

# Controlling the Morphology of Nanostructured Poly(fluorenyleneethynylene) Film by a Simple Method

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## 1. Introduction

The polymer devices based on the conjugated polymers have been rapidly progressed in recent years, and the monochromatic display with polymer light-emitting devices is used for consumer products. The easiness in the film fabrication is one of the most important features for polymer materials. That is, large films are easily produced by simple and low-cost technologies such as spin-coating and ink-jet printing. In these solution based techniques, the solidification of the polymer and film formation simultaneously occur under the exposure to the solution vapor. This scenario is quite useful if one want to obtain smooth and dense film, which is usually used for polymer light-emitting device application for example.

On the other hand, studies on the electrochemical and sensor applications of conjugated polymer have longer history than the modern applications such as light-emitting devices, photovoltaic devices, and field-effect transistors. These rather traditional applications incorporate transport phenomena of molecules and ions in the polymer film, in contrast to the modern applications in which only electrons and holes are supposed to mobile, and thus the high surface area film promoting fast insertion/desertion of species is favorable for them.

We have recently shown that the electrophoretic deposition of a conjugated polymer poly(3-octadecyl thiophene) from colloidal suspension yields a nanoporous film. [1] It is also evident that the nanostructured poly(3-octadecylthiophene) films incorporate no macroscopic pin-holes from the demonstration of polymer light-emitting device from the nanostructured film. [2] Moreover, since the recent studies show the device characteristics are strongly affected by the morphology of the polymer film used therein, the nanostructured conjugated polymer film may be interesting material also for the modern applications including photovoltaic devices.

In this report, we show the electrophoretic deposition of fluorene-based blue-emitting polymer, poly(9,9-dioctyl fluorenyl-2,7-ylene ethynylene) (POFE), [3] yielding nanostructured films. A simple method to control the particle size is also mentioned.

## 2. Experimental

Figure 1 shows the molecular structure of POFE. All chemicals including POFE purchased from Aldrich were used as received. Like poly(3-octadecylthiophene), POFE is soluble in toluene but insoluble in acetonitrile. And the

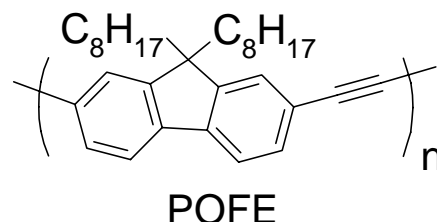


Fig. 1 Molecular structure of POFE.

same procedure could be used to obtain colloidal suspension. That is, 3 ml of 1.0 g/l toluene solution of POFE is poured into 27 ml of acetonitrile, to obtain 10 ml of 0.1 g/l suspension of POFE.

To control the size of colloidal particle, the acetonitrile: toluene ratio was changed as follows: 3 mg of POFE was dissolved in 3.0, 1.0 and 0.5 ml of toluene at first, and they were poured into 27, 29 and 29.5 ml of acetonitrile to obtain 0.1 g/l suspension with acetonitrile: toluene ratio = 9:1, 29:1, 59:1 respectively.

The electrophoretic deposition was carried out by application of DC voltage between a pair of ITO-coated glass plates soaked in suspension charged in a glass cuvette.

The characterization of film was carried out by using a Hitachi U-3410 spectrophotometer, a Hitachi F-2500 fluorescence spectrophotometer, and a Burleigh Metris 2000 atomic-force microscope.

## 3. Results and Discussion

As shown in Fig. 2, the scattering of light at visible region becomes strong as decreasing the toluene content in the suspension, indicating that the colloidal particle in the POFE suspension becomes larger. This phenomenon is clearly observed by naked eye. The suspensions are stable, and no notable change such as precipitation was observed for more than two weeks.

The fluorescence of colloidal suspensions is much weaker than the toluene solution. It is usually observed that the fluorescence from a conjugated polymer becomes weaker by solidification, and this is reasonably understood in terms of strengthened interchain interaction due to solidification. Therefore, the solidification of POFE to form colloidal particle is expected. It was also confirmed that POFE used is insoluble to acetonitrile-toluene (9:1) mixture.

The electrophoretic deposition of POFE film could be carried out by the method described above. When the

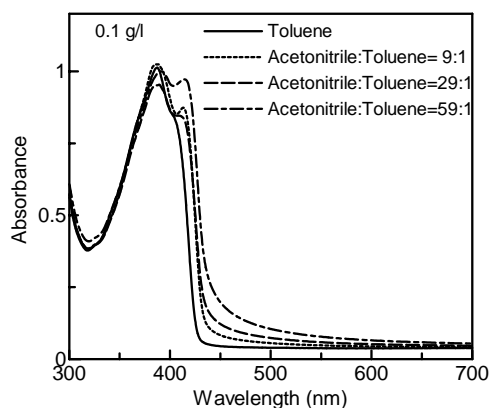


Fig. 2 Optical absorption spectra of POFE suspensions.

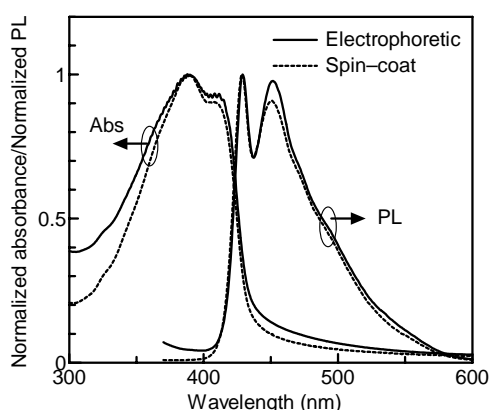


Fig. 3 Optical absorption and photoluminescence spectra of POFE films deposited by spin-coating and electrophoretic deposition

voltage applied between two ITO electrodes 5 mm apart exceeds 100 V, the film deposition was clearly observed. Contrary to the case of poly(3-octadecylthiophene), the film was deposited on the positively biased electrode, indicating that the colloidal particles of POFE in the suspension are negatively charged. The optical absorption and photoluminescence spectra of electrophoretically deposited POFE film is essentially the same as those of spin-coated film, as indicated in Fig. 3.

Figure 4(a) shows the atomic-force microscopy image of POFE film electrophoretically deposited from the 9:1 suspension. It is clearly indicated that the submicron particles constitute the film. The approximate diameter of particles is found to be 80 nm. The mechanism of nanostructure formation can be explained as follows: The solidification of polymer to form colloidal particle occurs in suspension prior to film formation. Then, the solid nanoparticles are collected by the electrophoretic force to form film, and the drying of the film takes place in non-solvent atmosphere to preserve the nanostructure. This is in contrast to the traditional film processing technique from polymer solution, in which the solidification and the film formation simultaneously take place

The variation of colloidal size due to variation of toluene content shown in Fig. 1 is directly transferred to the

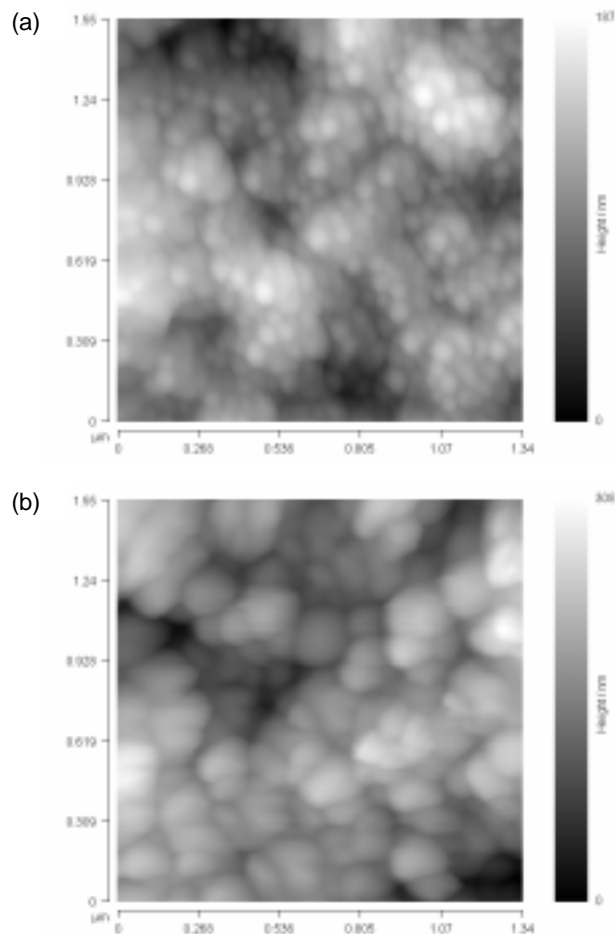


Fig. 4 AFM images of electrophoretically deposited POFE films from (a) 9:1 and (b) 59:1 suspensions.

nanostructured film. As shown in Fig. 4(b), the approximate diameters of particle are found to be 180 nm for the film deposited from the 59:1 suspension, indicating that the size of nanoparticles constituting the film becomes larger as the toluene content of suspension becomes lower.

#### 4. Conclusions

The nanostructured films of fluorene-based blue-emitting polymer, poly(9,9-dioctyl fluorenyl-2,7-ylene ethynylene) by electrophoretic deposition was mentioned. The colloidal particle size could be tuned by simply changing the solvent: non-solvent ratio, although the mechanism of size variation is not clarified at this stage. The morphology of nanostructured film reflected the colloidal particle size in the parent suspension.

#### Acknowledgements

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#### References

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