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Preparation of polyaniline dispersions with different assembly structure

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Polyaniline (PANI) dispersions with different assembly structure were prepared using sodium dodecyl benzene sulfonate (SDBS) as surfactant. Based on the images from the microscopy, it was found that the assembly structure of the PANI dispersions could be changed with different preparation conditions, including the concentration ratio of SDBS to HCl, SDBS to aniline and aniline to ammonium persulfate. UV-Vis spectra, conductivity and size distribution of the dispersions were also measured. The dispersions showed good stability and existed without precipitate at least half a year. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Polyaniline (PANI) is one of the most promising conducting polymers due to its easy preparation, unique doping mechanism, cheap materials, good chemical and environment stability and so on. Based on the above merits, PANI has been comprehensively used in many fields, especially in various electronic devices and sensors [1–3]. However, its poor solubility limited its application as conducting materials. To overcome this obstacle, people have used functionalized protonic acids, such as dodecylbenzenesulfonic acid (DBSA) or camphorsulfonic acid (CSA) to dope PANI and obtained conducting products soluble in many kinds of organic solvents [4, 5]. Another effective approach involves preparing PANI in colloidal dispersion. This approach allows formation of conducting PANI in aqueous solution in one step, and the so-obtained PANI dispersion can be directly used to prepare conducting film and hence application in different devices. So dispersion has been considered as the link between basic research and commercial application of PANI [6]. PANI dispersion is typically prepared via the aid of steric stabilizer, including poly-(vinyl alcohol) [7, 8], poly (N-vinylpyrrolidone) [7, 9–12], poly (vinyl methyl ether) [13], polyacrylamide [14], hydroxypropylcellulose [15] and so on. Besides, many surfactants, such as DBSA [16–19] and sodium dodecyl sulfate (SDS) [20–22] have also been used to prepare stable PANI dispersion. However, many of the researches focused on the microscopic morphology of the particles in the dispersion and few reported the entire assembly structure in the dispersion system. On the other hand, R. Madathil et al. have used sodium dodecyl benzene sulfonate (SDBS) to prepare PANI gel by adding HCl to convert SDBS to its acid form, DBSA [23]. In our experiments, we found changing the acid concentration would generate a stable PANI dispersion and no gel was formed. Here, we made a detailed study of its assembly structure in different preparation conditions and we are sure it will help us to further understand the interaction between PANI and the surfactant.

2. Experiments

2.1. Materials

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

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2.2. Preparation of PANI dispersion

A typical experiment was done as follows: SDBS aqueous solution with different concentration was mixed with small amount of HCl solution (0.36 M). The acid was used to convert SDBS to its acid form DBSA and provide H^+ to induce the polymerization of aniline. Aniline was dissolved in the above solution under stirring. Ammonium persulfate (APS) in powder state was then added into the mixture solution and stirred for 1 min. The so-obtained solution was kept unstirred at 25°C for about 2 h until the color turned dark green, which indicated the emeraldine salt had been formed. Different preparation conditions were listed in Table I and the total volume of the solution was 1.0×10^{-4} m^3.

2.3. Characterization

A drop of PANI dispersion was dropped onto a piece of microslide and put into the oven under 60°C in order to remove the solvent and then a film was formed. A microscope (Olympus BX51) was used to observe the structure of the films obtained from different conditions.

Optical spectra were recorded on UV-2550 UV-Vis spectrometer. 2.0×10^{-7} m^3 of dispersion was diluted with 1.0×10^{-5} m^3 of deionized water for the measurement and deionized water was used for background.

Conductivity of dispersions was gathered with a standard conductometric cell composed of two blank platinum electrodes. DDS-11A meter operating at 1 kHz frequency was used in the experimental set-up and the measurement was carried out at 25°C.

A laser-scattering particle size distribution analyzer (Zeta 3000) was used for measurement of the PANI particle size distribution on diluted dispersion at 25°C.

3. Results and discussion

3.1. Formation and stability of PANI dispersions

As discussed in many papers, the surfactants, such as SDS and DBSA, form micelles in the aqueous solution at first and provide local places for the polymerization of aniline [18, 22]. They often act as both surfactant and dopant. In the experiment, we consider the free surfactants that are not used for the dopant work as steric stabilizer and hence depress the precipitation of PANI. If the free surfactants are not adequate, the PANI precipitate will be generated. From Table I, we can see a low SDBS concentration (Sample 5) or high aniline concentration (Sample 12 and 13) both result in the generation of precipitate. On the other hand, when the acid is used in excess, precipitate can also be generated which is perhaps due to the damage of the micelles (Sample 3 and 4). Furthermore, when aniline/APS ratio is lower or higher than 1, PANI dispersion in its emeraldine state cannot be obtained, which can be directly seen from the dispersions' color (Sample 8, 9 and 10). Apart from these factors, PANI dispersions can exist without any precipitate at least half a year and they can be diluted by deionized water for many times without generation of precipitate, indicating their high stability or nearly solution characteristic. It should be noted that a high concentration of SDBS or low concentration of HCl would greatly decrease the rate of polymerization of aniline.

3.2. Assembly structure of PANI dispersions

Typical PANI particle in its dispersion shows granular morphology with a particle size in the range of tens to hundreds of nanometers. However, there are so few reports about the structure of PANI dispersion, which may help us to understand its assembly and utilize it in certain aims. Though our results are based on the observation of the films formed by the dispersions, we believe the results can reflect the different assemblies of the PANI dispersions.

Fig. 1 gives the dispersions' structure with different amount of HCl added into the solution at fixed other conditions. As can be seen from the images, a low concentration of HCl results in a loose network structure (Fig. 1a and b). On the contrary, from Fig. 1c and d, one can observe a relatively smooth surface. Further observation proves

TABLE I Preparation conditions, formation and conductivity of the PANI dispersions

Sample	Aniline (g)	APS (g)	SDBS (M)	HCl (10^{-6} m^3)	Dispersions color	Precipitation	Conductivity (mS/cm)
1	0.093	0.228	0.025	1.65	Dark green	No	13.23
2	0.093	0.228	0.025	3.3	Dark green	No	13.42
3	0.093	0.228	0.025	6.6	Dark green	Slight[a]	16.83
4	0.093	0.228	0.025	10	Dark green	Slight	19.70
5	0.093	0.228	0.01	3.3	Dark green	Yes	12.97
6	0.093	0.228	0.05	3.3	Dark green	No	15.05
7	0.093	0.228	0.1	3.3	Dark green	No	18.23
8	0.093	0.114	0.025	3.3	Fawn	Slight	09.90
9	0.093	0.456	0.025	3.3	Brown	No	18.39
10	0.093	0.62	0.025	3.3	Brown	No	21.60
11	0.047	0.228	0.025	3.3	Dark green	No	13.63
12	0.186	0.456	0.025	3.3	Dark green	Yes	17.80
13	0.372	0.912	0.025	3.3	Dark green	Yes	25.02

[a] The precipitate will diminish by slightly shaking the bottle and the dispersion will be formed again.

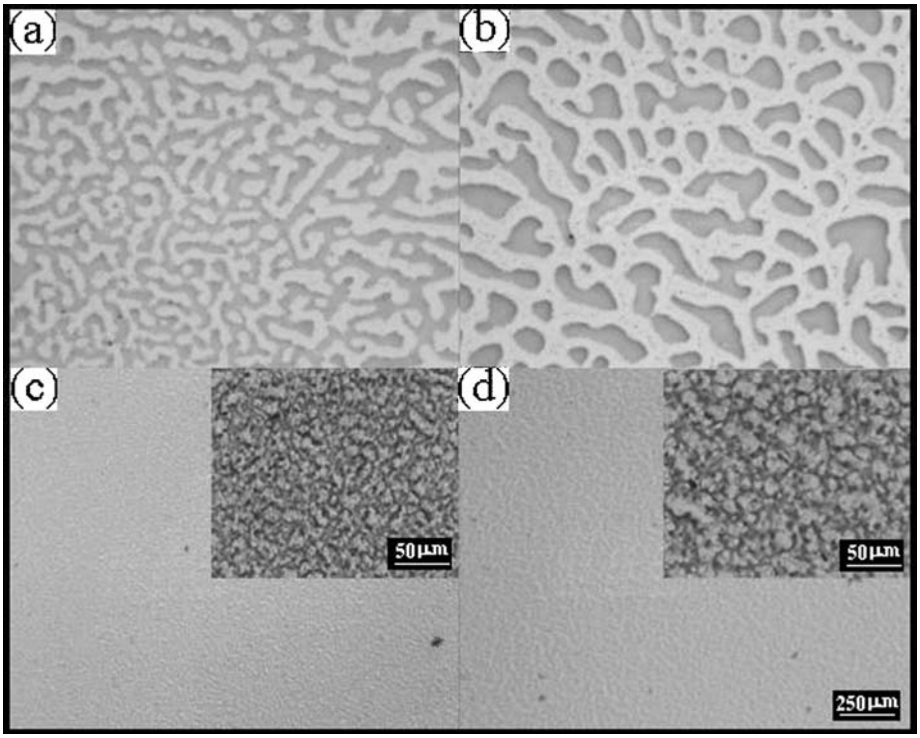

Figure 1 Microscopy images of PANI dispersions with different amount of HCl (a) 1.65×10^{-6} m^3, (b) 3.3×10^{-6} m^3, (c) 6.6×10^{-6} m^3 and (d) 1.0×10^{-5} m^3).

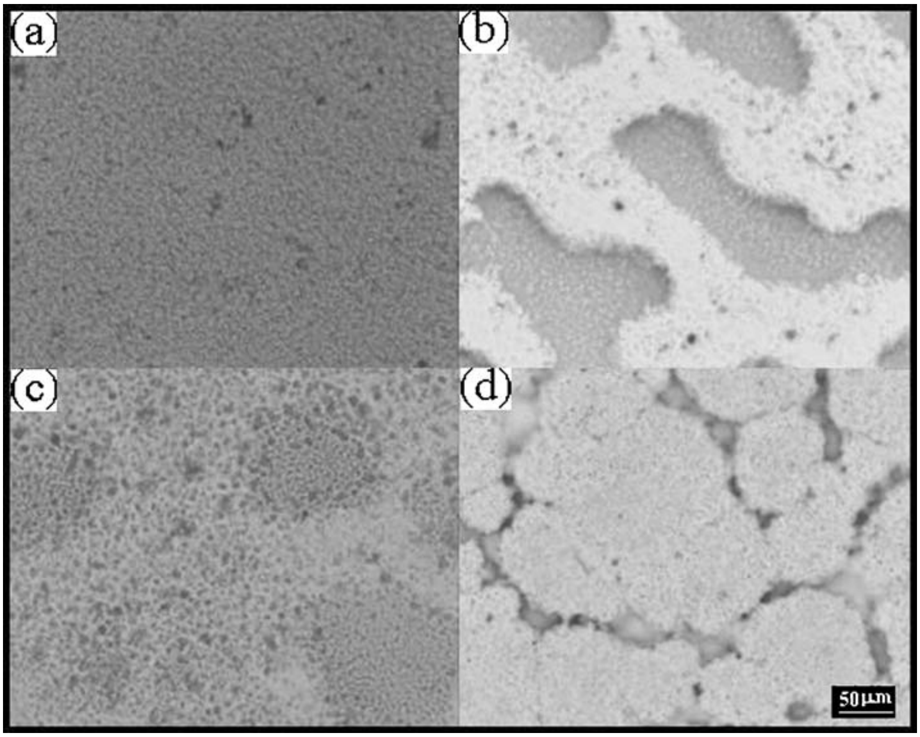

Figure 2 Microscopy images of PANI dispersions with different concentration of SDBS (a)0.01M, (b)0.025M, (c)0.05M and (d)0.1M).

that they are net-linked with a compact structure (insets of Fig. 1c and d). This may be resulted from the quicker polymerization rate, which holds back the free surfactants to extent and construct a network structure similar to that in Fig. 1a and b. Though they appear homogeneous, Sample 3 and 4 show slight precipitate because of their relatively high acid concentration (Table I) [22].

The different structure by only changing the concentration of SDBS is presented in Fig. 2. As discussed in Section 3.1, a lower SDBS concentration results in precip-

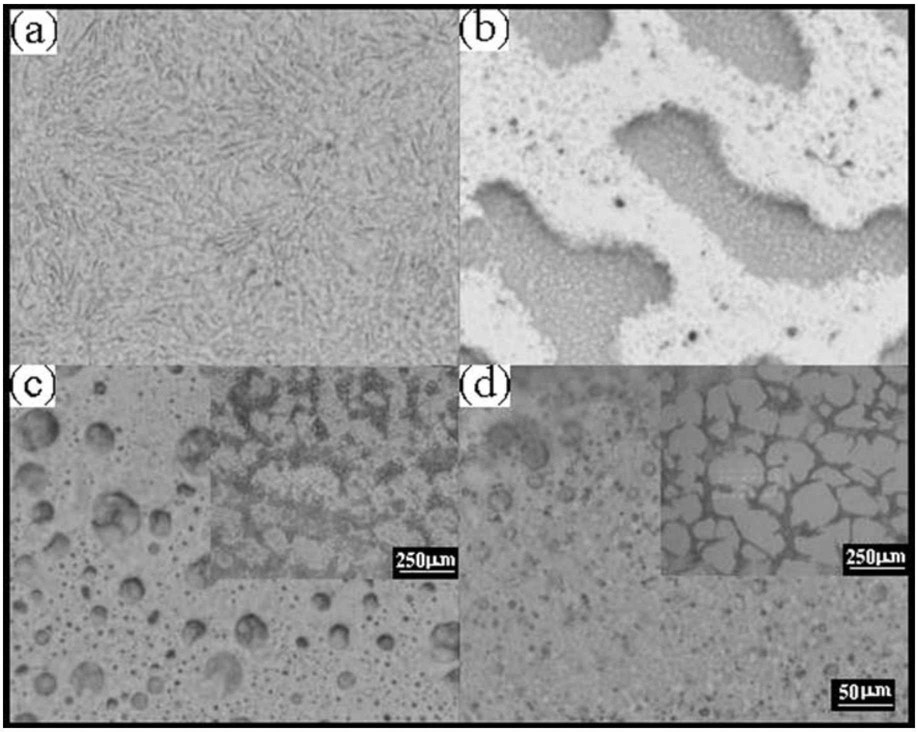

Figure 3 Microscopy images of PANI dispersions with different aniline/APS ratio (a) 2:1, (b) 1:1, (c) 1:2 and (d) 1:2.7).

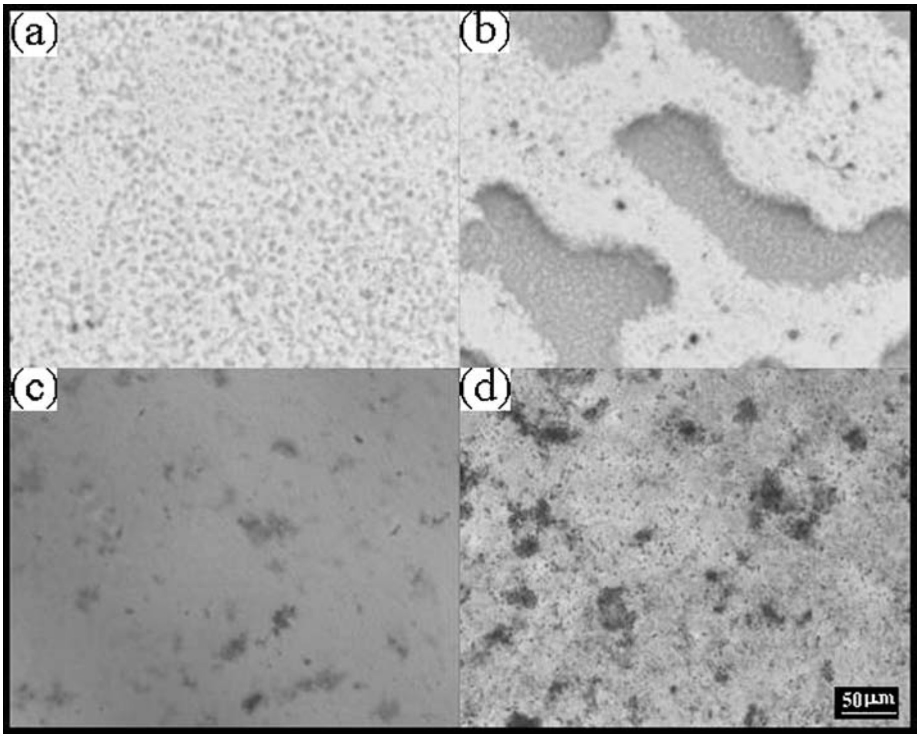

Figure 4 Microscopy images of PANI dispersions with different amount of aniline (a) 0.047 g, (b) 0.093 g, (c) 0.186 g and (d) 0.372 g).

itation of PANI (Fig. 2a) and this can be ascribed to fewer surfactants to stabilize the PANI particles. With increasing the SDBS concentration, a better network structure is formed and hence keeps the PANI from precipitating.

Different aniline/APS ratio will also affect the structure of the PANI dispersion, as shown in Fig. 3. When the APS is not sufficient to polymerize the aniline, fiber-like structure is presented probably due to the existence of a large amount of oligomers. On the contrary, if excess APS is used, the aniline will induce over-oxidization and generation of oil aggregation, though the network structure still exists (Fig. 3c and d).

From Fig. 4, the dispersions' structure obtained from different aniline concentration, a higher aniline concentration is expected to produce precipitate because the free surfactants cannot afford to support the PANI particles.

3.3. UV-Vis spectra of PANI dispersions

A typical absorption spectrum of PANI dispersion has two absorption peaks at about 330 and 420 nm and one absorption peak maximum at 790 nm. The first two peaks often combine to emerge as a platform. The peak at 330 nm arises from π-π^* electron transition within benzenoid segments and the peak at 420 nm, accompanied by the absorption with 790 nm as the maximum peak is related to the doping level and formation of polaron [16, 18].

As can be seen from Fig. 5, the UV-Vis spectra of the PANI dispersions with different amount of HCl, the absorption peaks at around 330 and 420 nm show little difference, while the peaks at 790 nm give out unlike results with both absorption position and intensity. The absorption maxima shift toward the longer wavelength region from 779 (Sample 2, 3.3×10^{-6} m^3 of HCl) to 781 (Sample 4, 1.0×10^{-5} m^3 of HCl), 788 (Sample 3, 6.6×10^{-6} m^3 of HCl) and 792 nm (Sample 1, 1.65×10^{-6} m^3 of HCl). This phenomenon perhaps results from the different dispersion structure as shown in Fig. 1. When more acid is used, the absorption maximum shifts to longer wavelength by comparing Sample 1 with 2 and Sample 3 with 4. The shift may be originated from different doping level and intra-chain conformation. It appears that Sample 3 shows maximum absorption intensity, indicating it has relatively more content of doped PANI.

The absorption spectra of PANI dispersions with different SDBS concentration are given in Fig. 6. The spectra show that a higher concentration of SDBS will result in a lower absorption intensity, which may attribute to the fact that more SDBS can decrease the polymerization effect. On the other hand, the peak position at around 790 nm shifts from 796 (Sample 5, 0.01 M) to 779 (Sample 2, 0.025 M), 782 (Sample 6, 0.05 M) and 750 nm (Sample 7, 0.1 M), indicating the decrease of doping level. Though Sample 2 and 6 show little difference at this absorption position, the peaks around 330 and 420 nm give out dissimilar results. Unlike the typical spectra of doped PANI, the peaks around 330 and 420 nm of Sample 6 and 7 do not form a good platform. This can be ascribed to the insufficient polymerization of aniline in higher SDBS concentration at fixed HCl content because the surfactant will compete with aniline to interact with the H$^+$ in the solution.

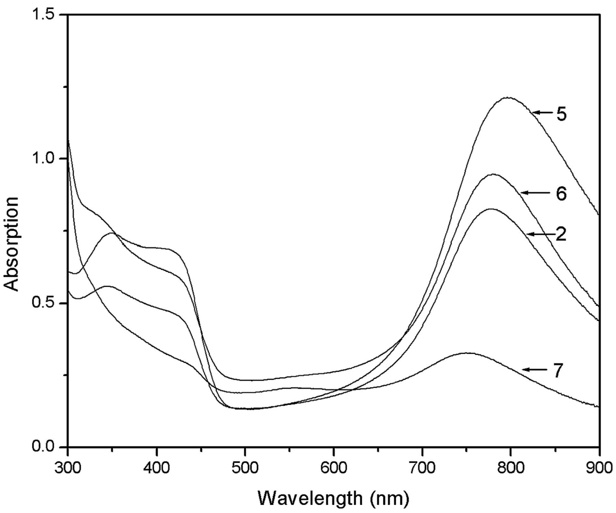

Figure 6 UV-Vis spectra of PANI dispersions with different concentration of SDBS (The concentration of the SDBS can be found in Table I as the numbers refer to).

Fig. 7 shows the spectra of PANI dispersions with altering aniline/APS ratio from 2:1 to 1:3. It is found that deficient or excess APS will both lead to the unsuccessful polymerization of aniline in SDBS solution, which can be concluded from the decrease and even diminish of the

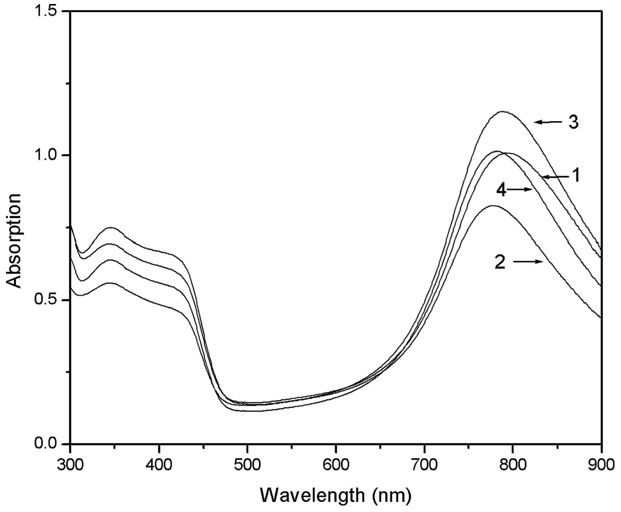

Figure 5 UV-Vis spectra of PANI dispersions with different amount of HCl (The amount of the HCl can be found in Table I as the numbers refer to).

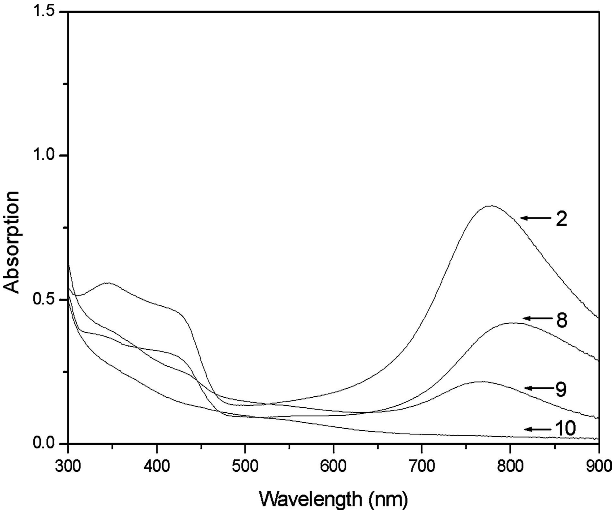

Figure 7 UV-Vis spectra of PANI dispersions with different aniline/APS ratio (The aniline/APS ratio can be found in Table I as the numbers refer to).

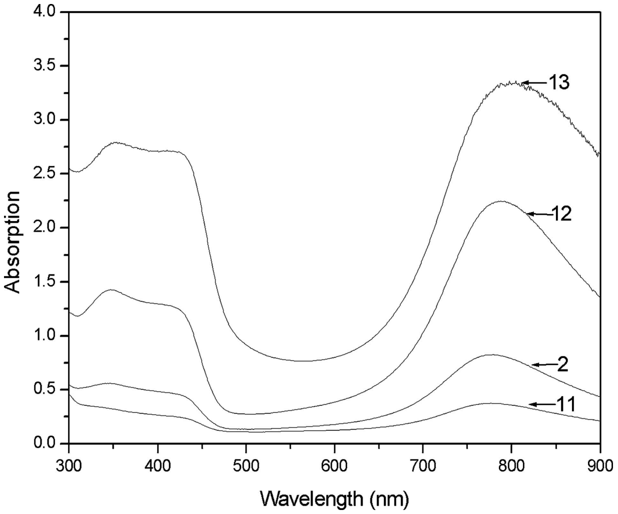

Figure 8 UV-Vis spectra of PANI dispersions with different amount of aniline (The amount of aniline can be found in Table I as the numbers refer to).

peaks around 420 and 790 nm when the ratio is lower or higher than 1.

Increasing the concentration of aniline at fixed aniline/APS ratio and concentration of HCl and SDBS will result in the increase of absorption intensity at any position as presented in Fig. 8, indicating more doped PANI existing in the dispersion. In addition, the position around 790 nm at maximum shifts to longer wavelength accompanying by the increase of the content of PANI, which may depend on its molecular mass, degree of oxidation and supermolecular level [24].

3.4. Conductivity

The conductivity of the PANI dispersions may be mainly affected by two factors, i.e., formation of PANI and content of the ions, especially the ammonium sulfate produced by the reduction of ammonium peroxydisulfate in the dispersion. From the results of different samples' conductivity as listed in Table I, one can find that in these systems, the later one plays a major role, that is, the conductivity of the dispersions increases with the amount of reactants. This should be attributed to the low concentration of aniline and hence relatively few PANI forming in the dispersion.

3.5. Size distribution

We tried to measure the size distribution of different PANI dispersions by using dynamic light scattering. The results show that the size of the particles in the dispersion is in the range of 10 to 70 nm, however, we cannot make a conclusion on how the particles change in different dispersions. We consider this result may own to the following reasons: (1) the dispersion is under a dynamic process, (2) the difference among the dispersions is not so evident, (3) the surfactant may disturb the measurement and (4) the concentration of the samples is very low.

4. Conclusions

PANI dispersions with different assembly structure were prepared using SDBS both as surfactant and dopant with the aid of acid. It was found that the molar ratio of SDBS/aniline, SDBS/HCl and aniline/APS would all affect the assembly structure of the PANI in the dispersion and hence the dispersions' optical absorptions. The dispersions showed excellent stability and nearly solution characteristic, though their conductivity was only in the range of tens of mS/cm and affected by the presence of ammonium sulfate. The PANI dispersion with kinds of structure can be applied for sensors and other electronic devices.

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