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Morphology and thermostability of polypyrrole prepared from SDBS aqueous solution

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Summary

Polypyrrole (PPy) with microstructure was prepared in sodium dodecyl benzene sulfonate (SDBS) aqueous solution. The composition, morphology, structure and thermostability of the resulting PPy particles were collected by elemental analysis, scanning electron microscopy (SEM), fourier transformation infrared (FT-IR) spectra and differential thermal analysis (DTA). The yield and conductivity were also measured. Different preparation conditions including the concentration of the surfactant and the monomer, addition of acid or not and the kind of the oxidant were all investigated. The results showed there was an extrinsic relation between the morphology and the thermostability of the samples. Based on the relation, a possible mechanism was proposed that there might be two kinds of interaction between SDBS and PPy, i.e., inter- and intra-interaction.

1. Introduction

In recent years, polypyrrole (PPy) as one of the most promising conducting polymers has received comprehensive interests due to its excellent characteristics including easy preparation, environmental stability, high conductivity and so on. The mentioned merits lead PPy to behave wide potential applications in various fields, such as sensors, actuators and electric devices [1-4]. Therefore, to obtain PPy with excellent chemical and physical characteristics becomes more and more attractive. For this purpose, polymerization of pyrrole in different surfactant systems has been developed quickly, because surfactants can induce the pyrrole to grow in certain manners and hence result in PPy with ordered morphology, which will show superior properties to that from conventional aqueous solution [5,6]. On the other hand, the doping of the surfactant into the polymer backbone can improve the thermostability of the resulting products [7,8]. Among the conventional surfactants, cetyltrimethylammonium bromide (CTAB) is proved to be an effective one to guide for the formation of PPy nanofibers [9,10]. X. Zhang et al. further investigated the controllable synthesis of PPy nanostructures by using different kinds of surfactants, including CTAB, dodeyltrimethylammonium, octyltrimethylammonium, poly(ethylene glycol) mono-*p*-nonylphenyl ether and sodium dodecyl sulfate (SDS). They showed that using the former two and ammonium persulfate (APS) as oxidant could obtain PPy with ribbon wire-like structure, but the others could only generate sphere-like structure despite of the oxidant ($FeCl_3 \cdot 6H_2O$ or APS), except that when SDS was used, PPy without geometrical nanofeature would be formed [11]. B.P. Grady et al. have reported the formation of nanostructured PPy with controlled morphologies on atomically flat surfaces using adsorbed surfactant molecules as templates [12]. Apart from the above mentioned surfactants, sodium dodecyl benzene sulfonate (SDBS) is also used comprehensively for the polymerization of pyrrole. The influence of different preparation conditions on the structure, thermal stability and other properties of the resulting polymer have been investigated [13-18]. Their results showed the addition of surfactants could accelerate the polymerization and the PPy containing surfactant gave high thermal and hydrolytic stability in air, which could be caused by incorporation of anionic surfactant into the PPy as the co-dopant. However, a systemic investigation on the morphology of the PPy obtained from SDBS aqueous solution is rarely reported, which may help us further understand the interaction between the surfactant and the polymer. Therefore, we synthesized PPy with sub-micro structure in SDBS aqueous solution and investigated the extrinsic relation between its morphology, structure and thermostability with the aid of elemental analysis, scanning electron microscopy (SEM), Fourier transformation infrared (FT-IR) spectra and Differential thermal analysis (DTA) measurements. A possible mechanism was also proposed to explain the difference between the various samples.

2. Experimental Section

2.1 Materials

Pyrrole was distilled under reduced pressure and other chemicals were used as received without further purification.

2.2 Preparation of PPy

A typical experiment was done as follows: SDBS aqueous solution with certain concentration was mixed with or without small amount of acid (HCl, 1M). Pyrrole was dissolved in the above solution under stirring. $FeCl_3 \cdot 6H_2O$ or ammonium persulfate (APS) was then added into the mixture. The reaction was stirred for 6h and finally ca. 20 mL of acetone was poured into the system to finish the polymerization. The as-obtained precipitation was collected by filter, washed by deionized water and ethanol continuously and dried under vacuum at room temperature for 48h. After dried, the samples were dispersed in water for 1 h with stirring and filtered again so as to remove the remained free surfactants. The detailed preparation conditions were listed in Table 1 and the total volume of the solution was 100 mL. In this experiment, 0.1 M of pyrrole in 0.025 M of SDBS was selected to compare with other preparation conditions because apparent difference could be observed when the conditions were changed accordingly. Meanwhile, in order to avoid the produce of excess precipitates of $Fe(DBS)_3$, the molar radio of the monomer to the oxidant was kept at 1:1, though the optimum one was 1:2.3 [19,20].

Table 1. Preparation conditions of the polymerization of pyrrole in SDBS aqueous solution

Sample	SDBS (M)	Pyrrole (M)	Acid (HCl, 1M, mL)	Oxidant
1	0.01	0.1	/	$FeCl_3 \cdot 6H_2O$
2	0.025	0.1	/	$FeCl_3 \cdot 6H_2O$
3	0.1	0.1	/	$FeCl_3 \cdot 6H_2O$
4	0.025	0.05	/	$FeCl_3 \cdot 6H_2O$
5	0.025	0.2	/	$FeCl_3 \cdot 6H_2O$
6	0.025	0.1	1	$FeCl_3 \cdot 6H_2O$
7	0.025	0.1	/	APS

2.3 Characterization

The PPy composition was determined by elemental analysis using an elemental analyzer VarioEl.

The conductivity of powder pellets at room temperature was measured by a typical four-probe method (SDY-5).

The morphology of the samples was observed using SEM (SSX-550, Shimadzu) without gold coating.

FT-IR spectra of the samples were measured on an FTIR-8400s spectrometer (Shimadzu) in the transmission mode. Standard KBr technique was applied and the resolution of the measurements was equal to 4 cm^{-1}.

DTA was carried out from 25 to 700 °C at a heating rate of 10 °C/min under air atmosphere (ZCR-II). α-Al_2O_3 was used as reference.

3. Results and discussion

3.1 Elemental composition

Table 2 lists the elemental composition of PPy prepared from different conditions. The existence of S indicates the anionic surfactant, SDBS, is incorporated into the PPy structure in certain degree and the SDBS may also exist in the samples with the adsorption interaction with PPy. On the other hand, we only detect few amounts of Cl in all the samples, which shows the Cl^- has weaker ability to be the counter-ion in PPy chain in the presence of SDBS. For all the samples, the molar ratios of N to S are in the range from 2.27 (Sample 6) to 3.28 (Sample 3), indicating that for about three pyrrole rings one positive charge is created, which has to be balanced by the anion of oxidant molecule [20].

If we assume that SDBS acts as only dopant anion species for the PPy component, we can calculate an apparent doping ratio from S:N element molar ratio. As can be seen from Table 1 and 2, when the concentration of the surfactant is increased from 0.01 to 0.1 M, the doping ratio shows a contrary change. We consider that in the system with higher SDBS concentration, the interaction between the surfactants becomes stronger than that in the lower SDBS concentration system. Therefore, it is hard for the anionic section, DBS^-, incorporating into the PPy chain as dopant. Decreasing or increasing the monomer concentration to 0.01 or 0.2 M, respectively, enhances both the doping ratios of the resulting polymers. In the lower pyrrole concentration system, the opportunity for the SDBS acting as a dopant turns increased. On the contrary, the higher concentration of pyrrole may prevent the interaction between the surfactants.

Adding small amount of acid into the reaction solution will also result in the enhancement of doping ratio because of the increasing of the electrostatic interaction between H^+ and DBS^-. On the other hand, using APS as oxidant seems to increase the doping ratio of the obtained polymer, however, it should be noted that the reduced product of APS, SO_4^{2-}, may also take part in the polymerization as a dopant [14].

Table 2. Elemental composition of different samples and their corresponding yield and conductivity

Sample[a]	Elemental analysis (wt.%)				Doping ratio[b]	Yield[c]	Conductivity ($S \cdot cm^{-1}$)
	C	H	N	S			
1	65.54	5.67	9.66	8.35	0.76	0.93	5.8
2	67.56	5.99	9.83	6.98	0.62	1.36	0.56
3	68.35	6.18	9.63	6.62	0.60	1.58	0.35
4	66.92	5.92	8.53	9.00	0.92	1.03	0.72
5	65.63	5.53	9.59	9.37	0.85	0.79	0.71
6	67.13	5.85	9.30	8.03	0.76	1.18	0.62
7	62.19	5.20	11.23	9.41	0.73	1.25	0.2

[a] The numbers of the samples correspond to those in Table 1.

[b] 2·molar ratio of S/N [15].

[c] $g \cdot g^{-1}$ pyrrole.

3.2 Yield and conductivity

The yields of the PPy prepared from different conditions are listed in Table 2. We can find a higher yield is obtained in the system with higher SDBS concentration. Because SDBS can accelerate the polymerization rate and hence improve the polymerization of the pyrrole. A lower yield is found when a higher pyrrole concentration is used (Sample 5), which shows an incompleted polymerization occurs in this system. Meanwhile, adding acid or using APS as oxidant does not have much influence on the polymerization yield.

As for the conductivity of the different samples, a higher value of conductivity is expected when the sample has a higher doping ratio. However, Sample 1 shows the highest conductivity though it does not give the highest value of doping ratio. That is because the calculated doping ratio is based on the assumption that all surfactants act as dopant in the polymerization. Indeed, in a system with higher SDBS concentration, SDBS will act as not only dopant but also surfactant and the later effect will bring the SDBS into the resulting samples due to its adsorption interaction with the polymer. In these conditions, the bigger amount of surfactant anions containing bulky aliphatic chains can be a steric barrier for the charge transport in the PPy chains [20]. That Sample 7 with APS used as oxidant gives the lowest conductivity may be originated from the interaction between APS and the surfactant. In this system, PPy doped with sulfonate is hardly yielded, since the dissociation of the anionic surfactant is prevented due to the presence of the strongly electrolytic oxidant [14].

3.3 Morphology

3.3.1 Influence of SDBS concentration

The influence of SDBS concentration on the morphology of PPy is presented in Fig. 1. From the figure, we can find the PPy obtained from 0.01 M of SDBS shows almost all globular morphology with the diameter ranging from 200 to 400 nm (see Fig. 1a). An increasing concentration of SDBS to 0.025 M leads to agglomeration of the resulting PPy in certain degree. We can obtain globular, fiber and ever agglomerate particles in this system, which can be seen from Fig. 1b. The agglomeration turns obvious when 0.1 M of SDBS is used and nearly no globular particles can be found. The increasing of the interaction between the different components is considered as the reason to induce the above results. The polymerization of pyrrole in 0.01 M of SDBS is more like in aqueous solution than in the system with higher SDBS concentration, and gives out the similar globular particles as that in common aqueous solution. However, 0.025 M or 0.1 M of SDBS provides large amount of surfactant molecules that will have strong electrostatic or adsorption interaction with pyrrole, PPy and even the oxidant, $FeCl_3 \cdot 6H_2O$ and thereby the agglomeration becomes apparent.

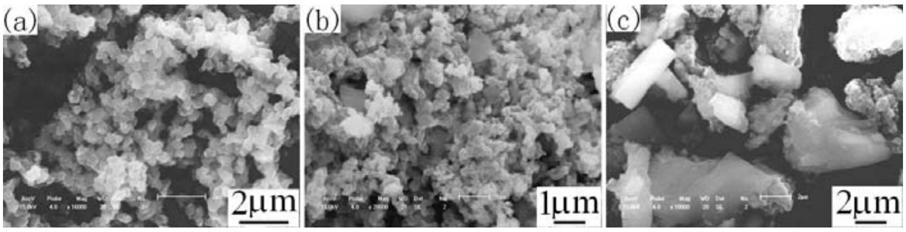

Fig. 1 SEM images of the PPy obtained from the systems with different surfactant concentration (a. 0.01 M; b. 0.025 M; c. 0.1 M)

3.3.2 Influence of pyrrole concentration

The morphology of the PPy obtained from the systems with different pyrrole and fixed SDBS concentration (0.025 M) can be observed in Fig. 2. When the pyrrole is as low as 0.05 M, no apparent agglomeration is found. The resulting PPy shows globular morphology and can further form fibers with the aid of the surfactants (Fig. 2a), which may construct micelles in the aqueous solution and then provide proper polymerization space. However, when a larger pyrrole concentration, such as 0.1 M, is used, the micelles will be destroyed because of the strong electrostatic interaction between SDBS and PPy,

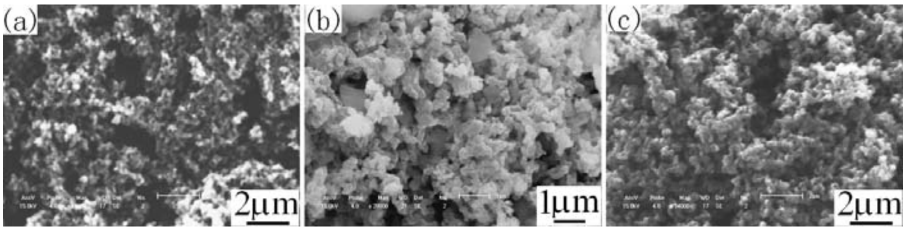

Fig. 2 SEM images of the PPy obtained from the systems with different pyrrole concentration (a. 0.05 M; b. 0.1 M; c. 0.2 M)

or even the oxidant, and the system results in globular and agglomerate particles with a few fibers still existing (Fig. 2b). It is interesting that the agglomeration turns weak as the pyrrole concentration reaches 0.2 M and the so-obtained PPy shows almost all globular morphology with the average diameter of ca. 300 nm (Fig. 2c). This is originated from the fact that the interaction between SDBS and PPy becomes relatively weak and the interaction between the reaction monomers turns strong.

Based on the above discussion in Section 3.3.1 and 3.3.2, we can find the morphology of the obtained polypyrrole may be controlled by the ratio of monomer pyrrole to surfactant SDBS, which can be confirmed by comparing the SEM images presented in Fig. 1 and 2. A high ratio of pyrrole to SDBS will lead to globular morphology without apparent agglomeration and a low ratio results in serious agglomeration, because the interaction between the surfactant and the monomer and also the oxidant becomes strong when a low ratio of pyrrole to SDBS is used. At the same time, the product from the reaction between SDBS and $FeCl_3{\cdot}6H_2O$, e.g., $Fe(DBS)_3$, will also affect the agglomeration when a low ratio of pyrrole to SDBS is used, since $Fe(DBS)_3$ has poor solubility in water (though it can redissolve partly in the solution with the progress of the polymerization reaction [14].)

3.3.3 Influence of acid

Adding 1 mL of acid (HCl, 1M) to the reaction system will also influence the morphology of the PPy, which can be concluded from Fig. 3. Compared with the sample without acid (Fig. 3a), the PPy with acid adding to the solution shows relatively homogeneous globular particles with the diameter of ca. 200 nm. This can be explained by the decreasing of the electrostatic interaction between SDBS and PPy since the H^+ will also have strong interaction with SDBS, which is consistent with the results of elemental composition.

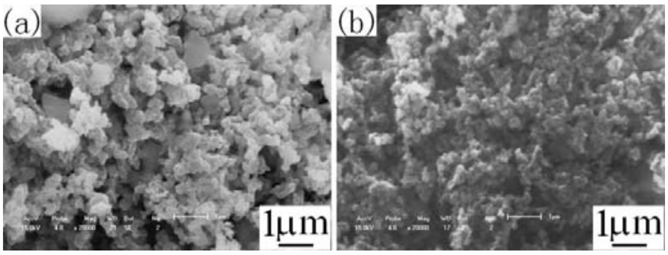

Fig. 3 SEM images of the PPy obtained from the systems with (b) and without (a) acid

3.3.4 Influence of oxidant

Using APS as oxidant will also decrease the degree of agglomeration, which can be seen from Fig. 4. This phenomenon can be originated from the changing of the electrostatic interaction between the oxidant and surfactant. The cation produced by $FeCl_3{\cdot}6H_2O$ will have certain interaction with the ion produced by SDBS and generate some kind of precipitate, e.g., $Fe(DBS)_3$. However, there will be less interaction between $S_2O_8^{2-}$ and DBS^-. Therefore, it can be expected that the agglomeration is impeded when APS is used instead of $FeCl_3{\cdot}6H_2O$. On the other hand, the size of the resulting PPy appears smaller than that in the system with $FeCl_3{\cdot}6H_2O$ as oxidant and it shows an average diameter of ca. 120 nm.

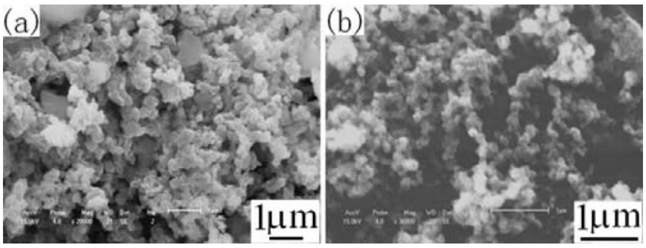

Fig. 4 SEM images of the PPy obtained from the systems with $FeCl_3 \cdot 6H_2O$ (a) and APS (b) as oxidants

3.4 FT-IR spectra

The FT-IR spectra of all the samples were collected and the results indicate the typical characteristics of PPy. Taking Sample 2 as an example (Table 1), as shown in Fig. 5b, the peaks at 1540 and 1454 cm^{-1} are corresponding to the stretching vibration of the C=C double bond of PPy and the C-N stretching vibration, respectively. The peaks at 1300 and 1176 cm^{-1} represent the =CH- in plane vibration [21,22], and the latter can also indicate that the PPy is in doping state [11]. The peak at 1032 cm^{-1} belongs to $–SO_3^-$ group of the dopant and the peaks in the range of 700-500 cm^{-1} correspond to S-O, C-S stretching modes, both above which imply that the sulfonic acid groups are introduced in the polymer backbone [8]. The weak peak around 2900 cm^{-1} is also found, which can further confirm the formation of the doping because this peak can be attributed to the stretching vibration mode of the methylene in the surfactant structure [11,21].

The FT-IR spectra of the samples by changing the concentration of the surfactants, adding acid to the system or using APS as oxidant appear no much difference with that of Sample 2. However, when the concentration of pyrrole is changed, the spectra of the obtained PPy give unlike results. A tendency of red shift can be observed when the monomer concentration is increased from 0.05 to 0.2 M (See Fig. 5), which may

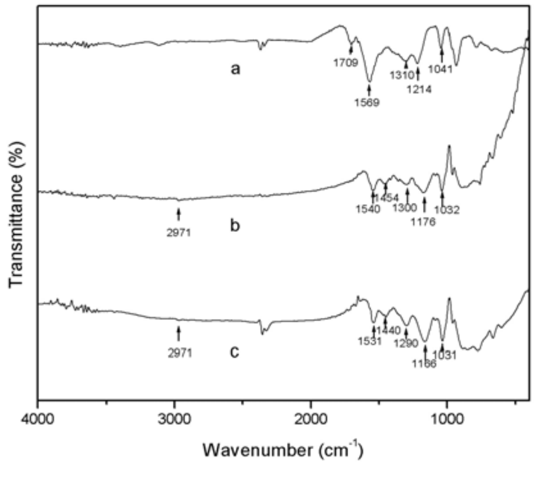

Fig. 5 FT-IR spectra of the PPy obtained from the systems with different pyrrole concentration (a. 0.05 M; b. 0.1 M; c. 0.2 M)

be induced by the change of the doping ratio and it can be found in Table 2 by comparing Sample 2 and 5. On the other hand, the peak at ca. 1450 cm^{-1} can hardly be found and an additional peak at ca. 1700 cm^{-1} is observed in the sample obtained in Sample 4 (see Table 1 and Fig. 5a), which indicates the PPy is slightly overoxidized during the growth process [23].

3.5 DTA

Typical DTA curve of doped PPy shows an exothermic peak at ca. 280 °C, which is related to the decomposition of PPy. Another peak at ca. 500 °C is attributed to the expulsion of the dopant [24]. In our experiments, the inherent relation between the morphology and themostability of the resulting PPy has been further investigated and a possible mechanism is proposed to explain the difference between the samples from different preparation conditions.

It is considered that there may be two kinds of interaction between SDBS and PPy, and here we name them as inter- and intra- interaction. The former can be designed as follows: the surfactant acts as a "bridge-bond" between the polymers through the adsorption or electrostatic interaction and it makes the resulting polymer form agglomerates. On the other hand, the latter refers to the doping of the sulfonate group into the polymer backbone. Apparently, the inter-interaction is weaker than the intra-interaction. Based on the above proposal, we discuss the thermostability of all the samples.

3.5.1 Influence of SDBS concentration

The DTA curves of the PPy obtained from the systems with different SDBS concentration are presented in Fig. 6. From this figure, one can find three or four exothermic peaks in all the samples. The peak below 100 °C can be attributed to the loss of the residual monomer or moisture content entrapped in the polymer matrix [24]. The peak at ca. 220 °C may be resulted from the decomposition of some

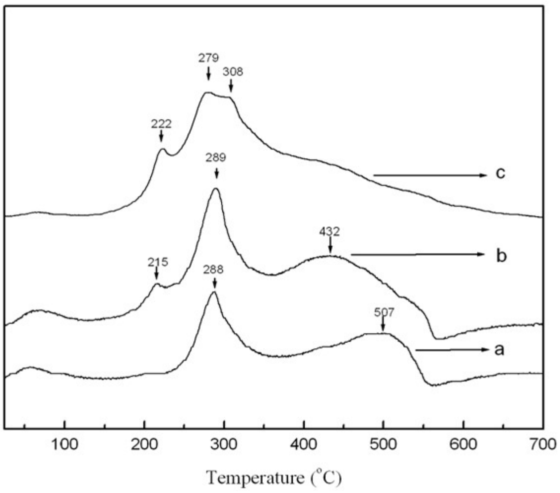

Fig. 6 DTA curves of the PPy obtained from the systems with different surfactant concentration (a. 0.01 M; b. 0.025 M; c. 0.1 M)

oligomer components. The PPy begins decomposition from ca. 250 °C and a maximum is found at ca. 290 °C. The peak around 450 °C can be related to the disruption of the interaction between SDBS and PPy.

As the surfactant concentration is as low as 0.01 M, the peak around 220 °C can hardly be found, indicating a good polymerization of the pyrrole. On the other hand, it gives a high temperature for the disruption of the interaction between SDBS and PPy, which means that an intra-interaction plays a main role in the resulting sample, and that the sample has a higher doping ratio also confirms our conclusion. However, when the concentration of the surfactant is increased to 0.025 M, the corresponding peak turns to 432 °C because the inter-interaction begins to make effect (see Fig. 1b). The same peak nearly eliminates when the SDBS concentration reaches 0.1 M and a shoulder peak is found at ca. 310 °C, which can be originated from the serious agglomeration of the PPy due to the dominant role of the inter-interaction between SDBS and PPy (see Fig. 1c).

3.5.2 Influence of pyrrole concentration

Fig. 7 shows the DTA curves of the PPy resulted from the systems with different monomer concentration. Comparing with their morphology as shown in Fig. 2, one can expect their peak positions. For example, the samples obtained from 0.05 and 0.2 M of pyrrole solutions (Sample 4 and 5 in Table 1) give higher temperature relating to the disruption between SDBS and PPy because they have less agglomeration effect than that from 0.1 M of pyrrole solution (Sample 2). In those conditions, the intra-interaction, i.e., the doping other than "bridge-bond" is predominant, which can be further confirmed by the higher doping ratios of Sample 4 and 5 than that of Sample 2.

3.5.3 Influence of acid

Addition of acid to the system will affect the morphology of the resulting PPy and hence their thermostability, which can be seen from Fig. 3 and 8. A peak around

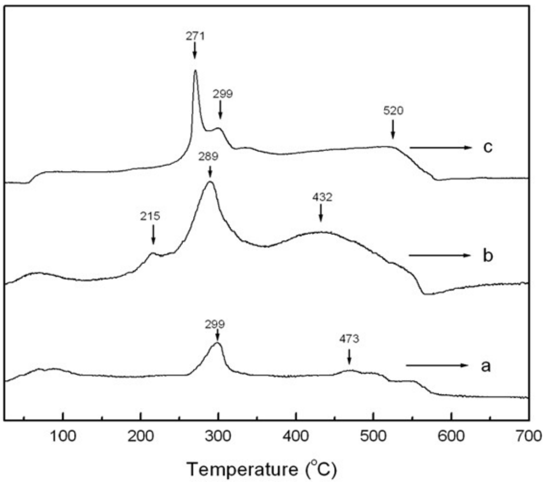

Fig. 7 DTA curves of the PPy obtained from the systems with different pyrrole concentration (a. 0.05 M; b. 0.1 M; c. 0.2 M)

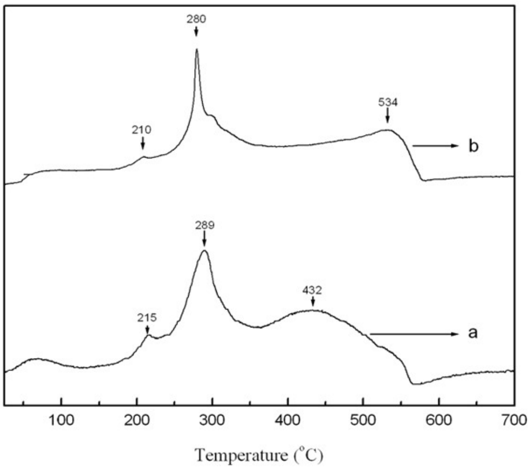

Fig. 8 DTA curves of the PPy obtained from the systems with (b) and without (a) acid

534 °C is found when acid is used in the polymerization process because, as we know, the addition of H^+ will help for the improvement of the doping ratio and then strengthen the intra-interaction between SDBS and PPy, which can be seen from Table 2 by comparing Sample 2 and 6 with the corresponding apparent doping ratios of 0.62 and 0.76, respectively.

3.5.4 Influence of oxidant

We have discussed above that using APS as oxidant will decrease the agglomeration of the PPy, thus the inter-interaction between SDBS and PPy is reduced due to the repulsion of SDBS and APS. On the contrary, the intra-interaction is enhanced accompanied by the increase of doping ratio (Table 2, Sample 2 and 7) under this condition and the resulting PPy shows a high temperature at ca. 538 °C, which can be seen in Fig. 9.

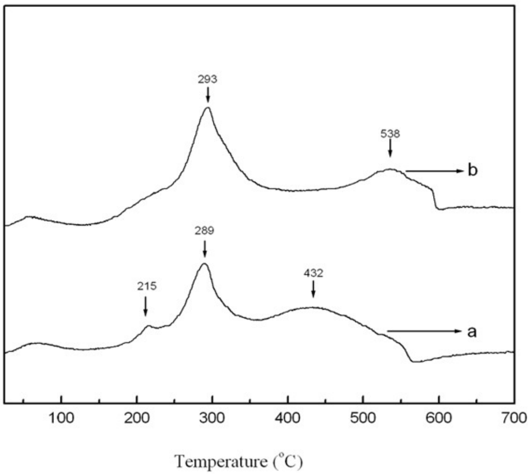

Fig. 9 DTA curves of the PPy obtained from the systems with $FeCl_3 \cdot 6H_2O$ (a) and APS (b) as oxidants

4. Conclusions

PPy with microstructure was successfully prepared from the SDBS aqueous solution and the composition, yield, conductivity, morphology, structure and thermostability of the resulting products were all investigated. The results showed that the concentration of the surfactant and monomer would both affect the agglomeration of the as-obtained samples. A low ratio of pyrrole to SDBS led to relatively serious agglomeration. On the contrary, high corresponding ratio would decrease the effect. Besides, addition of acid and using APS as oxidant would both increase the doping ratio and decrease the degree of the agglomeration. The FT-IR spectra indicated the PPy was in well-doped state. An extrinsic relation between the morphology and thermostability of the resulting PPy was observed and there might be two kinds of interaction between SDBS and PPy, i.e., inter- and intra-interaction. The inter-interaction played a main role in the PPy with serious agglomeration, so the products showed low temperature for the disruption of the interaction between SDBS and PPy. However, the PPy with homogeneous globular or fiber structure gave high corresponding temperature because the intra-interaction (doping) was predominant.

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