

Electrical Property and Stability of Electrochemically Synthesized Polypyrrole Films

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ABSTRACT: Polypyrrole (PPy) films doped with arylsulfonate dopants were prepared by electrochemical polymerization, to investigate the effects of various dopants on conductivities, thermal stabilities, and morphologies of PPy films. Also, HCl was added to those dopants as a cooperating dopant, to improve conductivity of PPy films. Conductivity of PPy film doped with the mixture of each dopant and HCl was improved. Temperature dependency on conductivity for PPy films doped with various dopants was investigated by heating them from 30 to 300°C. For the film

doped with TSA, DBSA, and AQSA, conductivity increased up to 150°C and then rapidly decreased, whereas the conductivity of other films decreased after 200°C as temperature increased up to 300°C. Moreover, the film doped with small size dopant such as TSA and HCl/TSA had an interconnected porous fibrillar-like morphology. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3659–3666, 2004

Key words: conducting polymers; polypyrrole (PPy); dopants; electrochemistry; films

INTRODUCTION

The intrinsic conducting polymers (ICPs) containing π -bonded or conjugated polymers have gained great importance with the discovery of doped polyacetylene (PA) in 1977 because of its potential application for electronic materials.¹ According to the results of previous research, electroconductivity of ICPs such as polyacetylene (PA), polyaniline (PANI), polythiophene (PT), and polypyrrole (PPy) varies with the kind of dopant used because of the differences in oxidation and reduction states.² Also, the ICPs allowed them to be applied in various electronic devices, solid battery electrodes, electrolyte of capacitor, EMI shielding materials, electrochemical ionic sensors, and camouflage sheets in spite of their short history.^{3–10} Among the ICPs, PPy has excellent environmental stability, easy synthesis, and higher conductivity than those of other conductive polymers.^{5,11,12} Because of its good intrinsic properties, PPy appears promising for use in various fields. However, the application of pyrrole black is limited because it is insoluble and infusible. Electrochemically synthesized PPy film was more useful for application in the field of electronic device because of the direct formation of conducting

polymers with control of film thickness and morphology.

In the general electropolymerization, the oxidation of a pyrrole monomer yields a radical cation at the initiation step. It is a pair of radical cations that couple to a dimer and deprotonate, producing a bipyrrrole. After the deprotonation step, the bipyrrrole is oxidized again and coupled with another oxidized segment. Deprotonation and reoxidation follow, and the process continues with the formation of oligomeric species and finally PPy.¹³

In general, the conductivity and the thermal stability of the PPy are strongly dependent on polymerization conditions such as concentration of pyrrole and dopant, the applied voltage, solvent used, reaction temperature, and kind of dopant.^{11,12,14} In a recent investigation of PPy doped with various protonic acids, it was found that HCl and sulfonic acid were the best dopants in terms of conductivity and stability. Because the interchain interaction and the conformation of conducting polymer are varied by change of chemical structure and the charge transfer with dopants, these also affected the conductivity and the thermal stability.^{15,16}

Compared with PPy film doped with HCl, the thermal stability of the film doped with sulfonic acid was enhanced.¹⁷ However, the conductivity of film doped with sulfonic acid was decreased because of its bulky structure. Moreover, many researchers have reported that the dopant mixtures induced high conductivity.¹⁸ To expand commercial applications for capacitors, rechargeable batteries and sensors, the conductivity and

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thermal stability of film is more important than physical property because of the temperature used. In this study, therefore, differences of conductivity between film doped with a single dopant and that of a dopant mixture were observed. To investigate the effect of dopant and dopant system, polymerization conditions, except kind of dopant, were fixed. PPy was then electrochemically synthesized with various single dopants and dopant mixtures with HCl. The changes of electrical conductivity, thermal stability, and morphology of prepared PPy films were investigated with various dopant systems.

EXPERIMENTAL

Materials

Pyrrole (Aldrich Chemical Co., Milwaukee, WI) was purified by vacuum distillation before use. Hydrochloric acid (HCl, Duksan Pure Chemical Co., Japan), *p*-toluenesulfonic acid (*p*-TSA, Yakuri Pure Chemicals Co., Japan), naphthalenesulfonic acid (NSA, Aldrich), dodecylbenzenesulfonic acid (DBSA), anthraquinone-2-sulfonic acid, sodium salt monohydrate (AQSA, Aldrich), and polystyrenesulfonic acid (PSSA, Polysciences, Warrington, PA) of special reagent grade were used without further purification.

Preparation of polypyrrole film

PPy films were prepared on a stainless-steel plate at constant voltage by electrochemical polymerization with various dopants. Then HCl of 1 : 1 molar ratio was added to those dopants as a cooperating dopant to improve the conductivity of PPy films. Polymerization was performed in aqueous solutions of 0.2 mol/L pyrrole and 0.1 mol/L dopant at 5°C for 2 h under a constant power source of 1.3 V. PPy films obtained from the working electrode connected with anode were washed with distilled water and dried *in vacuo* at 40°C for 24 h.

Measurement of conductivity and thermal stability

The conductivity of PPy film was measured according to ASTM D4496-87. A constant current was applied to the outer electrodes from a constant current source and the potential difference between the inner electrodes was measured with a Keithley 2000 digital multimeter (Keithley Instruments, Taunton, MA). The conductivity change with temperature variation was measured using a hot stage (Mettler Instruments, Greifensee, Switzerland) from 30 to 300°C at a heating rate of 10°C/min. In addition, to investigate of stability of film at constant temperature, resistance was measured with a multimeter at 100, 150, and 200°C for 20 h. The multimeter was interfaced to a personal computer by an RS-232C port for automatic data col-

lection. PPy film surfaces from different dopant systems were observed by FE-SEM (JSM-6330F, JEOL, Tokyo, Japan). The dimension of formed droplets with dopants was analyzed by image analysis. To consider the effect of the dopant itself on thermal stability for PPy film, TGA (Model 2960, TA Instruments, New Castle, DE) of sodium salt of sulfonic acid was performed.

The conductivity of PPy film doped with various dopants was measured using a standard four-probe method, and for measuring conductivity variation with temperature, a four-probe cell was inserted in the hot stage.

In general, the conductivity decay with time was proportional to the square root of thermal treatment time, indicated by the following equation:

$$(\sigma_0 - \sigma) / \sigma_0 = 1 - \frac{R_0}{R} = At^{1/2}$$

where σ_0 is the initial conductivity, σ is the conductivity, R_0 is the initial resistance, R is the resistance, A is the conductivity decay parameter, and t is the treatment time.

RESULTS AND DISCUSSION

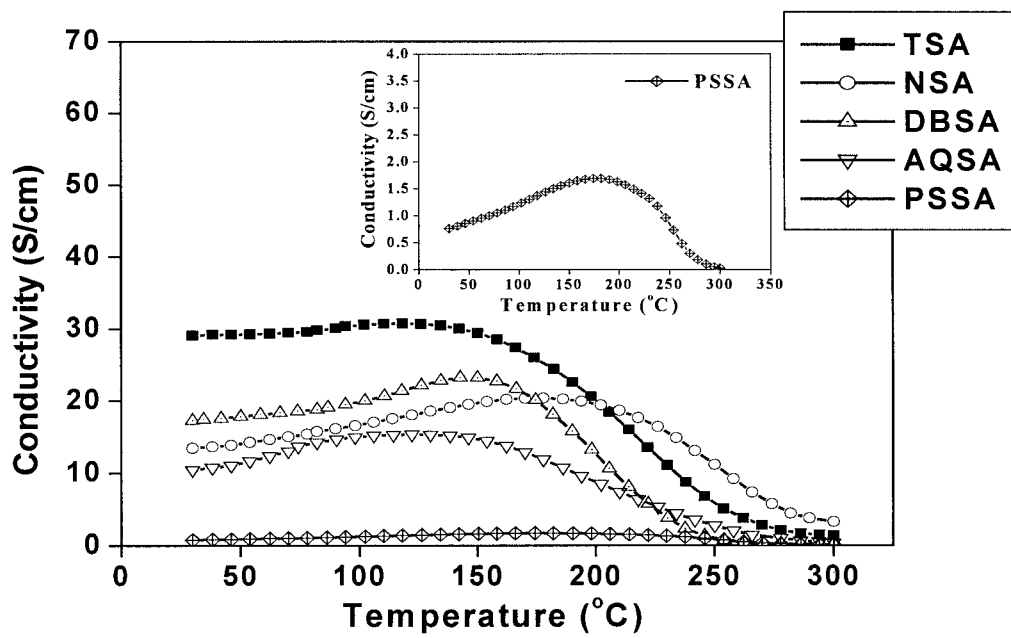
Conductivity of PPy film

The conductivity of PPy films was changed by current density, synthesis temperature, monomer and dopant concentration, and series of dopant.² Optimum conditions of electrochemical polymerization such as temperature, concentration, and current density were previously determined by other researchers.^{11,12,14} Polymerization was performed in an aqueous solution of 0.2 mol/L pyrrole and 0.1 mol/L dopant at 5°C for 2 h under a constant power source of 1.3 V.

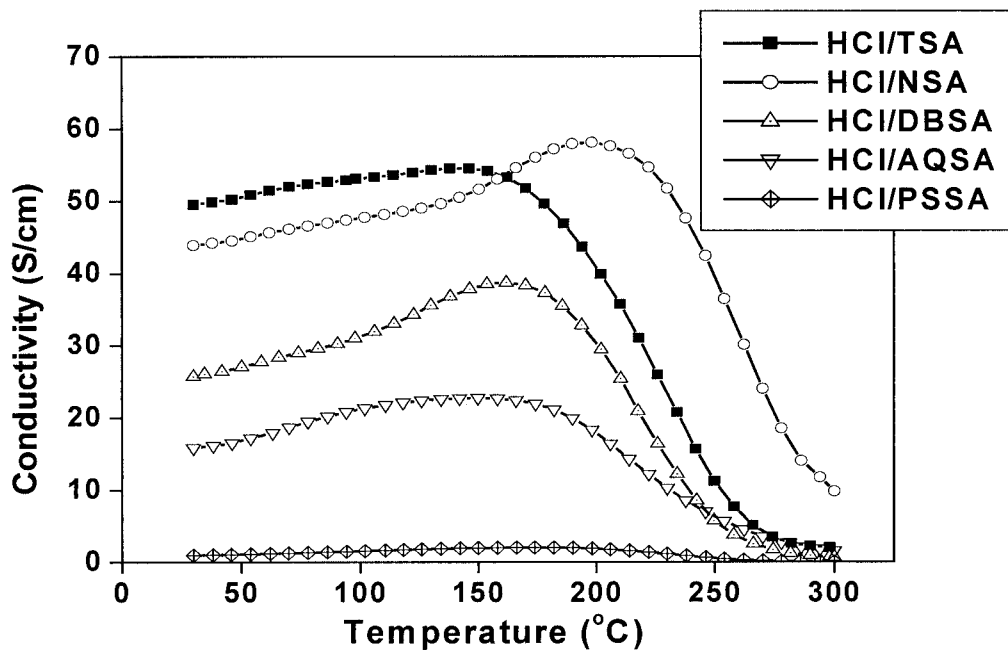
Conductivities of the PPy films doped with various single dopants and their mixtures were measured to investigate differences of conductivity with dopant

TABLE I
Conductivity of PPy Film Doped with Various Single Dopants and Dopant Mixtures

Dopant used	Conductivity at room temperature (S/cm)
TSA	28.6
HCl/TSA (1/1)	48.9
NSA	13.1
HCl/NSA (1/1)	43.3
DBSA	11.2
HCl/DBSA (1/1)	15.2
AQSA	9.0
HCl/AQSA (1/1)	15.3
PSSA	0.8
HCl/PSSA (1/1)	1.0



(a) single dopant



(b) dopant mixture

Figure 1 Conductivity changes with increasing temperature on electropolymerized PPy film doped with various dopants.

size and dopant system. As shown in Table I, changes in the conductivity are related to different conformations of PPy molecules induced by the dopant ion.^{11,15} As the molecular mass of dopant decreases, the con-

ductivity of film increases because the more planar and smaller dopant anion leads to formation of more conductive PPy films. As the size of dopant increases, the conjugation length (i.e., the length of an intramo-

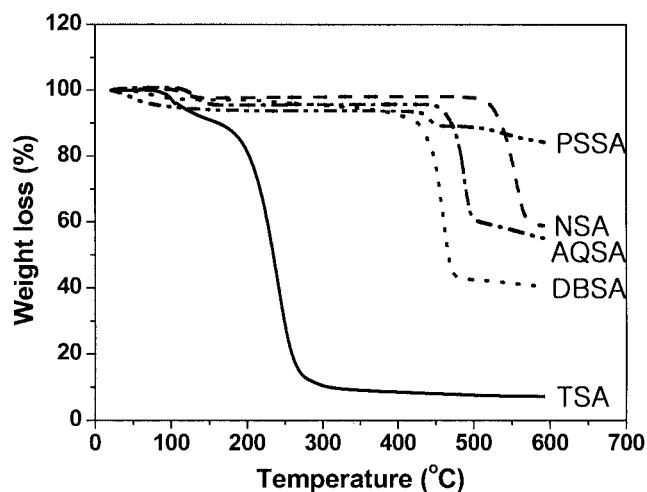


Figure 2 TGA curves of dopant anion with N_2 purging at the scan rate of $10^\circ\text{C}/\text{min}$.

lecular conduction path) of a polymer chain decreases. In addition, as the size of dopant increases, the inter-chain interaction of film is reduced because of the steric hindrance of dopant. Therefore, the conductivity of film doped with a relatively large size dopant was decreased.¹⁶

By mixing each dopant with HCl, the conductivity of PPy film was improved.¹⁸ Generally, the conductivity of film doped with inorganic anions such as Cl^- , ClO_4^- , SO_4^{2-} , and HSO_4^- is higher than that of the film doped with aromatic dopants because of the smaller molecular structure and stronger acidity.^{19–21} Therefore, the conductivity of film doped with the dopant mixtures with HCl was higher than that of the single dopant used in the same dopant series.

Thermal stability of film doped with various dopants

Temperature dependency

The dopant anion used during polymerization has a profound influence on the stability of the resulting film. Figure 1 shows changes in the conductivity of electrochemically synthesized polypyrrole film doped with various dopants and dopant mixtures as the temperature increases. For the film doped with TSA, DBSA, and AQSA, the conductivity increased as the temperature increased up to about 150°C and then rapidly decreased, whereas the conductivity of the film doped with NSA and PSSA started to decrease as the temperature reached 200°C .

The initial increase in conductivity can be considered by the fact that molecular chains of polymer are fully rearranged by heating and offer a flowing route to electrons.

In the case of a dopant mixture system, the temperature dependency of conductivity revealed a trend

similar to that of a single dopant. As the molecular size of single dopants and cooperating dopants with HCl was increased, the temperature dependency on the conductivity of PPy film was decreased. Moreover, TGA result of dopant, as shown in Figure 2, confirmed that the thermal stability of PPy film was closely related with stability of the dopant.

Ageing temperature and time dependency

To investigate the thermal stability of film, the thermal ageing of the PPy films was performed at 100 , 150 , and 200°C for 20 h in an oven. Figure 3 shows the ratio of the conductivity values of PPy film before (σ_0) and after (σ) ageing at a certain temperature for 20 h.

From the result of temperature dependency of conductivity, the degree of the conductivity decrement of PPy film at 100°C was not much greater than that at other temperatures. The conductivity of PPy film decreased gradually as the temperature increased. More than 90% of the film conductivity was lost at 150°C and was completely lost at 200°C .

Generally, the conductivity of PPy doped with HCl, compared against sulfonic acid, is substantially decreased with elevated temperature.¹⁶ As shown in Figure 3, however, the conductivity decrement of the PPy film doped with a single dopant system is larger than that with the dopant mixture system at 100°C . After thermal ageing at 100°C for 20 h, the conductivity of PPy film with a single dopant system was decreased to just 30% of the initial conductivity, whereas the conductivity of PPy film with a dopant mixture system was maintained up to more than 60% of the initial conductivity. Evaporation of dopant is difficult for treating PPy film at 100°C because the interactions between dopant and polymer were higher than the evaporation ability of the dopant. It is considered that interaction between the polymer and chlorine anion was stronger than the interaction between the polymer and other sulfate anions up to 100°C , given that the electron negativity of the chlorine anion is much larger than that of sulfate anion. As the ageing temperature increased to 150 and 200°C , the conductivity was greatly decreased by evaporation of HCl used as a cooperating dopant.

On the other hand, the conductivity decrement of PPy film doped with DBSA showed a tendency to differ from that of other films, given the structural difference between DBSA, which has a long alkyl chain, and the other sulfonic acid. These results also confirmed conductivity decay parameters for each film at each ageing temperature.

In addition, conductivity measurements with time of thermal ageing were performed on PPy film at 100 , 150 , and 200°C , as shown in Figure 4. Conductivity of thermally aged PPy films doped with TSA, HCl/TSA, NSA, and HCl/NSA was decreased, whereas conductivity of

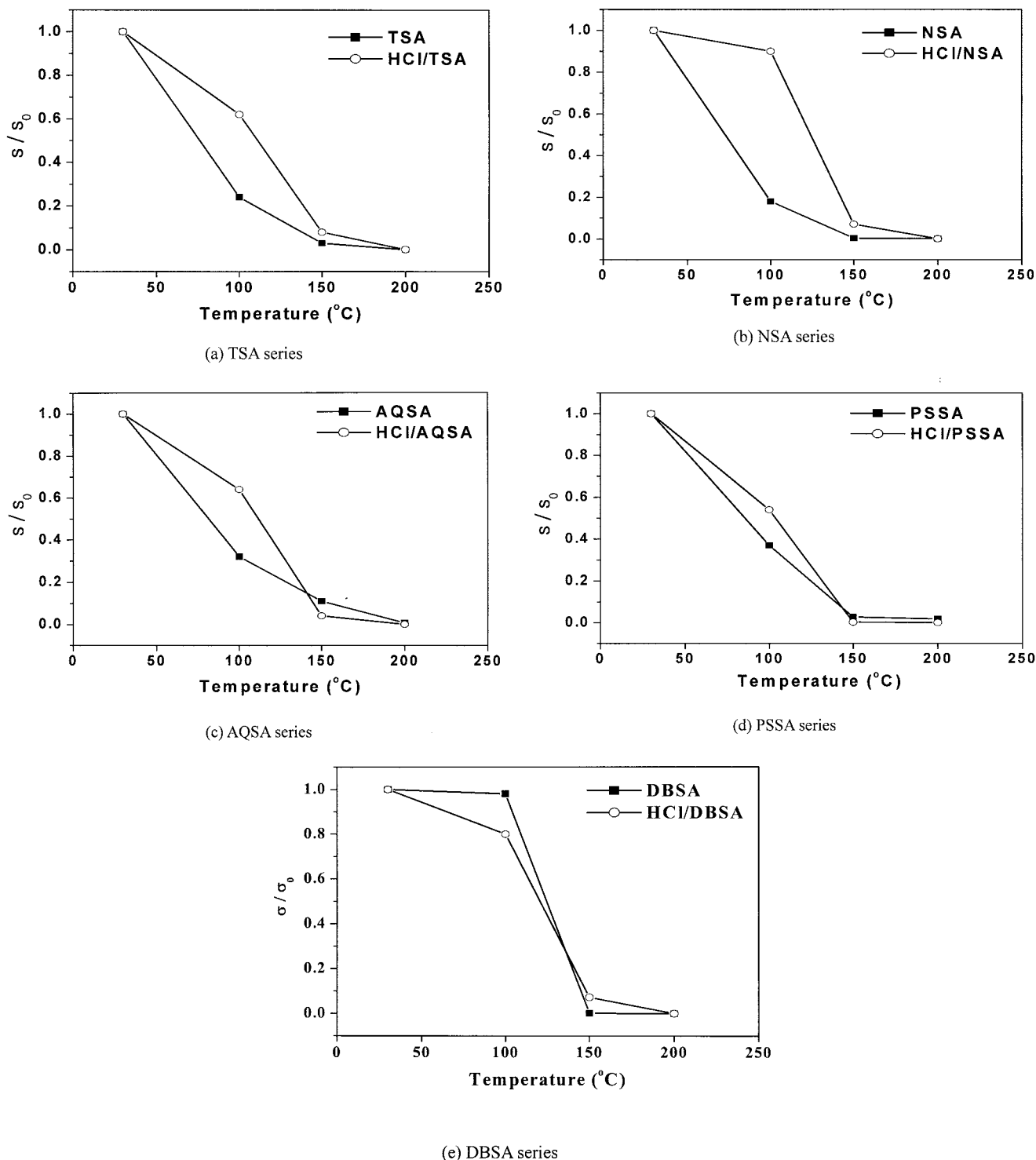


Figure 3 Relative conductivity of aged PPy film under air at room temperature, 100, 150, and 200°C after 20 h (σ_0 : initial conductivity; σ : after ageing for 20 h at a certain temperature).

PPy film doped with DBSA and HCl/DBSA was slightly increased at 100°C because the long alkyl chain of DBSA may be fully rearranged by heating and is then supposed to offer a flowing route to electrons.²²

As ageing temperature increased to 150 and 200°C, the conductivity decrement rate increased. Because of

interaction with HCl, the conductivity of PPy film doped with dopant mixtures was more stable than that doped with single dopants up to 100°C. However, the conductivity of PPy film rapidly decreased at 200°C, especially those with dopant mixture. It was hypothesized either that the dopant used was decom-

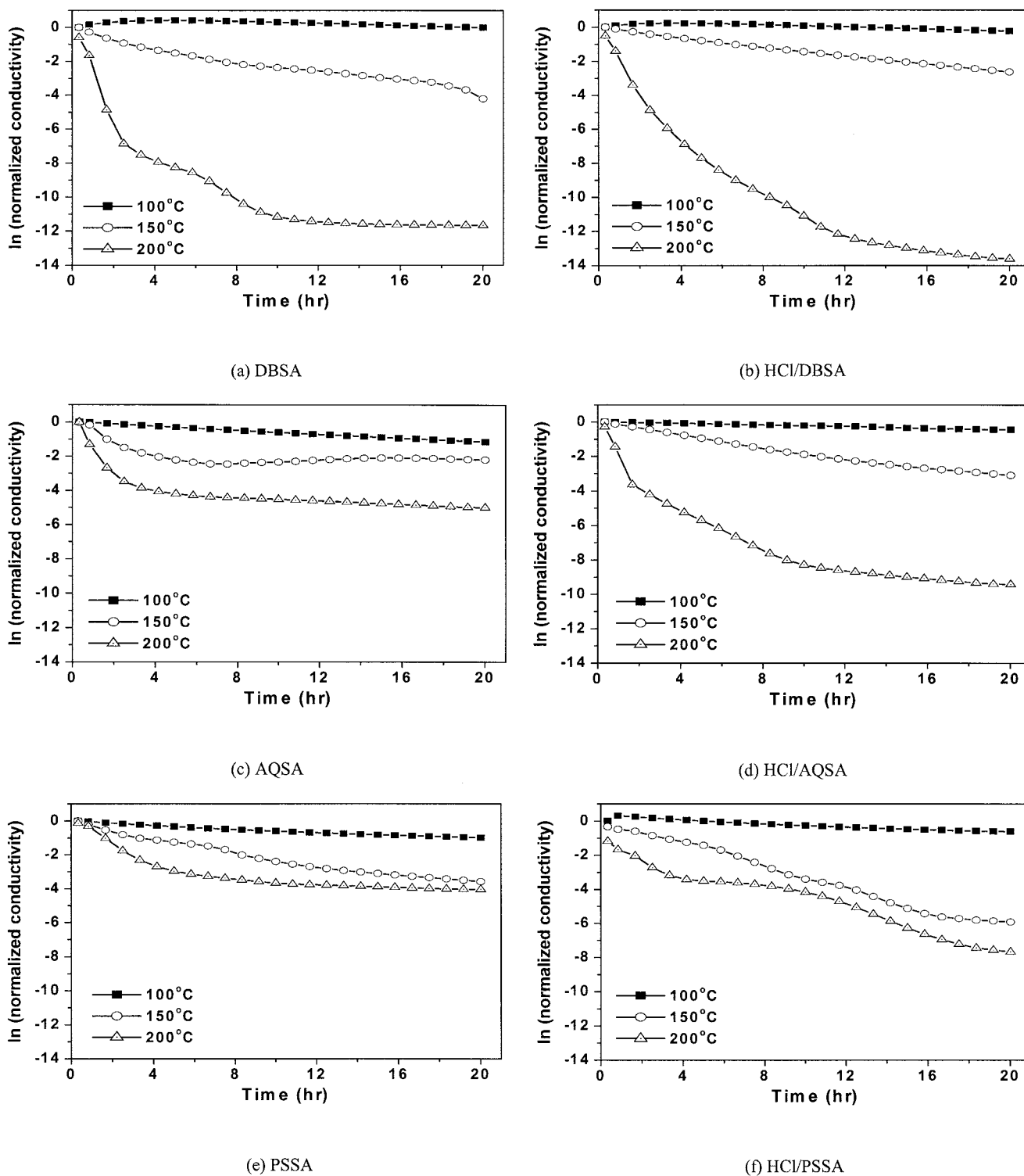
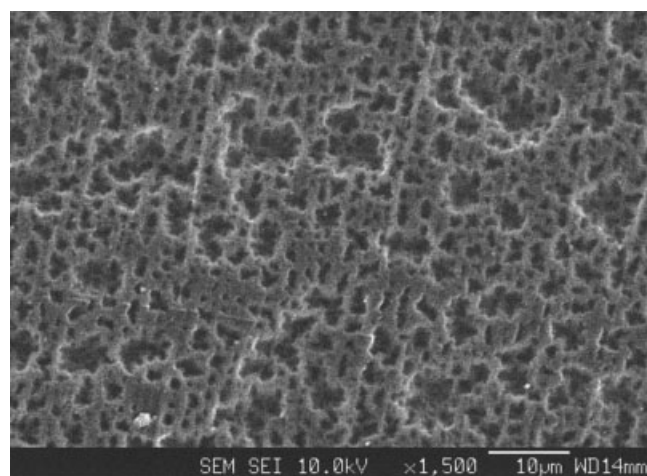


Figure 4 Conductivity decay of PPY films in air at 100, 150, and 200°C for 20 h.

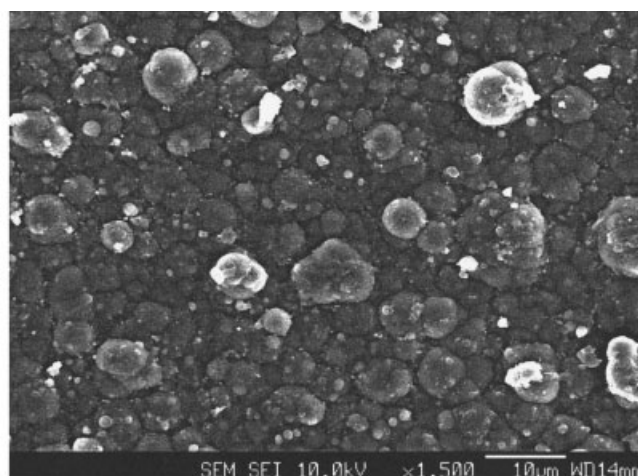
posed or that the linkage between PPy chain and dopant was broken. In other words, the initial conductivity value of film was increased and maintained well up to 100°C by addition of HCl; however, conductivity was reduced significantly by decomposition of HCl at higher temperature.

Morphology of electrochemically synthesized polypyrrole

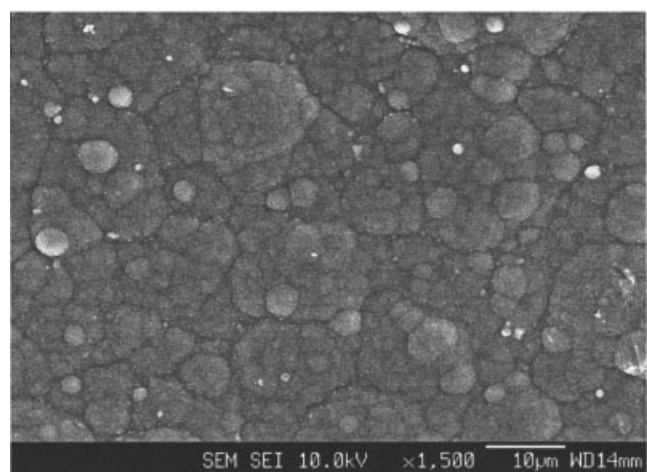
The morphology of PPy is affected by the dopant applied, solvent, and fundamental condition of polymerization such as applied voltage, concentration of chemicals, and reaction temperature.¹¹ The support-



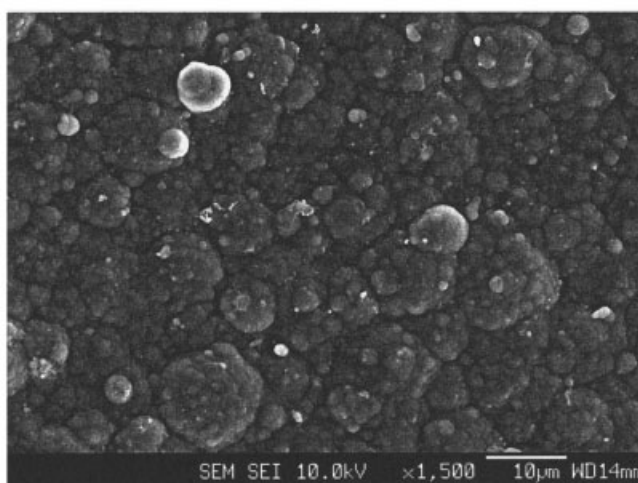
(a) HCl/TSA



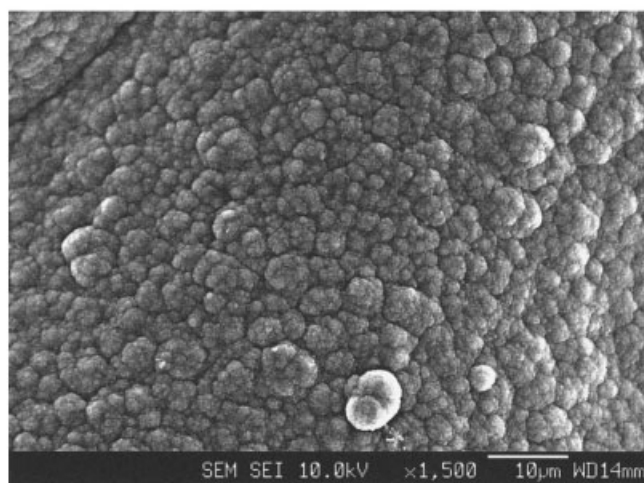
(b) HCl/NSA



(c) HCl/DBSA



(d) HCl/AQSA



(e) HCl/PSSA

Figure 5 Surface morphology of films doped with various dopants ($\times 1500$).

TABLE II
Droplet Dimension of PPy Film Doped with Dopant Mixtures

Dopant mixture	Area (μm^2)	Aspect ratio	Maximum diameter (μm)	Minimum diameter (μm)	Mean diameter (μm)
HCl/NSA	28	1.3	6.5	4.9	5.6
HCl/AQSA	16	1.1	4.4	3.8	4.1
HCl/DBSA	14	1.2	4.3	3.7	4.0
HCl/PSSA	10	1.4	4.0	2.7	3.3

ing dopant and dopant system have a great influence on the morphology of electrodeposited PPy, as shown in Figure 5. Electrochemically synthesized PPy films have either compact globular surface structure or open fibrillar morphology.²³ Film doped with a small size dopant, such as HCl/TSA, has an interconnected, porous, fibrillar-like morphology [Fig. 5(a)]. This fibrillar-like morphology of PPy film doped with TSA series was obtained from PPy that exhibited a progressive nucleation. The conductivity of film with fibrillar morphology was higher than that of film with globular morphology because of the interaction between polymer chains.²⁴ However, film doped with another sulfonic acid system, except TSA, was characterized by a globular form resembling a "crocodile-skin" surface [Fig. 5(b)–(e)]. Data concerning droplets formed by a dopant mixture system are shown in Table II by image analysis. For film doped with HCl/DBSA and HCl/PSSA, as the molecular mass of dopant cooperating with HCl increased, droplets were reduced in size and were well dispersed because of the improved dispersion efficiency by surfactant function of added sulfonic acid.

CONCLUSIONS

Polypyrrole films were prepared by electrochemical polymerization with various dopants and dopant mixtures to investigate the effects of various dopants on the conductivity, thermal stability, and morphology of PPy films.

As the molecular mass of dopant decreased, the conductivity of film increased, which was attributed to the more planar and smaller counter ion, resulting in the formation of more conductive PPy films. For the film doped with TSA, DBSA, and AQSA, the conductivity increased as temperature increased up to about 150°C and then rapidly decreased, whereas the conductivity of film doped with NSA started to decrease as temperature increased up to 200°C. Generally, the conductivity on PPy films doped with dopant mixtures was more stable than that of films doped with single dopants. However, in the case of DBSA series, which has a long alkyl chain, the decrement rate of conductivity differs from that of other films because of the structural difference. The dif-

ference may be attributed to a thermal annealing effect, by which the conformation of the polymer molecules rearranged into a more expanded form, leading to an increased conjugation length.

Electrochemically synthesized PPy films have either compact globular surface or open fibrillar morphology. The film doped with small size dopant such as HCl/TSA had an interconnected porous fibrillar-like morphology. The conductivity of film with fibrillar morphology was higher than that with globular morphology because of the interaction between polymer chains.

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