Stability of Polyaniline Synthesized by a Doping–Dedoping–Redoping Method

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ABSTRACT: Stability, including thermal stability, conductivity stability in air and after thermal treatment (100–200°C), of the polyaniline (PANI) films synthesized by a doping–dedoping–redoping method was investigated. It was found that thermogravimetric analysis (TGA) curves undergo three steps: loss of water or solvent, dedoping and decomposition, and those depend on the counterions. Compared with PANI films doped with camphor sulfonic acid (CSA) in *m*-cresol, the thermal stability of the doped PANI films is improved by the new method, and thermal stability in the order of PANI–H_3PO_4 > PANI–*p*-TSA > PANI–H_2SO_4 > PANI–HCl, PANI–$HClO_4$ > PANI–CSA was observed. The conductivity of the doped PANI films at room temperature was reduced after thermal treatment, and it is dependent of the counterions. It was found that the conductivity stability of PANI–*p*-TSA and PANI–CSA is the best below 200°C. When the doped PANI films were placed in air, their conductivity decrease slowly with time due to deproton, and also depends on the counterions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 615–621, 1999

Key words: polyaniline stability; doping–dedoping–redoping method

INTRODUCTION

In general, a granular morphology of polyaniline (PANI) doped with HCl reported by MacDiarmid et al.[1] was observed. In our laboratory, recently, a unusual porous morphology of PANI films synthesized by a new method termed "doping–dedoping–redoping" was observed.[2] Besides the unusual morphology, the resulting PANI films synthesized by the new method also exhibit high conductivity at room temperature, 200–300 S/cm,[2] which was one order of magnitude higher than that of PANI doped with HCl, and is comparable with the results of PANI films doped with camphor sulfonic acid (CSA) in *m*-cresol.[3] Compared with PANI–CSA reported by Cao et al.,[3] the counterions of PANI–CSA were replaced with conventional acids such as HCl, $HClO_4$, H_2SO_4, H_3PO_4, and *p*-toluene sulfonic acid (*p*-TSA) in the new method proposed by the authors.[2] It has been demonstrated that the resulting PANI chain still kept the expanded conformation like PANI–CSA in *m*-cresol, which may be the reason that high room-temperature conductivity can be obtained by the new method. In addition, the stability of PANI films is very important in the practical application of PANI, such as a thermal process. A series of articles concerning the thermal stability of PANI have been reported in the literature.[4–11] It was found that thermal stability of PANI salts depends on the counterions used.[6] Thus, it is very interesting to investigate the effect of the synthesis method and counterions on the thermal sta-

Figure 1   TGA curves of PANI films synthesized by the doping–dedoping–redoping method: (a) in nitrogen; (b) in air.

bility of doped PANI films, which has not yet been published in the literature.

In this article, the thermal stability of PANI films synthesized by the new method was measured by thermogravimetric analysis (TGA) as a function of counterions. The effect of thermal treatment on the conductivity of the PANI films synthesized by the new method is reported. Moreover, the stability of conductivity in air and the effect of water on conductivity are also discussed.

EXPERIMENTAL

The preparation process of the free-standing films of PANI synthesized by the doping–dedoping–redoping method were reported previously.[2] First, free-standing films of PANI were prepared by casting PANI–CSA solution in m-cresol onto a glass substrate.[3] The resulting films (i.e., PANI–CSA) were dedoped by 3% NH_3 solution to get emeraldine base (EB) films, and then the EB films were redoped by HCl, $HClO_4$, H_2SO_4, H_3PO_4, and p-TSA to reach the maximum conductivity. The

room-temperature conductivity of the resulting PANI films was measured by a four-probe method using ADVANTEST R6142 Programmable DC Voltage/Current Generator and a KETHLEY 196 System DMM. To investigate the effect of thermal treatment on the resulting PANI films, the samples were heated at 100, 150, and 200°C in air and argon, respectively, then their room temperature conductivity was measured. The samples for measuring the stability of conductivity in air were stored in a paper bag, which allows slow circulation of air.

Thermal stability of the PANI films was investigated by thermogravimetric analyzer (Perkin-Elmer, TGA7). Air and nitrogen were used as the purge gas at a flow rate of 40 mL/min. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

TGA curves of the PANI films synthesized by the new method measured in N_2 and air atmosphere are shown in Figure 1. Three results can be sum-

Table I Related Data of TGA Curves of PANI Films Measured in Nitrogen

	EB	PANI–CSA/ *m*-cresol	PANI– CSA	PANI– HClO$_4$	PANI– HCl	PANI– H$_2$SO$_4$	PANI– *p*-TSA	PANI– H$_3$PO$_4$
Second step weight loss (%)	20	35	25	24	16	18	40	10
Onset temp. (°C)	511	190	270	250	280	280	290	300
Third step weight loss (%)		25	20		20	10		
Onset temp. (°C)		450	450		490	510		

marized as follows: (1) the TGA curves of PANI films synthesized by the new method undergo two or three steps: loss of water or solvent, dedoping or decomposition initiated by dopants, and decomposition of PANI chains. This is consistent with the results reported by conventional method.[1] For the first-step weight loss, for instance, both emeraldine base (EB) form and emeraldine salt forms (ES) of PANI films synthesized by the new method with HCl, HClO$_4$, H$_2$SO$_4$, H$_3$PO$_4$, *p*-TSA, and CSA show 2–4% weight loss at the temperature between 60 and 100°C, which is attributed to the loss of water or other solvents.[4,5] After the initial weight loss, for example, EB shows a slow weight loss, which may be assigned to the loss of low molecular-weight oligomer, and does not show significant weight loss until 510°C, where PANI chains begin to decompose. However, it was noted that all ES forms of PANI films begin to decompose at a temperature much lower than the decompose temperature of EB. Therefore, the second-step weight loss of ES may be initiated by dopants. PANI films doped with HCl and H$_2$SO$_4$ show the third-step weight loss around 500°C, which correspondents to the decomposition temperature of EB form of PANI; (2) the thermal stability of the PANI films synthesized by the new method strongly depends on the counterions used, and the related data are given in Table I. As shown in Table I, the initial decomposition temperature of PANI was estimated to 190°C for PANI–CSA, 250°C for PANI–HClO$_4$, 280°C for PANI–H$_2$SO$_4$ and PANI–HCl, 290°C for PANI– *p*-TSA, and 300°C for H$_3$PO$_4$, respectively. The stability of ES with different acids is in the order of PANI–H$_3$PO$_4$ > PANI–*p*-TSA > PANI–H$_2$SO$_4$ > PANI–HCl, PANI–HClO$_4$ > PANI–CSA. This indicates that PANI–H$_3$PO$_4$ is the most stable

samples synthesized by the new method. It showed the second weight loss, from 300 to 400°C, decomposed slower than other samples over 400°C, and still kept 60% of its original weight at 900°C. The reasons for that may be due to following facts: (1) H$_3$PO$_4$ is a acid with a high boiling point, and it is inert for oxidation and reduction. (2) It is possible that benzene segment of PANI can condense with H$_3$PO$_4$ to produce phosphoamide, because the NH bond is one of the weakest bonds and nitrogen atoms in benzene segment is the most reactive atom in PANI chains, phosphoamide can stabilize the PANI chain. For other dopants such as HCl, HClO$_4$, H$_2$SO$_4$, CSA, and *p*-TSA, on the other hand, the less thermal stability compared with H$_3$PO$_4$ may be due to the facts that HCl is violate, HClO$_4$ is a violate strong oxidant, H$_2$SO$_4$ is also an oxidant at a high temperature, and CSA or *p*-TSA are unstable at a high temperature. (3) The thermal stability of doped PANI–CSA films synthesized by the new method is similar to the results reported by Cao et al.,[11] in which PANI–CSA decomposes above 200°C, corresponding to the decomposition temperature, 193–195°C,[12] of the CSA itself.

As shown in Figure 2, PANI redoped with CSA has better stability that PANI doped with CSA in *m*-cresol. Its second-step weight loss begins at 270°C, much higher than that of PANI–CSA films cast from *m*-cresol, which may be due to residual *m*-cresol and free CSA.

The TGA results in air are similar to those in nitrogen at temperature below 200°C. This indicates that the reaction between O$_2$ and PANI is not remarkable below 200°C. Most samples decompose completely between 600 and 700°C, except for PANI doped with H$_3$PO$_4$, which decomposed gradually over 600°C, and still kept 30% of

Figure 2 Comparison of TGA curves of the doped PANI films synthesized by a different method.

its weight at 900°C [Fig. 1(b)]. Some samples show less weight loss in air than in N_2 between 200 and 600°C, such as PANI doped with H_3PO_4 and p-TSA, which indicates that PANI absorbs O_2 between 200 and 600°C in air.[5]

Effect of Thermal Treatment on Room Temperature Conductivity

Although, except for the loss of water below 100°C, TGA data show little weight loss below 200°C, thermal treatment below 200°C greatly affects room-temperature conductivity of doped PANI films. The effect of thermal treatment on the conductivity of PANI films synthesized by the new method is shown in Figure 3, and related data are given in Table II. It was found that the room-temperature conductivity of doped PANI with different dopants after thermal treatment at 100°C in air decreases with the heating time [Fig. 3(a)]. All samples show a fast initial decrease of conductivity. When they were treated for a longer time, conductivity of all samples drops slowly, and approaches to a constant value. The initial decrease of conductivity may result from the loss of water. This is consistent with the following experimental evidences: (1) considering the TGA data (Fig. 2), it can be found that the weight loss at temperatures between 50 and 100°C is due to the loss of water, and samples lose most water very quickly.[2] (2) It has been demonstrated that the moisture in doped PANI affects its conductivity.[13–16]

After thermal treatment at 100°C, moreover, it was noted that the conductivity of PANI–CSA and PANI–p-TSA is more stable than other sam-

ples. The relationship between conductivity and thermal treatment time for PANI films treated at 150°C is similar to that of samples at 100°C, except for the decrease of conductivity quickly [Fig. 3(b)].

After thermal treatment at 200°C for 1 h [Fig. 3(c)], conductivity of PANI doped by CSA drops to lower than 10^{-5} S/cm, which is the lowest limit of the measurement of our instrument. But PANI films doped with H_2SO_4, H_3PO_4, and p-TSA show much better thermal stability than PANI–CSA. After heating at 200°C for 4 h, their conductivity is still in the range of 10^{-2}–10^0 S/cm.

This result suggests that the thermal stability of conductivity treated at a high temperature (e.g., 200°C) is improved by the method proposed by the authors.[2] Moreover, it was noted that the thermal stability of conductivity of most samples

Figure 3 Room-temperature conductivity of PANI films treated at different temperatures in air: (a) 100°C; (b) 150°C; (c) 200°C.

Table II   Change in Conductivity of Doped PANI Films Synthesized by the New Method After Thermal Treatment at Different Temperatures in Air

Dopants	$(\sigma_T/\sigma_0)100\%$[a]		
	100°C	150°C	200°C
CSA	70	20	3.0×10^{-6}
p-TSA	50	20	0.55
H_2SO_4	50	10	6.0
H_3PO_4	55	8.0	3.5
$HClO_4$	40	6.0	0.10
HCl	20	5.0	6.0×10^{-5}

[a] σ_0, before thermal treatment; σ_T, thermal treatment in air for 3 h.

cannot be significantly improved when the samples were heated in argon. This is consistent with the fact that there is little difference in the weight loss below 200°C between samples heated in air and nitrogen. As an exception, room temperature conductivity of PANI–HCl treated at 200°C in Ar for 4 h is two orders of magnitude higher than that in air, due to air oxidation occurring during thermal treatment of PANI–HCl in air.

Besides moisture, in general, it is reasonable to believe that conformation changes or chain arrangement,[5] deproton, the reaction between dopants and PANI chains, the reaction between O_2 and PANI as PANI was heated in air, and the decomposition of PANI or counterions are reasons that result in the decreasing of the conductivity of PANI films after thermal treatment at a high temperature. But from TGA results, we can see that there is no significant weight loss from 100 to 250°C in doped PANI films except for PANI–CSA. Therefore, there is no significant decomposition for other samples below 200°C, and the conformation changes may be the main factor affecting conductivity. Because the large size of p-TSA and CSA do not favor the twist of PANI chains, PANI doped by CSA and p-TSA is apt to keep the expanded conformation, which is essential for PANI to keep high conductivity.[17] PANI–CSA becomes unstable at 200°C, because CSA begins to decompose at 193–195°C.[12] It is reasonable that by substitute CSA with other counterions, the thermal stability of conductivity of PANI at a high temperature (>200°C) can be improved. HCl is a volatile liquid, so that PANI doped with HCl loses HCl gradually above 50°C.[4] The decrease of con-

ductivity of PANI–HCl is mainly due to the loss of the dopant. This is the reason that the conductivity of PANI–HCl drops more quickly than that of other samples. H_2SO_4 and H_3PO_4 are acids with high boiling point; PANI films doped by them do not lose dopants, but the reaction between dopants and the PANI chain[5] may decrease the conductivity at a high temperature.

The Stability of Conductivity in Air

From TGA results, it can be found that PANI films made by the new method contain about 2–4% water. The effect of moisture on conductivity is different for different counterions. Moreover, it was demonstrated that water affects the room-temperature conductivity of doped PANI films synthesized by the convenient method[1]; many articles have been published in the literature.[13–16] Thus, the effect of moisture on the conductivity of PANI films synthesized by the new method was measured as a function of dopants, and the results are given in Table III. As shown in Table III, when the samples were dried in a vacuum disecator with silica gel for 48 h, the conductivity of all redoped samples decreased about 10–50%, depending on the dopants used, i.e., water has the largest effect on the conductivity of PANI–H_2SO_4, whose conductivity drops 50% after drying, while it has the least effect on the conductivity of PANI–CSA and PANI–p-TSA, whose conductivity decreases about 10%. If the samples were kept in air at 25°C and 35–45% humidity, the samples absorb moisture. Their conductivity recovers and approaches to the original values. It was interesting to note that moisture does not affect the conductivity of PANI–CSA films cast from m-cresol solution.

In addition, the stability of the conductivity in air for the doped PANI films depends on the counterions as shown in Table III. After 6 months in air, the conductivity of PANI films redoped with H_2SO_4, p-TSA and PANI–CSA films cast from m-cresol solution hardly decreases, while, there is about a 40% decrease in conductivity of PANI film doped with HCl and $HClO_4$. Thus, the change in conductivity for the PANI films redoped with HCl and $HClO_4$, which is volatile acids and easy to dedope, may be attributed to the loss of water and dopants.

Conclusion

The stability, such as thermal stability, stability of conductivity in air, and after thermal treat-

Table III   The Stability of Conductivity of PANI Films Redoped by Different Dopants and PANI Films Doped with CSA in *m*-Cresol, When They Were Kept in Air

Conductivity	HCl	HClO$_4$	H$_2$SO$_4$	H$_3$PO$_4$	*p*-TSA	CSA	CSA/*m*-Cresol
σ_0 (S/cm)	270	320	200	260	250	270	300
σ_1 (S/cm)	190	210	100	170	220	220	300
σ_2 (S/cm)	240	260	150	230	240	260	300
σ_3 (S/cm)	160	220	200	190	310	270	280

σ_0 is initial room temperature conductivity of doped PANI films synthesized by the new method; σ_1, after drying in a vacuum for 48 h; σ_2, after drying in a vacuum for 48 h and kept in air for another 48 h at 25°C and 35–45% humidity; σ_3, after placing in air for 6 months after redoping.

ment, of the PANI films synthesized by the doping–dedoping–redoping method was measured as a function of counterions. The main results are summarized as follows:

1. The TGA curves of the PANI films synthesized by the doping–dedoping–redoping method undergo two or three steps: loss of water or solvent (50–100°C), dedoping (250–300°C), and decomposition (>500°C), depending on the counterions, which is consistent with observations of the conventional method. In comparison with doped PANI–CSA synthesized by the conventional method,[3] the thermal stability of the doped films was improved by the new method proposed by the authors. Moreover, it was found that PANI–H$_3$PO$_4$ is the most stable in both air and nitrogen. One reason for this may be due to a high boiling point of H$_3$PO$_4$ dopant, which is inert for oxidation and reduction. Others may result from condensation reaction between amide segments of PANI and H$_3$PO$_4$ dopant to produce phosphoamide, which can stabilize the PANI chain.

2. Effect of the thermal treatment at temperatures between 100 and 200°C on the room-temperature conductivity of the PANI films synthesized by the new method was measured as a function of counterions. It was found that the conductivity decreases with an increase of the heating temperature. It was noted that the conductivity of PANI–CSA and PANI–*p*-TSA are the most stable below 200°C, while the stability of PANI films doped with H$_2$SO$_4$ and H$_3$PO$_4$ are much better than the PANI–HClO$_4$ and

PANI–HCl after thermal treatment at a high temperature (200°C).

3. The conductivity of the doped PANI films synthesized by the new method in air also decreases slowly with time due to loss of water or dedoping, which is consistent with observations reported from the conventional method. However, the stability of conductivity in air strongly depends on the counterions. Over 6 months in air, for instance, the conductivity of PANI film doped with H$_2$SO$_4$, *p*-TSA, and CSA changes little, while there is about a 40% decrease in conductivity of PANI films doped with HCl and HClO$_4$ due to a high boiling point.

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