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Antioxidative Dopant for Thermal-Resisting Polypyrrole and Its Mechanism

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In order to improve the thermal stability of the electric conductivity of polypyrrole (PPy), a series of aromatic sulfonate derivatives having acid-type substitute groups, such as –COOH, –OH, and $-SO_3H$, were used as dopants. The PPy doped with these dopants showed excellent thermal stability of their electric conductivity, even at 150 °C in air. Especially, 2-hydroxy-5-sulfobenzoic acid, having one –COOH and one –OH, provided the highest thermal stability; the doped PPy maintained 95% of its initial conductivity, even after heating for 8 h at 150 °C in air. Furthermore, the PPy showed 20-times higher stability against long-term heating at 125 °C for 1000 h in comparison with PPy doped with *p*-methylbenzenesulfonic acid, which is conventionally used to provide high thermal stability. The thermal-stabilization mechanism has suggested that dopants having acidic substituents should suppress proton dissociation from the N-position of the PPy main chain and keep the π-conjugation structure by supplying a proton from the acidic groups. Such a proton supplement was confirmed by the IR spectroscopy of deuterized PPy.

Since the electric conductivity of polypyrrole (PPy) was confirmed by Diaz in 1979, many efforts have been made to increase the electric conductivity.[1,2] There have been many reports on the electric-conduction mechanism and chemical structure of conductive polymers, such as PPy, polyaniline (PAn), polythiophene (PTh), etc.[3,4] PPy is the most stable electrically conductive polymer, and its wide feasibility is well-known. Therefore, it has been applied in the electronic field as capacitors, electrodes for batteries, sensors, etc.[5—7] Structural analyses using NMR and Raman spectroscopy were reported by Truong et al. and Tachikawa et al.,[8—10] as related to its autoxidation. In general, a high electric conductivity of conductive polymers is attained by dopants which stabilize the polaron and bipolaron states as counter anions.[6,11—13] However, those states are unstable against oxidation by a nucleophilic attack of an oxygen molecule to radicals or localized charges.[14] Especially, destruction of the π-conjugated structure by oxygen binding is enhanced at high temperature, which results in a remarkable decrease in the conductivity.[15] Because such oxidation is initiated due to the formation of radicals or a change in the polarized states by the elimination of hydrogen (or proton), it is important to prevent any conductivity decrease by supplementing the eliminated hydrogen (or proton).[16]

We have found a new type of dopant which provides a high electric conductivity and high thermal stability for the host PPy.[17] They are a series of aromatic sulfonate derivatives with acidic substituents, such as carboxyl or hydroxy groups, which provide excellent thermal stability of the electric conductivity, which has until now never been reported. Though the thermal stability is considered to be the most important issue for the application of electric conductive polymers, studies of the thermal resistance of electrically conductive polymers have been very few compared with the other thermally resistive polymers. In this paper, the thermal stability of PPy using the new type of dopants are described, and the stabilization mechanism of the new dopants is discussed using spectroscopical analyses.

Experimental

Materials. Pyrrole was purchased from Kanto Chemical Co. and purified by distillation. All additives and dopants are listed in Tables 1 and 2 and numbered. They were purchased from Kanto Chemical Co.

Electropolymerization of Pyrrole. PPy films were prepared on 4 cm×4 cm stainless-steel electrodes by electropolymerization[3,17] at 2.5 mA cm^{-2} for 20 min vs. an Ag/AgCl electrode as a reference under nitrogen in distilled acetonitrile solutions containing 0.1 M freshly distilled pyrrole ($1 M = 1 mol dm^{-3}$) and 0.1 M supporting electrolytes, the sodium salts of dopants. The resulting PPy film was washed three times with distilled water and then acetone, and dried in vacuo for 12 h at room temperature. Films having a thickness of 20—50 μm were obtained as a free-standing type. Deuterium-labelled PPy was synthesized by electropolymerization of pyrrole-d_5 (Aldrich) in the same way as described above.

Density of PPy. The density of the electropolymerized PPy films was calculated from the weight and apparent volume. The specific of PPy was measured using a density gradient centrifugation method. The density gradient (1.0—1.8 g cm^{-3}) was prepared by using CsCl aq solutions with different concentrations and then calibrated.

Thermal Property of PPy. The electric conductivity of the films was measured using a four-probe method based on the van der

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Table 1. Properties of PPy Added Various Antioxidants

No.	Additive	σ_p [a)]	$\sigma_{\text{B.H.}}$ / S cm^{-1}	$\sigma_{\text{A.H.}}/\sigma_{\text{B.H.}}$
1	2,6-Dinitrophenol	1.56	9	0.20
2	2,4-Dinitrophenol	1.56	18	0.06
3	Pentachlorophenol	1.43	13	0.35
4	2-Methyl-4,6-dinitrophenol	1.39	10	0.20
5	2-Hydroxy-3-nitrobenzoic acid	1.23	16	0.30
6	*p*-Nitrophenol	0.78	29	0.45
7	*p*-Hydroxybenzoic acid	0.45	18	0.34
8	*p*-Bromophenol	0.23	23	0.24
9	*p*-Hydroxybenzaldehyde	0.22	38	0.29
10	3,5-Di-*t*-butyl-4-hydroxybenzaldehyde	−0.18	31	0.24
11	*p*-Methoxyphenol	−0.27	19	0.26
12	2,6-Di-*t*-butyl-phenol	−0.40	15	0.18
13	2,6-Di-*t*-butyl-4-methylphenol	−0.57	15	0.20
—	Non addition	—	23	0.26

a) σ_p: substituent constant.

Table 2. Properties of PPy Doped with Various Sulfonic Acid Derivatives

No.	Dopant	*d* of film / g cm^{-3}	*d* of PPy / g cm^{-3}	$\sigma_{\text{B.H.}}$ / S cm^{-1}	$\sigma_8/\sigma_{\max}$ (—)[a)]	$\sigma_{\text{A.H.}}$ / S cm^{-1}
14	Sulfoethanoic acid	0.73	1.49	3	0.18	—
15	7,7-Dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonic acid	1.35	1.40	130	0.13	—
16	*p*-Methylbenzenesulfonic acid	0.88	1.36	120	0.33	25
17	*p*-Aminobenzenesulfonic acid			Not polymerized		
18	2-Naphthalenesulfonic acid	1.07	1.37	50	0.65	10
19	*m*-Benzenedisulfonic acid	1.22	1.43	50	0.88	35
20	1,5-Naphthalenedisulfonic acid	—	—	80	0.88	64
21	*p*-Hydroxybenzenesulfonic acid	0.91	1.38	30	0.90	20
22	2,5-Dihydroxybenzenesulfonic acid			Not polymerized		
23	*p*-Sulfobenzoic acid	0.69	1.39	20	0.85	12
24	*m*-Sulfobenzoic acid	0.88	1.39	50	0.94	50
25	4-Sulfo-1,2-benzenedicarboxylic acid	0.57	—	25	0.68	15
26	2-Sulfo-1,4-benzenedicarboxylic acid	—	—	7	0.86	6
27	2-Hydroxy-5-sulfobenzoic acid	1.29	1.42	75	0.95	70
28	*p*-Dodecylbenzenesulfonic acid	1.20	1.32	25	0.25	5

a) σ_8: σ at 150 °C after 8 h heating. $\sigma_{\max}$: maximum σ while heating at 150 °C.

Pauw theory with a thermoset container. Generally, when a PPy film is heated from room temperature to 150 °C, the electric conductivity initially increases, shows a maximum ($\sigma_{\max}$), and then gradually decreases due to thermal degradation. We evaluated their thermal stability based on $\sigma_t/\sigma_{\max}$, where σ_t is the conductivity at 150 °C after heating for *t* h, and $\sigma_{\text{B.H.}}$ and $\sigma_{\text{A.H.}}$ are the conductivities at room temperature before and after heating at 150 °C, respectively. From the decreasing profiles of the electric conductivity at various temperatures, the time when the electric conductivity decreased to half of the initial conductivity ($t_{1/2}$ (s)) was determined. The decreasing rate constant (k) was calculated from $t_{1/2}$. For a measurement of the long-term stability, the temperature was set at 125 °C.

Spectral Analyses of PPy. Changes in the electric states of PPy films at room temperature before and after heating at 150 °C were measured by a reflective method using a UV-2200 (Shimadzu) at 150 °C. Changes in the IR spectra during heating were monitored using a MFT-2000 (JASCO).

Results and Discussion

The Electric Conductivity of PPy at High Temperature in Air. The electric conductivity of polypyrrole (PPy) electropolymerized and doped with *p*-methylbenzenesulfonic acid (**16**), which had been recognized to give a relatively high thermal stabilization,[13] was monitored at 150 °C in nitrogen and air, as shown in Fig. 1. Both samples have a similar profile at the beginning, namely the increment of the electric conductivity. This is considered to be an annealing effect that enhances the orientation of the PPy chains, as reported by Turcu et al.,[18] or a semiconductive effect. The conductivity of PPy in air decreased remarkably to 33% of $\sigma_{\max}$ after 8 h at 150 °C, the main reason of which is considered to be due to oxidation of the main chain, resulting in a loss of π-conjugation. Truong and other researchers reported

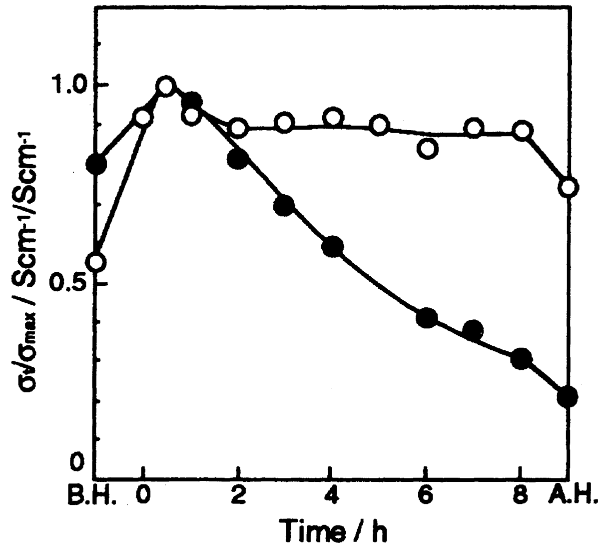

Fig. 1. The time courses of electric conductivity of polypyrrole (PPy) under (○) N_2 or (●) air.

that a decrease in the electric conductivity of PPy was caused by autoxidation, which was evidenced by an increase in the absorption bonds attributed to C=O and C–OH in FT-IR or Raman spectroscopy.[11] They also indicated the relationship between oxygen diffusion into PPy films and the occurrence of PPy oxidation.[11] On the other hand, in a nitrogen atmosphere, the electric conductivity showed a small reduction in conductivity to 89% of σ_{max}, and then maintained a constant value even after 8 h heating at 150 °C.[15]

Thermal Stabilization of the Electric Conductivity of PPy. It is generally considered for the thermal degradation of the usual polymers that the elimination of hydrogen from the polymer chains occurs at high temperatures, and an oxygen molecule reacts with the generated radical in air. In the case of PPy, this would stop the extension of the π-conjugation of PPy. First, antioxidants were added in order to scavenge the radical by supplying hydrogen to the main chain radical before oxygen binding. Considering the antioxidation mechanism for phenol derivatives as radical scavengers, hindered-type phenol derivatives having bulky or electron-donating groups, such as *t*-butyl or methyl groups, are favorable and are incorporated into the PPy. However, the thermal stability became considerably worse in comparison to that in the absence of such radical scavengers (Table 1). The most effective additive of the phenol derivatives was *p*-nitrophenol (**6**) which had an NO_2 group with a rather high electron-withdrawing property. This effect has already been reported by Fukuyama et al.[6] The above-described results suggest that the phenol derivatives may tend to become phenolates after supplying a proton, rather than becoming phenoxyl radicals after releasing hydrogen atoms. Namely, the suppression of PPy oxidation would be performed by the proton supply rather than the hydrogen supply. Furthermore, the bulky substituent is considered to lower the electric conductivity by disturbing the plane orientation of the PPy main chain. Moreover, the antioxidants physically incorporated into PPy have their effects continued for a short period at high temperature because of sublimation and/or phase separation.

From the exploration of antioxidative compounds to be incorporated into the PPy more effective and stably, we have proposed the aromatic sulfonate derivatives which acted as dopants and had more than one acidic substituent, such as a carboxyl (–COOH), hydroxy (–OH), or sulfo group ($-SO_3H$) to supply protons.[17] Figure 2 shows the change in the electric conductivity of PPy at 150 °C in air. As references, we studied dopants without any acidic substituents, such as **16**[8] or alkylnaphthalenesulfonic acid (**18**),[13] which have been reported to have a high thermal-stabilization effect. The PPy with these dopants showed a significant reduction of the electric conductivity at 150 °C, while the dopants with acidic substituents, i.e., 2-hydroxy-5-sulfobenzoic acid (**27**), showed a remarkable thermal-stabilization effect that had never been reported. Table 2 summarizes the thermal stability of PPy with various dopant anions, including acidic aromatic sulfonates. A significant decrease in the electric conductivity after heating at 150 °C was observed for 5 samples from the top. All of them do not have any acidic substituents. On the other hand, dopant anions having acidic substituents showed high thermal stabilities. Especially, *m*-sulfobenzoic acid (**24**) and **27** showed an excellent thermal stability; namely, there was no decrease in the electric conductivity for this heating condition.

Figure 3 gives the change in the electric conductivity of PPy doped with **16**, **21**, **24**, and **27** at 125 °C for 1000 h. A dopant having acidic substituents, such as carboxy and/or hydroxy groups, also showed an excellent thermal stability against long-term heating. The half-lives of the electric conductivity of PPy doped with **16**, **21**, **24**, and **27** were 20.0, 33.9, 83.9, and 108.1 h, respectively. Therefore, a dopant having a carboxy group has a higher stability than that having a hydroxy group, and a dopant having two such

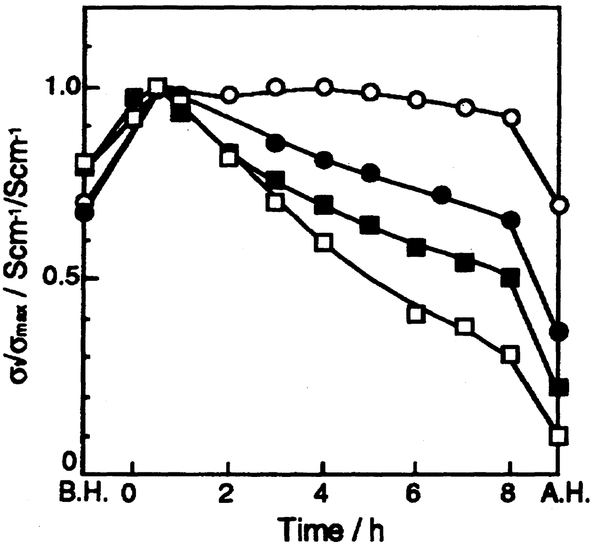

Fig. 2. Thermal stabilization of electric conductivity of PPy by dopant against heating at 150 °C in air: (○) **27**, (●) **18**, (□) **16**, (■) **16**+**6**.

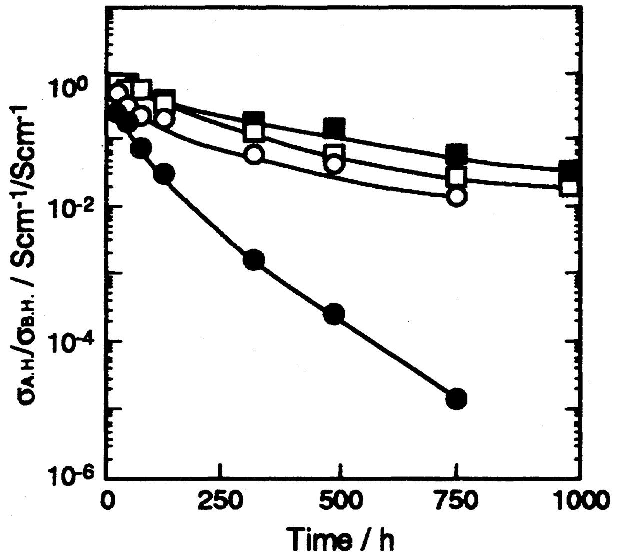

Fig. 3. Long-term stability of PPy at 125 °C in air: (●) **16**, (○) **21**, (□) **24**, (■) **27**.

acidic substituents showed the highest long-term stability. Especially, decreasing the ratio of the electric conductivity for PPy with **27** after 1000 h-heating was only 1/20. While a considerable decrease was observed for PPy with **16**, it was $1/10^5$ after 750 h-heating, and the conductivity became impossible to measure.

The surface of the PPy film obtained by electroxidative polymerization using scanning electron microscopy (SEM) can be confirmed as the cauliflower-like growth of PPy. The decrease in the electric conductivity of PPy should mainly be due to the oxidation of PPy by oxygen. The stability is considered to be related to the density or oxygen permeability of the PPy films, because the membrane permeability would depend on the density of the membrane if the kind of polymer was the same. Table 2 also shows the apparent density of the PPy film calculated from its weight and apparent volume measured by SEM, as well as the specific gravity of PPy. The apparent density of the film had a wide range from 0.57 to 1.35 $\mathrm{g\,cm^{-3}}$, depending on the morphology of the film, such as a sponge-like structure. However, the specific gravity (density) of PPy was from 1.32 to 1.49 $\mathrm{g\,cm^{-3}}$ with a narrower distribution. There was no relationship in the filling factors calculated from the densities of the film and PPy with thermal stability. For example, because samples doped with **15** and dodecylbenzenesulfonic acid (**28**) had high filling factors, they were expected to have a low oxygen permeability, and thus high thermal stability; however, their thermal stabilities were quite low. Therefore, the membrane density or oxygen permeability, which is thought to be influenced by the filling factor, does not always lead to a higher thermal stability.

Electric State by UV-vis Spectroscopy. The electric states, such as the polaron and bipolaron of PPy, can be clearly observed by UV-vis spectroscopy. The refractive UV-vis spectra were used to analyze the electric states of PPy during heating at 150 °C in air. The spectral changes of PPy doped with **27** were compared with PPy doped with **16**, and are shown in Fig. 4. Before heating, polaron and bipolaron bands were observed at around 500 and 700 nm for both samples, respectively.[19,20] The bipolaron peak of the **16** system was lowered during heating, corresponding to a decrease in the electric conductivity. Though the PPy doped with **27** showed a small reduction in the bipolaron peak at the beginning of heating, 86% of the electric conductivity was maintained, even after 8 h of heating. According to the band energy, the bipolaron structure affords the main portion of the electric conduction. Therefore, a reduction in the bipolaron structure due to heating should result in a decrease in the electric conductivity. As a conclusion, maintenance of the bipolaron structure of PPy by **27** expresses the high thermal stability of PPy versus heating.

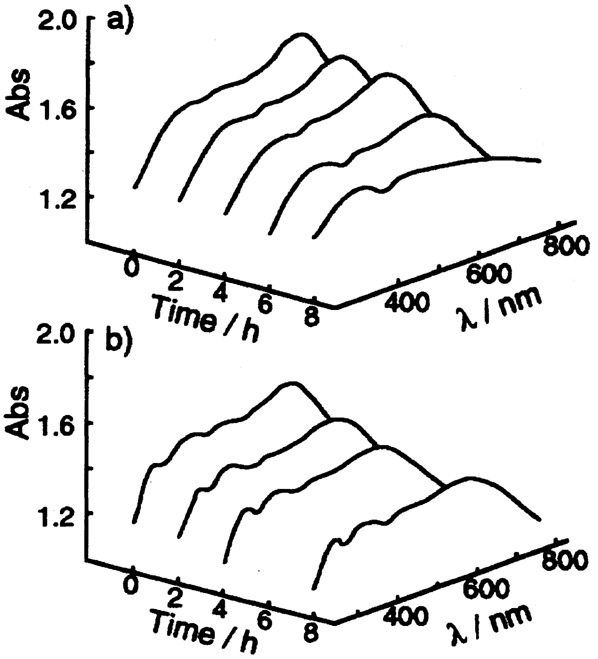

Fig. 4. Change of UV spectra of PPy doped with **16** (a) or **27** (b) heating at 150 °C in air.

Microscopical IR Observation of Deuterized PPy. The above-described results suggest that the effect of high thermal stabilization would be expected for compounds having acidic substituents, such as –COOH, –OH, and $-SO_3H$. Namely, at high temperature, the elimination of hydrogen or protons from the PPy main chain is considered to be suppressed due to their supplement from the dopants. Therefore, we prepared electropolymerized PPy films in which all hydrogen atoms were replaced with deuterium atoms, and the change in the IR spectra during heating at 150 °C in air was observed with microscopic IR.[3,21] This method can provide a high S/N ratio, even for PPy films, which were difficult to observe using normal IR because of the π-conjugated polymers. As shown in Fig. 5(a) and (b), deuterized PPy has a C–D bending vibration mode at 1020 $\mathrm{cm^{-1}}$, and N–D bending vibration modes at 1420 and 1535 $\mathrm{cm^{-1}}$. There was no significant change in the C–D mode during heating, whereas a peak shift was observed for the N–D modes. Especially, 1535

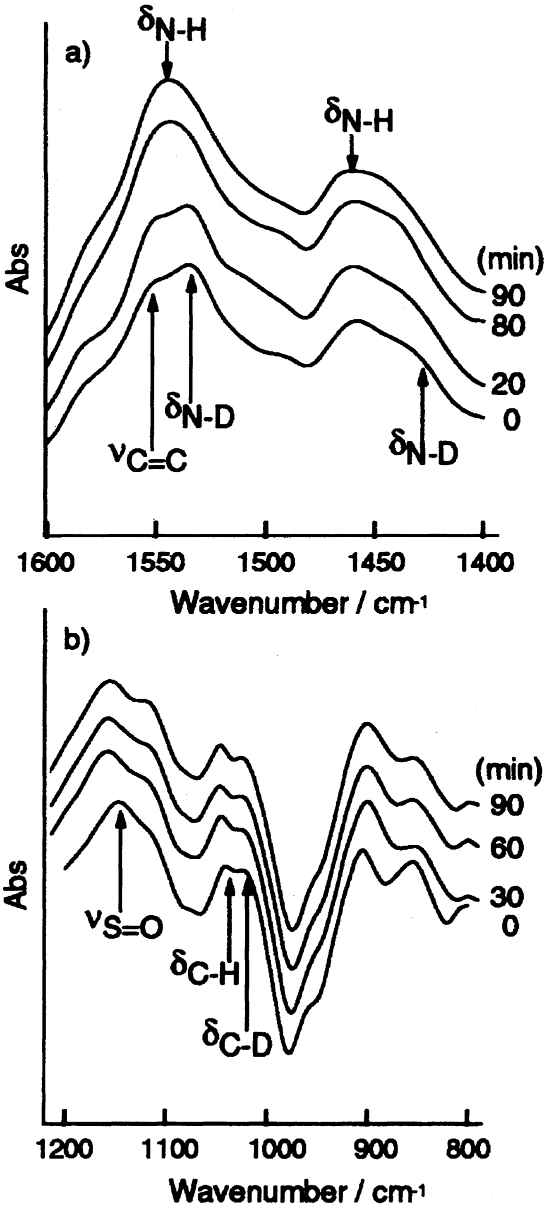

Fig. 5. Change of IR spectra of d-PPy/**27** heating at 150 °C.

cm^{-1} shifted to 1545 cm^{-1} after heating for 90 min in air, strongly suggesting a D–H exchange among the N–D of the PPy main chain and the proton of the acidic substituents of **27**, while **16** with no acidic groups showed a decrease in the N–D bending mode, followed by a slow appearance of the C=O vibration mode at 1716 cm^{-1}.

From the IR spectral change of deuterized PPy, proton dissociation from the N-position of PPy should result in a reduction in the positive charge of the main chain with a bipolaron structure, resulting in the so-called dedoping. Such a dedoping process leads to a disappearance of the bipolaron structure and the production of chemically instable points on the main chain; also, autoxidation would proceed from such unstable PPy points during heating in air. Lei and Martin[16)] prepared PPy doped with superoxide anions by interaction of pristine PPy with O_2. From their FT-IR and XPS data, after the exposure of the polymer to O_2 for 20 h at room temperature, deprotonation of the pyrrole nitrogen was confirmed. Because our PPy was doped electrochemically with aromatic sulfonate, the doping level of the superoxide anion should be low; however, a similar process would occur during long-time heating at high temperature.

On the other hand, **27**, which has acidic substituents, would suppress proton dissociation from the N-position of PPy due to an increase in the proton concentration in the polymer matrix and by maintaining the bipolaron structure. The protons should be supplied from the acidic groups of the dopant. Especially, at high temperatures above 200 °C, **27** converts to *p*-hydroxybenzenesulfonate by releasing CO_2, which was confirmed by IR, Raman, and GC-MS. However, the OH group remaining after the elimination of CO_2 would contribute to the thermal stabilization of PPy.

Conclusions

By incorporating aromatic sulfonates having acidic substituents into PPy as dopants, the thermal stability of the electric conductivity was remarkably improved. The degradation of the electric conductivity would have been due to proton dissociation from the N-position of the PPy main chain, the destruction of the bipolaron structure of the PPy main chain due to the proton supplement from acidic substituents of the dopant. Aromatic sulfonate having acidic substituents should be a useful dopant for providing the high electric conductivity and proton to the proton-deficient position of the PPy. This would contribute to the prevention of an initial change in the PPy structure, thus maintaining the bipolaron structure. The construction of this system should be useful in the application fields for electron conductive polymers in electric devices because of the high chemical stability in air, which has been a serious problem for electron-conductive polymers.

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