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Fabrication of High Quality Thin Film of PPV Derivative Polymers Using a Spincoating Method

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Abstract
We report in this work the results of fabricating high quality MEH-PPV and MEH-PPB thin films using spincoating method by proper choice of a solvent, weight concentration and spinning speed. It is found that the films prepared from toluene solutions of weight concentration around 5 % at spinning speeds of 2000 rpm show the highest quality of uniform thickness of d = 540 nm for MEH-PPV and d = 450 nm for MEH-PPB with normalized surface roughness (R_a/d) of 0.3 % for MEH-PPV and MEH-PPB.

Keywords: *Thin film, Spincoating, PPV-derivatives, MEH-PPV, MEH-PPB, Surface roughness*

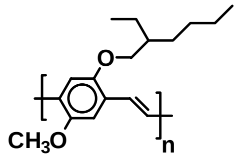
Abstrak
Dalam tulisan ini dilaporkan hasil fabrikasi film tipis MEH-PPV dan MEH-PPB yang berkualitas baik dengan menggunakan teknik spincoating melalui pemilihan parameter yang tepat yaitu meliputi jenis pelarut, konsentrasi dan kecepatan rotasi. Film-film yang dibuat dengan menggunakan pelarut toluen dengan konsentrasi 5 % dan kecepatan rotasi 2000 rpm menunjukkan kualitas yang baik dengan ketebalan d = 540 nm untuk film MEH-PPV dan d = 450 nm untuk film MEH-PPB. Kedua jenis film tersebut juga memiliki kerataan relatif (R_a/d) yang cukup baik yaitu sebesar 0,3%.

Kata kunci: *Film tipis, Spincoating, PPV dan turunan, MEH-PPV, MEH-PPB, Kehalusan permukaan*

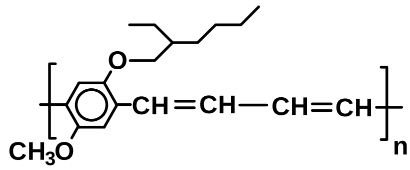
1. Introduction

Among the dozens of photonic polymers of conjugated chain, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-1,3-butadiene-1,4-diyl] (MEH-PPB) belong to the most intensively studied species due to their remarkable electroluminescent and nonlinear optical properties along with other supporting characteristics favorable for their photonic device applications. Unfortunately, the fabrication of high-quality films from these polymers has so far suffered from the problems of insufficient surface smoothness and optical transparency. We have shown from our previous work on the fabrication of poly(N-vinylcarbazole) (PVK) film using spincoating technique, that high quality film could be achieved by optimizing the processing parameters consisting of the choice of solvent, polymer concentration (c_w), spinning speed (ω) and spinning temperature (T)[1,2]. Among those processing parameters, the solvent has the most crucial influence on the film quality manifested by its surface smoothness and transparency. It was found[2] that beside a high solubility, the solvent used for spincoating should also have a low volatility and low hygroscopic property. A highly volatile solvent will cause an orange peel effect[2-5], while a highly hygroscopic solvent will result in a cloudy film[2,3,5].

In this report, we present the result of film fabricating from substituted PPV namely MEH-PPV and MEH-PPB. The basic repeat unit of MEH-PPV is monomer of PPV grafted with side chains of methoxy and ethylhexyloxy groups and that of MEH-PPB is a similar molecule containing two double bonds in its vinyl chain are shown in Fig. 1. These PPV derivatives are known to be soluble in a number of solvents such as chloroform, tetrahydrofuran (THF), 1,4-dioxane, toluene, chlorobenzene, methylene chloride, and 1,1,2,2-tetrachloroethane (TCE)[6]. The choice of solvent will be explained and the process of fabrication along with the results of various characterizations of the films will be described in this paper. Further, the α and β exponents in the scaling law derived previously on the basis of a rheological model[7,8] will also be determined from the data obtained in this experiment.



(a)



(b)

Figure 1. Molecular structure of MEH-PPV and MEH-PPB

2. Experiments

The polymers of MEH-PPV and MEH-PPB were obtained from Prof. Hoerhold's research group at the University of Jena. A description of the method used to synthesize these polymers can be found in Reference [6]. The thin films were spincoated on fused silica substrate at room temperature from the solutions of MEH-PPV (M_w = 25,000 (GPC) and T_g = 68 °C)) and MEH-PPB (M_w = 20,000 (GPC) and T_g = 86 °C) in toluene which was chosen according to criteria explained in the following paragraph. Prior to the deposition process, the fused silica substrates (35 mm x 25 mm x 1 mm) were cleaned for 15 minutes in an ultrasonic bath containing 1 % Hellmanex solution, and then rinsed successively with Milli-Q (pure water) water and ethanol. They were subsequently dried by blowing them with nitrogen gas immediately after being taken out from the ethanol solutions. In the mean time, the polymer solutions were filtered using 0.45 μm microphore filter to ensure their purity and homogeneity.

The choice of solvent was made by examining first of all the pertinent constants of various MEH-PPV and MEH-PPB solvents as given in Table 1. A consideration of low volatility and low hygroscopic requirement immediately narrows down the list of solvent to toluene, chlorobenzene and TCE for spincoating process at room temperature. Indeed, a problem of film transparency related to the used of 1,4-dioxane solvent has been reported on the fabrication of diflourophenyl-polydiphenylenevinylene (DFP-PDPV) film[11]. We finally settled for toluene since the films produced are free from the undesirable effects, and the films dry more rapidly than those spincoated from chlorobenzene and TCE solutions.

Table 1. Characteristics of solvents used for MEH-PPV and MEH-PPB[9,10]

No	Solvent	T_b (°C)	density (g cm^{-1})	Solubility (J cm^{-3})^{0,5}	Solubility in water at 25 °C (ppm)
1	Chloroform ($CHCl_3$)	61	1.4832	19.028	7.5000E+03
2	Tetrahydrofuran (C_4H_8O),	65	0.8892	19.129	1.0000E+06
3	1,4-dioxane ($C_4H_8O_2$)	101	1.0337	20.163	1.0000 E+06
4	Toluene ($C_6H_5CH_3$)	111	0.8669	18.346	5.4240E+03
5	Chlorobenzene (C_6H_5Cl)	132	1.1058	19.264	3.9070 E+02
6	1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$)	146	1.5953	20.485	2.9000 E+03

The process of spincoating was carried out under the same condition and in the same manner as described in Reference[1,2] except that the spincoating temperature is fixed at room temperature in this experiment. The characterizations of the resulted films were also carried out in the same fashion as described previously[1,2].

3. Results and Discussion

The films of MEH-PPV and MEH-PPB prepared using toluene are both transparent with a light orange color and red color, respectively. The as measured UV-Vis-Nir spectra were corrected by subtracting the reflection losses at the air/film and film/substrate interfaces using method described previously[12]. The resulted spectra show maximum absorption at 477 nm and 490 nm and the absorption edge at 570 nm and 600 nm for MEH-PPV and MEH-PPB, respectively. The film surface also appears smooth without any visible orange peel pattern as confirmed by its surface profile traces shown in Fig. 2 where a square dip in the trace is a result from scratching the film using sharp needle for evaluating the film thickness. This surface quality is mainly attributed to the appropriate choice of solvent. The thicknesses of these films are quite homogeneous as confirmed by the absence of perceptible interference fringes. The aluminum inset used for substrate holder in the film preparation is believed to provide a uniform temperature on the substrate and hence contributes to the above mentioned film quality.

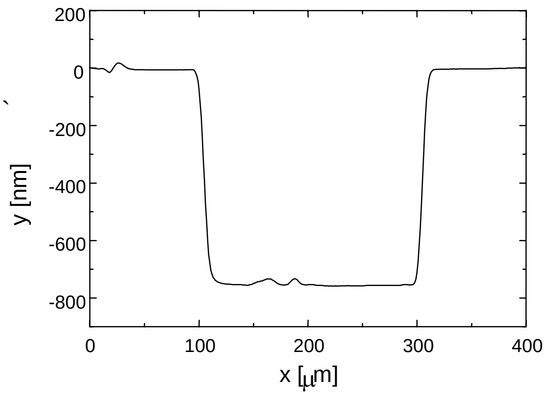


Fig. 2. Surface profile trace of MEH-PPV film of thickness of (749 ± 10) nm prepared from toluene solution

The processing parameters such as spinning speed and solution concentration display a systematic influence on the film thickness of MEH-PPV as described by Fig. 3. A log-log plot of thickness (d) versus spinning speed (ω) for $c_w = 3$ % or $c_w = 5$ % given in Fig. 3.a are both linear with the same slope of $\alpha = -0.50 \pm 0.02$. This result is consistent with a scaling law derived previously on the basis of a rheological model[7,8] where $d \sim \omega^{\alpha}$. Similarly, the thickness of film also increases with the polymer concentration (c_w) and satisfies a relationship of $d \sim c_w^{\beta}$ where $\beta = 1.61 \pm 0.04$ is a slope of log-log plot of thickness versus polymer concentration, which is not shown in this paper. We note from Fig. 4.b that the normalized surface roughness (R_a/d) of MEH-PPV film prepared with 5 % weight concentration in this experiment is about 2.0 ± 0.7 nm and practically independent of ω between 1000 rpm and 4000 rpm. The same can not be said however for the case with $c_w = 3$ % in the lower spinning speed variation. Still, as we found as a whole, the normalized roughness of MEH-PPV films prepared in this experiment varies within 0.3 % to 0.6 % of its mean. This remarkably low surface roughness is a further of the proper choice of solvent.

Fig. 4.a presents the log d – log ω plots for MEH-PPB films prepared with different c_w 's. It is obvious that this result exhibits virtually the same characteristics revealed by Fig. 3.a, differing only in the value of α which is given by $\alpha = -0.53 \pm 0.03$ in this case. An examination of the log d – log c_w relationship yield the value of $\beta = 1.49 \pm 0.01$. These results as a whole strongly attest to the validity of the scaling laws $d \sim \omega^{\alpha}$ and $d \sim c_w^{\beta}$ which can be expressed by the general relationship

$$d_2 = d_1 \left(\frac{\omega_2}{\omega_1}\right)^{\alpha} \left(\frac{c_{w2}}{c_{w1}}\right)^{\beta} \qquad (1)$$

with $\omega_1 = 2000$ rpm, $c_{w1} = 5$ %. We then find that d_1 (ω_1, c_{w1}) = 542 nm for MEH-PPV films, while d_1 (ω_1, c_{w1}) = 450 nm for MEH-PPB films, with the corresponding values of α and β given above.

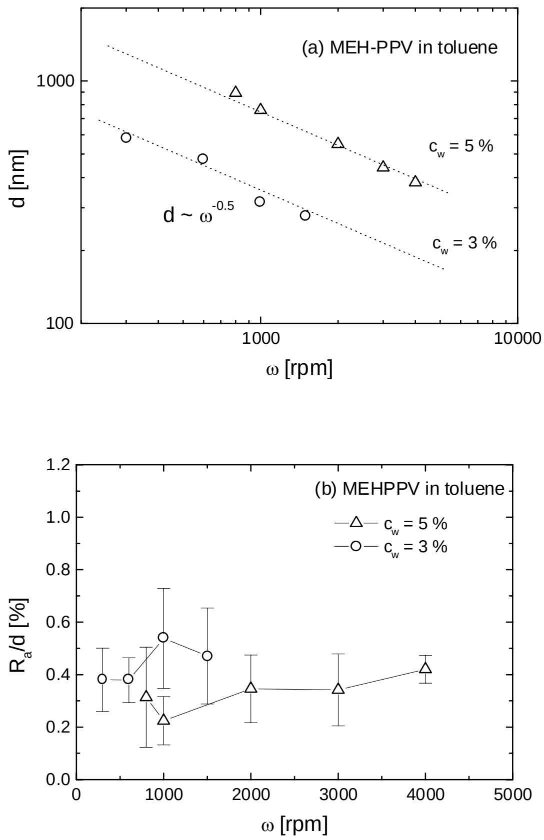
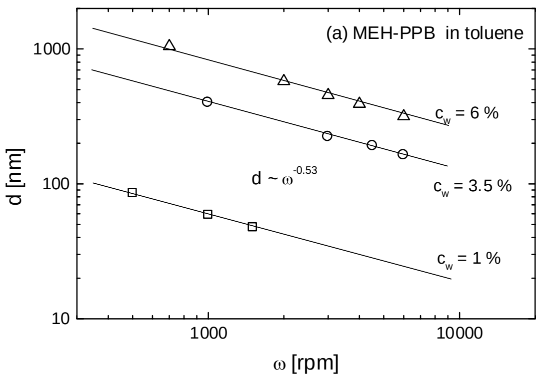


Fig.3 Dependence of thickness (a) and surface roughness (b) of MEH-PPV films on the spinning speed.

We note further that in both cases film spincoated at higher spinning speeds (2000 rpm – 4000 rpm) are generally much better surface quality. The unusually low surface roughness of MEH-PPB films spincoated at ω = (2000 – 4000) rpm is evidenced by the exceedingly small range of its deviation in R_a/d (0.3 % - 0.32 %). Spincoating films from solutions of low concentrations can not be carried out at higher spinning speed and the resulted films have less desirable surface quality.



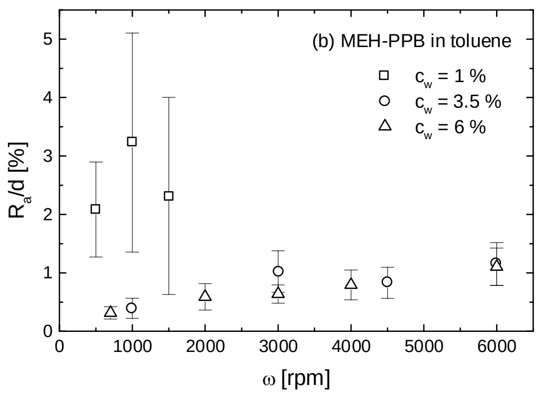


Fig. 4 Dependence of thickness (a) and surface roughness (b) of MEH-PPB films on the spinning speed.

4. Conclusion

In summary, we have demonstrated in this experiment that a proper choice of solvent, spinning speed and polymer concentration, has resulted in transparent MEH-PPV and MEH-PPB films of smooth surface and uniform thickness. In addition to the crucial influence of the choice of solvent, the experimental result also indicates the favorable choice of ω and c_w for the fabrication process. The optical quality of the films including their absorption and waveguide transmission characteristics will be reported elsewhere.

Acknowledgements

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