

## Fabrication and Evaluation of Nanostructured Conducting Polymer Films

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The electrophoretic deposition of nanostructured films from colloidal suspensions of a conjugated polymer poly(3-octadecylthiophene), PAT18, as well as the preparation of the suspension by a simple mixing method, is reported. A colloidal suspension of PAT18 was prepared by pouring a toluene solution of the polymer into acetonitrile, which is not a solvent for the polymer. It was found that the suspension obtained was stable for more than two weeks, and the stability was related to the concentration of the polymer therein. In comparison with a toluene solution of PAT18, the colloidal suspension shows a considerable red-shift in the optical absorption and photoluminescence spectra, as well as a quenched photoluminescence, indicating the solidification of PAT18 in the suspension. The electrophoretic deposition of a PAT18 film from the colloidal suspension was successfully carried out. The film shows almost the same optical absorption and photoluminescence spectra as those of a spin-coated film. On the other hand, an atomic force microscopy study revealed a nanostructured surface morphology of the electrophoretically deposited films. Such nanostructured films are expected to be promising materials for electrochemical and sensor applications.

Key words: conjugated polymers, nanostructure, electrophoretic method, colloidal suspension

### 1. INTRODUCTION

Conjugated polymers have attracted much interest from both fundamental and practical points of view in recent decades.<sup>[1]-[3]</sup> The  $\pi$ -conjugated electron system on their main chain provides unique electronic and optical properties, so that, to date, many electronic devices using conjugated polymers, including electroluminescent devices, photovoltaic devices, and field-effect transistors have been extensively studied.<sup>[4]-[10]</sup> The case with which large-sized, uniform thin-films can be fabricated by wet-processes seems to be one of the most fascinating advantages of the conjugated polymers.

The spin-coating technique is quite a convenient method, and thus has been very widely used to prepare polymer electronic devices. However, this technique is one of the most uneconomical methods, because most of the solution dropped on the substrate is blown away during the spinning of the substrate. Moreover, it is hard to obtain patterned films using this technique. This situation has stimulated the development of coating methods other than the spin-coating for conjugated polymers. Layer-by-layer deposition allows the deposition of polymer films of molecular-sized thickness.<sup>[11], [12]</sup> The ink-jet printing technique is a very powerful method for obtaining micro-patterned polymer films,<sup>[13], [14]</sup> although it "draws" the polymer as lines, so that, in principle, the throughput of this method seems to be limited.

Coating methods that are assisted by an electric field allow the deposition of materials not as lines, but as planes. Moreover, they are inherently compatible with patterned deposition, because the deposition area mimics the shape of electrode. Electrochemical polymerization is widely used to deposit conjugated polymers, however, the films obtained are doped with ionic impurities and, therefore, they are in a conducting state, which is not favorable for most of the electronic device applications that utilize the polymers as semiconductors. Recently, it has been reported that an electroluminescent poly(*p*-

phenylene vinylene), PPV, derivative film was successfully obtained by electrodeposition from an aqueous solution of the polymer salt.<sup>[15]</sup> Unlike the conventional electrochemical polymerization method, the film obtained using this technique is in an undoped state, which is suitable for electronic devices. However, the deposition time reported was rather long (as long as ten minutes), and the incorporation of ionic impurities, which may accelerate the degradation of the electronic device, seemed to be unavoidable.

On the other hand, many research groups are now focusing their attention on the correlation between the device characteristics and the morphology of the polymer films used therein. If we pick up field-effect transistors for example, it has been reported that films of regioregular poly(3-hexylthiophene) deposited by the same method, for example, spin-coating, but from different solvents, can exhibit different hole mobilities spanning a few orders of magnitude.<sup>[16]</sup> A similar morphology dependence in the device characteristics of photocells has also been reported.<sup>[17]</sup> Therefore, the development of a way of controlling the morphology of conjugated polymer films is very important.

Electrophoretic deposition, which is based on the electrical collection of small, charged particles dispersed in dielectric liquids, is one of the most widely used coating methods capable of patterning. This paper reports that the electrophoretic deposition of conjugated polymers from a colloidal suspension is a quick and efficient way for obtaining thin films of soluble conjugated polymers. Poly(3-octadecylthiophene), PAT18, was used as a test material to check our idea. An atomic force microscopy (AFM) study of the surface morphology of the film deposited from the suspension reveals the nanostructured feature of the films, which is not achieved by conventional methods, such as spin-coating. A simple way to prepare a colloidal suspension of the conjugated polymer is also noted.

## 2. EXPERIMENTAL DETAILS

Regiorandom PAT18 was polymerized and purified according to the literature procedure.<sup>[18]</sup> That is, 4 g of  $\text{FeCl}_3$  was dissolved in 100 ml of chloroform in a flask, and 2 g of 3-n-octadecylthiophene (TCI) was added dropwise to the solution, then the solution was stirred for 18 h at  $-15^\circ\text{C}$  under a flow of nitrogen. The solution was poured into excess methanol to quench the reaction. The crude polymer was collected by filtration and repeatedly washed with methanol, using a Soxhlet apparatus for over 24 h, thus obtaining 1.7 g of the undoped PAT18 powder used in this study. Acetonitrile and toluene were used as received from Wako Pure Chemicals.

Colloidal suspensions of PAT18 were prepared as follows: 2 mg of PAT18 were dissolved in 2 ml of toluene. The solution was then poured into 18 ml of acetonitrile, which is not a solvent for PAT18, and an 0.1 g/l colloidal suspension of PAT18 was obtained. Colloidal suspensions of PAT18 in an acetonitrile/toluene mixture (9:1 volume ratio) of various concentration, ranging from 0.01 to 0.5 g/l, were obtained in the same manner, but by varying the concentration of the toluene solution. The highest concentration of colloidal suspension we could obtain was 0.5 g/l: the limiting factor was the solubility of PAT18 in toluene, which is approximately 5 g/l.

The apparatus used for the electrophoretic deposition is schematically illustrated in Figure 1. About 2 ml of suspension was put into a glass cell that was 1 cm wide, 1 cm long, and 3 cm high. A DC voltage of up to 300 V was applied between two ITO-coated glass plates (10  $\Omega/\text{sq.}$ ; plates 5 mm apart) soaked in the suspension. The films thus obtained were washed with clean acetonitrile and dried in air.

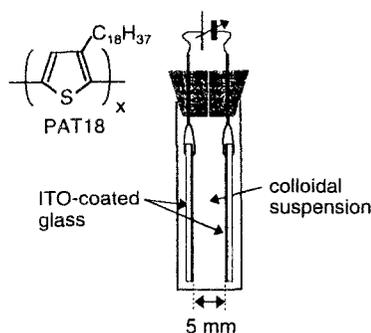


Fig. 1. Schematic illustration of the setup used for the electrophoretic deposition. The molecular structure of PAT18 is also shown.

The optical absorption spectra were measured by an Hitachi 3410 spectrophotometer. A glass cell with a 1 cm optical path was used for the liquid samples. The photoluminescence spectra were taken with a homemade setup including a photomultiplier tube (Hamamatsu R928) combined with a monochromator and a Xe-arc lamp (75 W) combined with another monochromator as the excitation source. Throughout this study, the excitation wavelength used was 400 nm. A glass cell (0.1 cm optical path) was used for the liquid samples, and the emission from the excited face was measured to minimize the modulation due to self-absorption. The AFM images were collected by a Burleigh Metris 2000 system operated in the non-contact mode in air.

## 3. RESULTS AND DISCUSSION

### 3.1 Colloidal suspensions of PAT18

A colloidal suspension of PAT18 in an acetonitrile/toluene mixture (9:1 volume ratio) was obtained by the simple mixing method described in the 2. Experimental details. It was confirmed that no PAT18 powder would dissolve in the acetonitrile/toluene mixture, even when the temperature exceeded the boiling point of the mixture. This indicates that we obtained a colloidal suspension, and not a typical solution, by the mixing method.

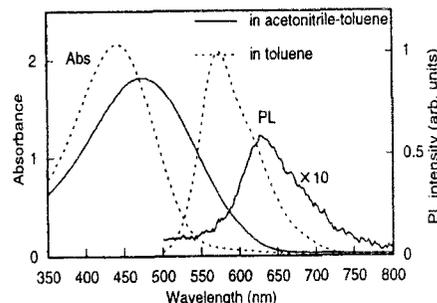


Fig. 2. Optical absorption and photoluminescence spectra of a colloidal suspension of PAT18 (0.1 g/l) in an acetonitrile/toluene (9:1 volume ratio) mixture, and a toluene solution of PAT18 (0.1 g/l).

Figure 2 shows the optical absorption and photoluminescence spectra of an 0.1 g/l PAT18 colloidal suspension in an acetonitrile/toluene mixture (9:1). The corresponding spectra of a toluene solution of PAT18 (of the same concentration) are also shown for comparison. It is well-known that poly(3-alkylthiophene)s, PATs, including PAT18, shows a pronounced solvatochromism.<sup>[19]</sup> That is, PATs in poor solvents such as anisole mimic the solid state properties of PATs, and show a considerable red-shift in the absorption spectrum, compared with those in good solvents, such as toluene and chloroform. The optical absorption spectrum of a colloidal suspension of PAT18 is almost the same as that of PAT18 dissolved in poor solvents.

The photoluminescence from a colloidal suspension of PAT18 is considerably weaker than, and shows a red-shift in comparison with, a toluene solution of PAT18. This may be due to the fact that, in an acetonitrile/toluene mixture, PAT18 solidifies to form colloids, thus enabling the energy transfer from higher excited states to the lowest one, as well as the quenching of the luminescence by defects such as the surface states of the colloid.

Photographs of the colloidal suspensions of various concentrations of PAT18, as well as the 0.1 g/l toluene solution of it, are shown in Figure 3 (a). These clearly indicate the transparency, and the color-shift from the toluene solution, of the colloidal suspensions. No notable aggregation or precipitation of colloids was found for over two weeks in the suspensions containing 0.02 g/l of PAT18 or more, indicating that they are relatively stable. On the other hand, in more dilute suspensions, namely less than 0.02 g/l, aggregation and precipitation occurred within two weeks, as shown on the right-hand side of Figure 3 (b) and (c). It is known that the stability of a suspension has its origins in the repulsive force between the colloidal particles. Therefore, it seems reasonable that

the suspension becomes unstable when it is too dilute, although the detailed mechanism that determines the stability of the present suspensions is not clear. Further investigations, including the dependence of the stability of the suspensions on the solvent ratios, as well on the alkyl chain length of the PAT are in progress.

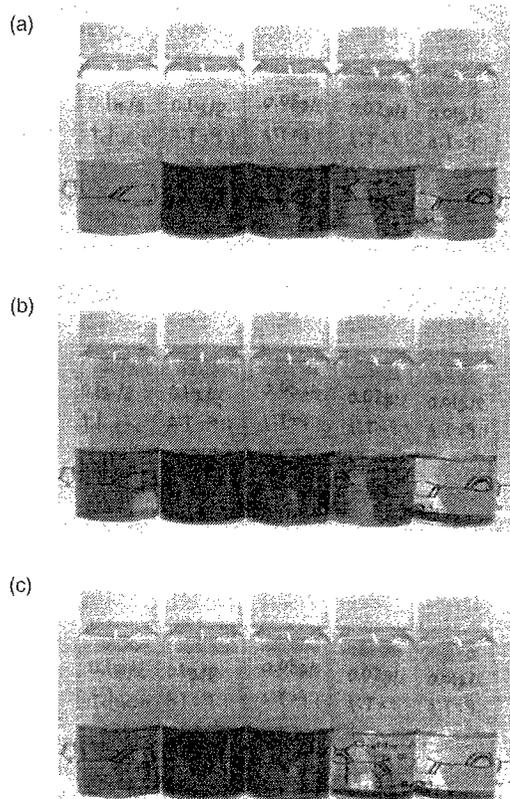


Fig. 3. Photographs of PAT18 colloidal suspensions of various polymer concentrations taken: a) just after preparation; b) after 6 days; and c) after 11 days. The toluene solution of PAT18 is also shown for comparison. From the left: 0.1 g/l toluene solution, 0.1, 0.05, 0.02, and 0.01 g/l colloidal suspensions. Note that the 0.01 g/l suspension in (b) and (c), as well as the 0.02 g/l suspension in (c), become inhomogeneous and colorless due to precipitation.

### 3.2 Electrophoretic deposition and characterization of films

The electrophoretic deposition of PAT18 from the colloidal suspensions was carried out with the setup illustrated in Figure 1. When the voltage applied exceeded 50 V, the deposition of a PAT18 film started immediately on the negatively biased indium tin oxide (ITO) electrode. For example, applying 100 V for 5 s in an 0.1 g/l suspension resulted in a film whose peak absorbance was approximately 0.35. Since PATs, including PAT18, are known as p-type semiconductors, it is reasonable to assume that a colloid of PAT18 is positively charged, and therefore that electrophoretic deposition would occur at the negatively biased electrode.

On the other hand, no film deposition was observed in an 0.1 g/l toluene solution of PAT18 on applying 200 V for 20 s, indicating that the individual polymer chains in a good solvent are so small that they are not effectively

driven by the electrophoretic mechanism. These observations are evidence not only that the deposition process in the acetonitrile/toluene mixture suspension of PAT18 is an electrophoretic one, but also that the polymer does indeed form colloids in the mixed solvents.

As can be seen in Figure 4 (a) and (b), both increasing the voltage and increasing the concentration of polymer in the suspension caused an increase in the thickness of the film deposited. However, as can be seen in Figure 4 (c), the thickness of the film deposited reached a plateau upon prolonged deposition, because the supply of polymer in the suspension was almost exhausted. That is, the total amount of polymer colloid formed was limited by the capacity of the glass cell used, and the suspension in the cell became almost colorless at that stage. Thus, electrophoretic deposition was found to be a quick and efficient method.

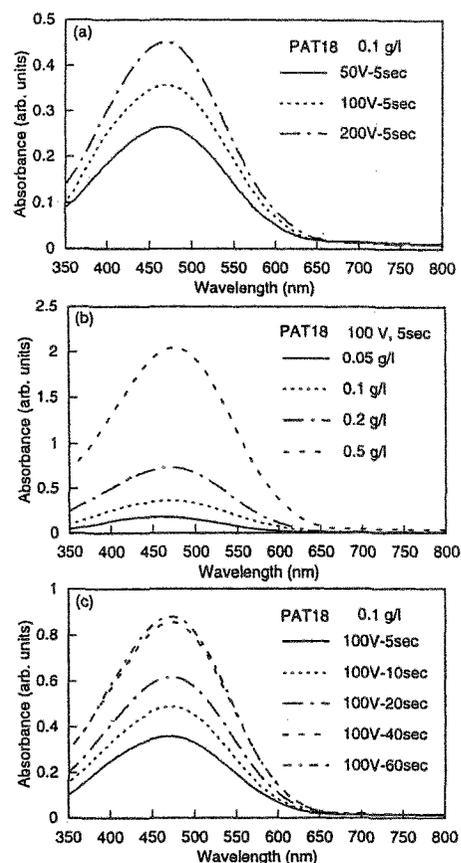


Fig. 4. Variation of the optical absorption spectra of PAT18 films deposited on ITO by electrophoretic deposition. Deposited: a) at various voltages (applied for 5 s) from 0.1 g/l PAT18 colloidal suspensions; b) at 100 V for 5 s, from colloidal suspensions of various PAT18 concentration; c) at 100 V, for various deposition periods, from 0.1 g/l colloidal PAT18 suspensions.

There is no pronounced difference in the optical absorption spectra between the electrophoretically deposited and the spin-coated films. The electrophoretically deposited film is as transparent as the spin-coated film, even in near IR region. The photoluminescence intensity of both films is also almost the same.

On the other hand, an AFM study revealed that the morphology of the PAT18 film produced by electrophoretic deposition differs from that of the spin-coated one. That is, whereas the surface of the spin-coated film is relatively smooth, a pronounced nanostructured surface was found in the electrophoretically deposited film. Apparently, the surface morphology of the electrophoretically deposited film reflects the colloidal feature of the parent suspension, that is, it consists of aggregated small particles that are about 0.1  $\mu\text{m}$  in diameter.

The peak absorbances for the spin-coated and electrophoretically deposited films were found to be almost the same, and about 0.45. The thickness of the spin-coated film (determined by the multiple beam interference method) was found to be approximately 200 nm. However, because of the pronounced porosity of the electrophoretically deposited film, the physical or geometrical thickness of the film deviates from that evaluated from the optical path. From the AFM images in Figure 7, the root mean square roughness was found to be 4 nm for the spin-coated film and 34 nm for the electrophoretically deposited film.

One of the most important factors distinguishing the present coating method from others is the difference in the elemental processes used to form the films. That is, electrophoretic deposition consists of two elemental processes: i) the polymer is solidified into small particles in suspension, and ii) these particles are successively collected, in a non-solvent environment (desirable for keeping the nanostructure), into a film. On the other hand, in other methods, such as spin-coating, the solidification and coating processes occur simultaneously in a solvent environment, and this may (by dissolution) deteriorate the nanostructure.

The unique, nanostructured morphology of the electrophoretically deposited film may provide quite a large surface area. Such films seem to improve the response speeds of electrochemical devices (such as secondary batteries) and sensor devices (such as gas sensors), because of their porosity, which may enable the fast absorption/desorption of dopants and target molecules. They also seem to be interesting materials for optical and electronic applications such as light-emitting diodes. It is worth noting that the method of preparing the colloidal suspension of conjugated polymer, as well as the electrophoretic deposition of a nanostructured, conjugated polymer film, is quite simple and apparently seems to be applicable to most of the soluble conjugated polymers, such as regioregular PATs, PPV derivatives, and polyfluorene derivatives.

#### 4. CONCLUSIONS

In this paper, the preparation of a colloidal suspension of poly(3-octadecylthiophene), PAT18, by a simple mixing method, and the electrophoretic deposition of nanostructured films has been reported. The experimental results can be summarized as follows:

- (1) A colloidal suspension of PAT18 was prepared by a simple mixing method, namely, pouring a toluene solution of the polymer into acetonitrile, which is not a solvent for the polymer. It was found that the suspension obtained was relatively stable, and this stability was related to the concentration of the polymer in the suspension.
- (2) The optical properties of a colloidal suspension of PAT18 differ considerably from those of a toluene solution of PAT18. That is, a considerable red-shift was observed in the absorption and photoluminescence spectra, and the photoluminescence efficiency was also considerably reduced, indicating the solidification of PAT18 in the suspension.
- (3) The electrophoretic deposition of a PAT18 film from a colloidal suspension of PAT18 was successfully carried out. The film showed almost the same optical absorption and photoluminescence spectra as those of a spin-coated film. However, an AFM study revealed the nanostructured surface morphology of the electrophoretically deposited films. Such nanostructured films seem to be promising materials for electrochemical and sensor applications. The simplicity with which a colloidal suspension of a conjugated polymer was prepared and the ease with which a nanostructured film was fabricated by electrophoretic deposition are promising for the extension of these methods to other soluble, conjugated polymers.

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