Thermal Stabilization of Polypyrrole by Incorporation of Aromatic Sulfonate Derivatives as Dopants

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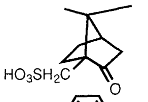
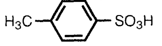
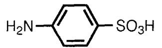
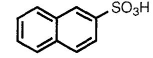
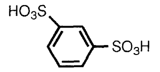
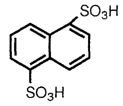
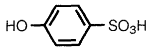
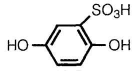
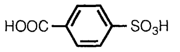
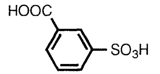
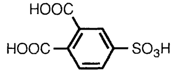
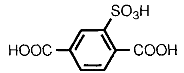
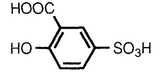
Thermal stability of electric conductivity of polypyrrole (PPy) was improved using aromatic sulfonate derivatives as dopants having mobile hydrogen in the form of acid groups such as sulfonic acid, carboxylic acid, or hydroxide groups. Particularly, when *m*-sulfobenzoic acid or 5-sulfosalicylic acid were used as dopants, the PPy showed high thermal stability of electric conductivity and kept 95% electric conductivity even after heating for 8h at 150 ℃ in air.

Electric conductive polymers have been widely studied for application to electronic devices such as capacitors, batteries, and transistors.[1] Particularly, polypyrrole (PPy) having a high electric conductivity and a high stability has been regarded as a good electrolyte material for solid electrolyte capacitors.[1-4] PPy can be easily obtained by chemical or electrochemical oxidation, in which anions are incorporated during the oxidation as dopants to produce the high electric conductivity. However, most of conducting polymers including PPy are degraded through oxygen and/or water attack in air at high temperature (>100 °C). Although there are an enormous number of papers related to the preparation conditions of PPy with high electric conductivity or mechanical stability, there are only several reports dealing with thermal stability.[3-8] High thermal stability and electric conductivity will provide conducting polymers with extremely wide applications for the practical operation of electronic devices.

PPy films doped with aromatic anions such as *p*-toluene sulfonate or naphthalene sulfonate are reported to have a thermal stability higher than aliphatic anions such as dodecyl sulfate or inorganic anions such as Cl^-, ClO_4^-.[8] The degradation of electric conductive polymers such as polycation-TCNQ[9] and PPy films[10] is significantly caused by a synergistic effect between oxygen and water vapor in a manner similar to the degradation of the commodity polymers, however, the stability of the electric conductivity is significantly improved in the dry nitrogen atmosphere. In addition, PPy electrochemically polymerized with *p*-nitrophenol as an additive was reported to show high thermal stability.[3] It is not sufficient to physically incorporate compounds having mobile hydrogen into PPy because of sublimation of the compounds such as *p*-nitrophenol under high temperatures.

In this study, we used aromatic sulfonate derivatives as dopants for PPy, and prepared the PPy films containing these dopants by electrooxidative polymerization. The dopants have mobile hydrogen and were electrostatically incorporated into PPy in order to suppress PPy oxidation. The thermal stability of the resulting polymers was evaluated based on their electric conductivity in air.

Table 1. Properties of PPy/dopant films

No.	Dopant	density (gcm^{-3})	$\sigma_{B.H.}$ (Scm^{-1})	σ_8/σ_{max} (-)[a]	$\sigma_{A.H.}$ (Scm^{-1})
1	$HOOC\text{-}CH_2\text{-}SO_3H$	0.73	3	0.18	–
2		1.40	130	0.13	–
3		0.88	120	0.33	25
4		not polymerized			
5		1.07	50	0.65	10
6		1.22	50	0.88	35
7		–	80	0.88	64
8		0.91	30	0.90	20
9		not polymerized			
10		0.69	20	0.85	12
11		0.88	50	0.94	50
12		0.57	25	0.68	15
13		–	7	0.86	6
14		1.29	75	0.95	70

a σ_8: σ at 150 °C after 8 h heating
σ_{max}: maximum σ while heating at 150 °C

Electrolyte solutions were used for the electropolymerization containing 0.1 M pyrrole and 0.1 M dopants in aquaous solutions. Pyrrole was purified twice by distillation under a nitrogen atmosphere. The electropolymerization of pyrrole was galvanostatically carried out at 2.5 mA/cm^2 for 20 min on a stainless steel (St) electrode (4 cm x 4 cm) in the solution. A St electrode of the same size was used as a counter electrode. The resulting PPy films were repeatedly rinsed with distilled water and acetone, and then dried in a desiccator for one day. The PPy films were peeled off the electrode as free standing films and dried *in vacuo* for 8h. The electric conductivity of the films was measured by the four-probe method, based on the van deer Pauw theory in a thermoset container.[11]

The relative conductivity (σ/σ_{max}) changes in the PPy with *p*-toluenesulfonate (**3**), **3** with *p*-nitrophenol, 2-naphthalenesulfonate (**5**), or *m*-sulfobenzoic acid (**11**) during heating at 150 ℃ are shown in Figure 1. When a PPy film is heated from room temperature to 150 °C, the electric conductivity initially increases because of an annealing effect[12] and shows a maximum σ_{max}, and then gradually decreases by thermal degradation. The electric conductivity at 150 ℃ after 8h is treated as σ_8. The σ before and after heating (r.t.) are also depicted in the same figure as B.H.

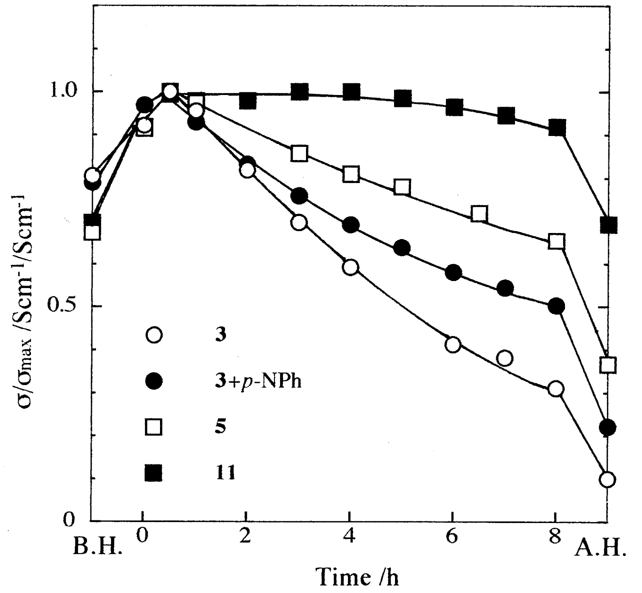


Figure 1. Thermal stability of PPy at 150°C in air. B.H. : Before heating (r.t.), A.H. : After heating (r.t.)

and A.H., respectively. Table 1 shows the structure of dopants corresponding to these numbers. **3** has generally been used as a dopant which produces a relatively high electric conductivity and a high thermal stability.[3] Under our experimental conditions, the σ/σ_{max} gradually decreased; the σ_8 was less than 25 % of σ_{max}. *p*-Nitrophenol was used as an additive to PPy where **3** was doped for thermal stabilization. In the experiment, *p*-nitrophenol aquaous solution (50mM) was soaked into the film of PPy with **3** until 20 mol% to pyrrole unit, and dried *in vacuo*. Though the adding effect was confirmed on the thermal stabilization,[3] σ/σ_{max} gradually decreased. After the measurements, a yellow oily material identified as *p*-nitrophenol was attached to the wall of the vessel, meaning the removal of the *p*-nitrophenol from the PPy by sublimation at 150 °C. On the other hand, **5** was also recently reported as a dopant of PPy,[8] and provides a higher thermal stability than the two dopants have already mentioned. However, a slow decrease in σ/σ_{max} was confirmed. These results indicate that dopants, which have been reported so far, show an insufficient thermal stabilities at 150 °C in air. On the other hand, reduction in the conductivity of PPy with **11** could not be observed even after heating for 8h at 150 °C in air as shown in Figure 1.

Table 1 summarizes properties of the electropolymerized PPy films doped with various dopants. The thermal stability of PPy could be evaluated using the electric conductivity ratio of σ_8/σ_{max} at 150 °C in air. Samples **1** to **5** have one sulfonate group and a relatively low thermal stability, while aromatic sulfonate derivatives with acid groups show a significantly higher thermal stability. The order of the stabilization effect of acid groups is -COOH > -OH > $-SO_3H$. PPy containing **11** or 5-sulfosalicylic acid (**14**) showed the highest thermal stability and kept 95% electric conductivity even after heating for 8h at 150 °C in air. It is also interesting that the dopants having the same substituent at different positions have different thermal stabilities (compare **10** to **11** and **12** to **13**). Dopants such as sulfo acetic acid (**1**), which has no aromatic group, were confirmed to have no thermal stabilization effect on PPy.

In spite of the same polymerization conditions, different densities of the resulting PPy films were obtained due to the different packing of dopants in PPy and/or PPy chains in the film. There is no relation of the density of PPy film to the initial electric conductivity, $\sigma_{B.H.}$, and to the thermal stability of the conductivity, σ_8/σ_{max}. Furthermore, there is also no relationship between $\sigma_{B.H.}$ and σ_8/σ_{max}, suggesting the orientation of PPy does not contribute to the thermal stability. The aromatic sulfonate derivatives having acid groups such as sulfonic acid, carboxylic acid, or hydroxide groups have a remarkable effect on the thermal stabilization. Preliminary, the activation energy for the thermal degradation were obtained, based on the assumption that the initial decrease obeys the first-order kinetics. **14** is as high as 41.3 kJmol^{-1}, in comparison with **3** (30.0 kJmol^{-1}). The half-life of the conductivity at 200°C for **14** is estimated to 16h showing remarkable stability.

The oxidation mechanism of commodity polymers is generally initiated from the elimination of hydrogen from the polymer, leading to the adduct of the oxygen molecule to the aromatic carbon radical and the resulting peroxide radical also takes hydrogen from the polymer. This oxidation cycle is repeated by absorbing oxygen molecules. Stabilization by antioxidants is due to the transfer of mobile hydrogen to the dehydrogenated site of the polymer before the adduct of oxygen. The acid groups of our dopants would work as the source of mobile hydrogen. Another important characteristic of the additives is the existence of at least one sulfonic acid group playing an important role in the electrostatically fixation of the additives to the polymer matrix. The more detail mechanism for oxidation and protection is under study.

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