value in the conductivity is investigating on.

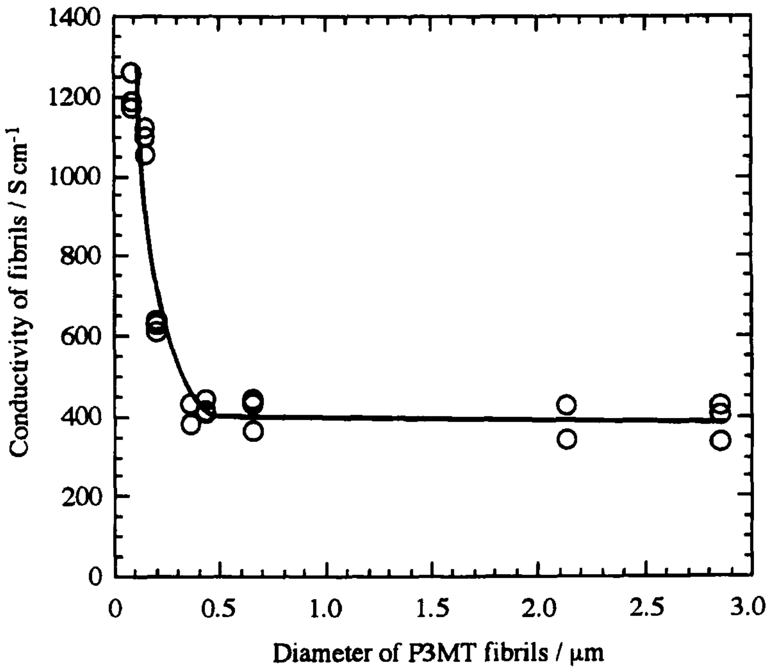

FIGURE 3 Conductivity of polythiophene fibrils as a function of its diameter.

Conclusion

The submicrometer-sized fibrils of poly-3-methylthiophene when polymerized in a structure with pores of aperture between 0.05 and 1.2 µm are formed through the following three stages; the growth nucleus generation, the thin-layer-deposition, and the spherical deposition. When the pore aperture becomes smaller, the thin-layer-deposition is remarkably easy to occur. From the simulated conductivity of the fibrils with each diameter, at the smaller pore aperture than a specific value, the thickness of the thin-layer-deposit having high-conductivity increases.

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