

# Effect of Physicochemical Properties of Solvents on Microstructure of Conducting Polymer Film for Non-Volatile Polymer Memory

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**Abstract**—The effect of physicochemical properties of solvents on the microstructure of polyvinyl carbazole (PVK) film for non-volatile polymer memory was investigated. For the solubilization of PVK molecules and the preparation of PVK films, four solvents with different physicochemical properties of the Hildebrand solubility parameter and vapor pressure were considered: chloroform, tetrahydrofuran (THF), 1,1,2,2-tetrachloroethane (TCE), and N,N-dimethylformamide (DMF). The solubility of PVK molecules in the solvents was observed by ultraviolet-visible spectroscopy. PVK molecules were observed to be more soluble in chloroform, with a low Hildebrand solubility parameter, than solvents with higher values. The aggregated size and micro-/nano-topographical properties of PVK films were characterized using optical and atomic force microscopes. The PVK film cast from chloroform exhibited enhanced surface roughness compared to that from TCE and DMF. It was also confirmed that the microstructure of PVK film has an effect on the performance of non-volatile polymer memory.

**Index Terms**—Non-volatile polymer memory, conducting polymer, solvent, solubility, microstructure, Hildebrand solubility parameter, vapor pressure

## I. INTRODUCTION

Recently, non-volatile polymer memory has been considered as a candidate for the next-generation non-volatile memory as an alternative to conventional flash memory based on floating gate transistor technologies. Non-volatile polymer memory has a sandwich structure of active material between two electrodes [1-6]. The active material mainly consists of metal nanoparticles (acceptor), conducting organic molecules or polymers (donor), and a polymer matrix (insulator matrix). The memory-effect phenomena of non-volatile polymer memory are reported to be attributed to charge transfer and trapping-detrapping processes [2-4]. Charge transfer [1] can occur at both the interface between nanoparticles and the conducting polymer, and the conducting polymer and electrodes; therefore, the interfacial properties need to be considered [7, 8] as a critical factor impacting the performance of the device. In this study, an attempt was made to control the interfacial properties of PVK films using solvents with different physicochemical properties of the Hildebrand solubility parameter and vapor pressure. In addition, the effect of the microstructure of PVK film on the performance of non-volatile polymer memory was investigated.

## II. EXPERIMENTAL PROCEDURES

Poly(vinyl carbazole) (PVK, Mw=700,000, TCI) was used as a matrix polymer. Chloroform, tetrahydrofuran (THF), 1,1,2,2-tetrachloroethane (TCE), and N,N-dimethylformamide (DMF) were used as solvents. The physicochemical properties of the solvents are shown in

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**Table 1.** Physicochemical Properties of Solvents at Room Temperature [9,10].

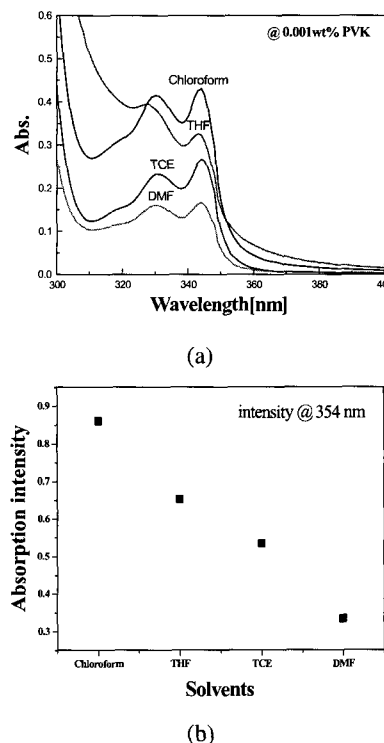
Solvent	b.p (°C)	Vp (mmHg)	$\delta$ (MPa <sup>1/2</sup> )	$\rho$ (g/cm <sup>3</sup> )
Chloroform	61	160	19.0	1.492
THF	65-67	129	19.4	0.889
TCE	147	8	20.1	1.586
DMF	153-155	2.7	24.8	0.944

b.p., boiling point; Vp, vapor pressure;  $\delta$ , Hildebrand solubility parameter;  $\rho$ , density.

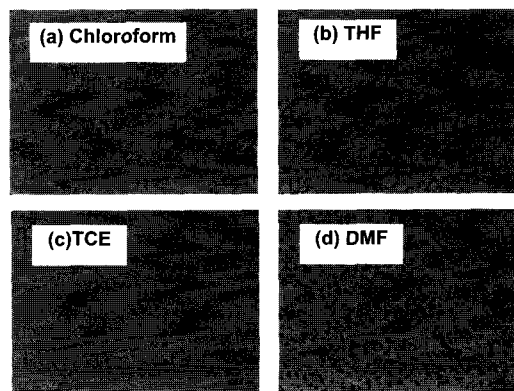
Table 1. A Cary 100 ultraviolet-visible (UV-vis) spectrometer (Varian Instruments) was used to investigate the solubility behavior of PVK in these different solvents. For UV-vis spectroscopy, the concentration of PVK molecules in a solvent was fixed at a weight fraction of 0.01%. A PVK film was formed on an aluminum electrode, which was deposited on a SiO<sub>2</sub> wafer, by spin coating the PVK polymer solution with a fixed concentration (0.8 wt%). The speed of spin casting was maintained at 2,000 rpm for 100 sec. Then, the film was baked at 120°C for 2 min. The surface roughness of the baked PVK films was measured using an optical microscope and a noncontact mode atomic force microscope (PSIA, XE-150). For the device fabrication, Au was evaporated onto the PVK film using a shadow mask at an evaporation rate = 0.5 Å/sec and pressure = 5×10<sup>-5</sup> Torr. The PVK layer was then formed by the same procedure as above-mentioned. The devices were cured at 300°C for 2 hrs to form Au nanoparticles within the PVK matrix. Finally, the formation of the top electrode was performed via evaporation using a shadow mask at a pressure = 5×10<sup>-6</sup> Torr. For the electronic measurement of the device, a programmable source meter (Keithley 2400, Keithley Instruments Inc., Cleveland, OH) was used with a computer interface.

### III. RESULTS AND DISCUSSION

The solubility of PVK molecules in the four different solvents was compared by observing the UV-vis spectrum of PVK solution (Fig. 1(a)). The characteristic peak around 354 nm was observed for PVK molecules in all the solvents. The intensity of each peak for PVK solutions prepared with the different solvents is summarized in Fig. 1(b). The peak intensity at 354 nm decreased as the Hildebrand solubility parameter of the solvents increased. The intensity for the PVK solution



**Fig. 1.** (a) Absorption spectra of PVK solutions (b) Absorption intensity at 354 nm



**Fig. 2.** Optical micrographs of spin-cast PVK films prepared from (a) chloroform, (b) THF, (c) TCE, and (d) DMF solutions. Length of scale bar is 100 μm.

prepared from chloroform was higher than any of the other solvents, implying that PVK has the highest solubility in chloroform.

The surfaces of PVK films were observed with an optical microscope (Fig. 2). Polymer aggregation did not occur in the PVK film prepared from all the solvents except for DMF, indicating that the Hildebrand solubility parameter of the solvents has to be lower than that of DMF for the solubilization of PVK molecules. However, the PVK film prepared from the chloroform and THF

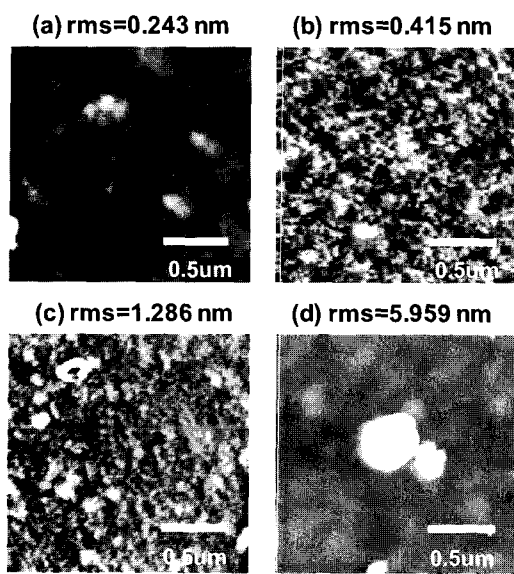


Fig. 3. AFM images of spin-cast PVK films prepared from (a) chloroform, (b) THF, (c) TCE, and (d) DMF solutions.

solutions had a higher surface roughness compared to that of the TCE solution, which results from Marangoni instability [11-13]. As shown in Table 1, chloroform and THF have a higher vapor pressure than TCE and DMF. During the spin coating process, solvents with high vapor pressure is vigorously evaporated from the surface, which results in the composition and temperature gradients in the thin solution film [11-13]. The local gradients of composition and temperature gave rise to a corresponding gradient of surface tension, inducing flow of the surface liquid layer on the substrate. As a result, the local surface tension gradients cause Marangoni convection [11-13].

Fig. 3 shows AFM images and the root-mean square (rms) values for the surface roughness of PVK films prepared with the four different solvents. It is remarkable that there were significant differences in the nano-topographical height of PVK thin films prepared from the four different solvents solutions. While the PVK films prepared with chloroform and THF exhibited low rms values, those prepared with TCE and DMF showed high rms values. This can be explained by the different solubility behavior of PVK in these solvents. The PVK solution prepared from chloroform showed the highest intensity of characteristic peak for PVK molecules (see Fig. 1). It indicates that PVK is highly soluble in chloroform. The high solubility of PVK in chloroform leads to the formation of PVK film with a lower nano-

topography. On the other hand, TCE and DMF insufficiently dissolve PVK molecules or swell PVK interchains, which resulted in the formation of a PVK film with higher nano-topography. Therefore, it can be concluded that the nano-topography of PVK thin film is significantly affected by the Hildebrand solubility parameter of a solvent.

To identify the correlation between the microstructure of PVK and the performance of the device, the current level of the devices was measured at the same read voltage. The device made with chloroform had a higher current level ( $1.5 \times 10^{-5}$  A at  $V_{\text{read}}=1$  V) than that of THF ( $3.4 \times 10^{-6}$  A at  $V_{\text{read}}=1$  V). On the other hand, the device made with TCE and DMF solutions shorted, which is attributed to the macro-/nano-topographical properties of the PVK films

#### IV. CONCLUSIONS

The effect of the Hildebrand solubility parameter and vapor pressure of solvents on the microstructure of PVK film was investigated. The PVK molecules were more soluble in the solvent with a low Hildebrand solubility parameter. Solvents with higher vapor pressure, chloroform and THF, induced Marangoni instability, which resulted in high surface roughness on the whole region of the substrate. On the other hand, from the images of AFM analysis, the surface of PVK film prepared from chloroform and THF solutions had low rms values in spite of induced Marangoni convection. It can be concluded that nano-scale surface roughness is dominated by the Hildebrand solubility parameter of a solvent, while micron-scale surface roughness is affected by the vapor pressure of a solvent. The current level of the device fabricated from the chloroform solution was higher than that from the THF solution. On the other hand, the devices fabricated from PVK solutions, which had TCE and DMF as the solvents, shorted. It can also be concluded that the microstructure of PVK film has an effect on the performance of non-volatile polymer memory.

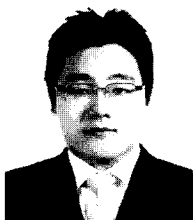
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In addition, he has taught industrial short courses, published three books in Korean, published 172 papers, given 227 talks, has issued 84 patents, and has submitted 147 patents.