

UV-VIS SPECTRA OF POLYANILINE DOPED WITH CAMPHOR SULFONIC ACID IN DIFFERENT ORGANIC SOLVENTS*

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Abstract The doping reaction of polyaniline with camphor sulfonic acid (CSAH) in different organic solvents was studied by UV-Vis spectroscopy. The experimental results show that the polaron band of the species was shifted to shorter wavelength when polyaniline was doped with CSAH in N-methyl-2-pyrrolidione (NMP) solvent, while the red shift of polaron band was observed when it was in N, N-dimethylformamide (DMF). It indicates that the influence of different processing solvents on the doping property of polyaniline is greatly different. N-methyl-2-pyrrolidione is a good solvent for polyaniline, polyaniline chain is unfolded in it. The interaction of NMP with CSAH is so strong that the resulting product is apt to dedoping, while the solubility of polyaniline in DMF is relatively low and polyaniline chain is in partly folded state. Thus the doping reaction is kinetically disadvantageous but thermodynamically advantageous.

Key words polyaniline; dope; camphor sulfonic acid; UV-Vis spectra

Doped polyaniline is a very promising conducting polymer, but its further application is greatly impeded by its poor solubility in organic solvent. N-methyl-2-pyrrolidione (NMP) is a well-known processing solvent for polyaniline. However the film cast from its NMP solution always shows less conductivity ($10^{-1} \sim 10^{-4} \text{ S} \cdot \text{cm}^{-1}$) than its conducting parent^[1]. Therefore it is necessary to investigate the interaction of doped polyaniline with different solvents in order to search for better processing solvent for doped polyaniline. Few reports have been made on the doping reaction of polyaniline in different organic solvents. In the present work, we investigated the doping reaction of polyaniline with camphor sulfonic acid in NMP or DMF by 'in-situ' UV-Vis spectroscopy and observed the blue shift or red shift phenomena of corresponding polaron band with time.

1 EXPERIMENTAL

Polyaniline was synthesized as reported by MacDiarmid et al^[2], and then changed to its intrinsic state labeled as PAN. By elemental analysis the composition of PAN is $\text{C}_{6.00} \text{H}_{4.48} \text{N}_{1.02}$. N-methyl-2-pyrrolidione (NMP) and N, N-dimethylformamide (DMF) were dried by activatory 4A molecular sieve and distilled under reduced pressure before use. Camphor sulfonic acid (CSAH) was analytically pure.

The solution was prepared by adding quantitative

amount of camphor sulfonic acid (CSAH) into NMP or DMF solution of polyaniline. The molar ratio of CSAH to -N= of polyaniline was 1:1. The UV-Vis absorption spectra were measured with a Shimadzu UV-1601PC spectrophotometer.

2 RESULTS AND DISCUSSION

2.1 UV-Vis Spectra of Polyaniline Doped with CSAH in NMP

Fig. 1 is the UV-Vis spectra of polyaniline before and after doped with CSAH in NMP. Curve 1 shows that undoped polyaniline has two absorption bands at 330 nm and 635 nm due to the excitation of the benzene and quinoid segments in polyaniline chain, respectively. When CSAH was dropped into the solution, the absorption band at 635 nm disappeared quickly except for the absorption at 330 nm, and the color of solution was changed from blue to yellowish green, and two new absorption bands at 430 nm and 800 nm were observed at the same time due to the excitation of corresponding polaron band^[3]: the former is a shoulder band and the latter a broad one. However the band at 800 nm was found to shift to 750 nm after 24 h. In fact the color of solution was turned to light blue after 6 days with the 800 nm band shifting to 670 nm, which indicates that CSAH doped polyaniline in NMP was undergoing apparently dedoping process. The relationship between blue shift of 800 nm-polaron band and time is shown in Fig. 2.

* Project supported by the National Natural Science Foundation of China

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Manuscript received Jan. 14, 1999

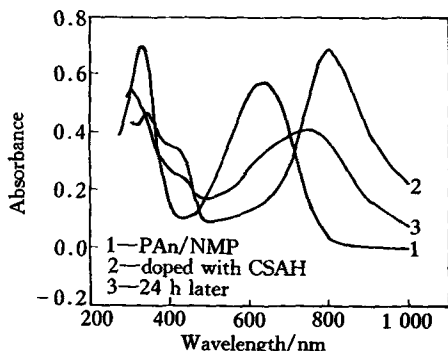


Fig. 1 UV-Vis spectra of polyaniline before and after doped with CSAH in NMP

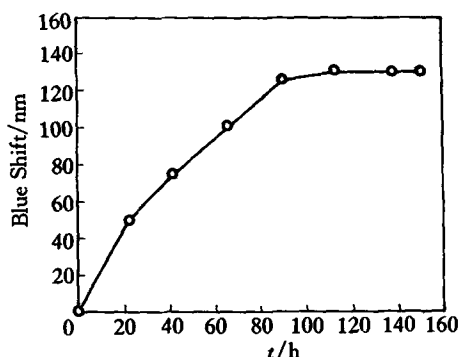


Fig. 2 The relationship between blue shift of 800 nm-polaron band and time

2.2 UV-Vis Spectra of Polyaniline Doped with CSAH in DMF

Fig. 3 is the UV-Vis spectra of polyaniline before and after doped with CSAH in DMF. Curve 1 shows that undoped polyaniline has two absorption bands at 330 nm and 625 nm due to the excitation of the benzene and quinoid segments in polyaniline chain, respectively.

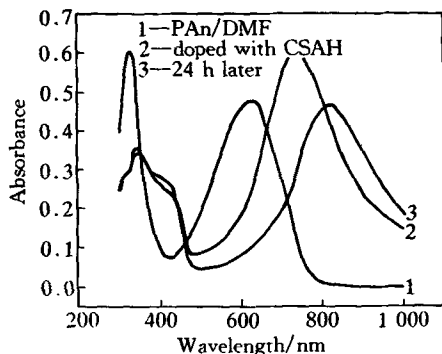


Fig. 3 UV-Vis spectra of polyaniline before and after doped with CSAH in DMF

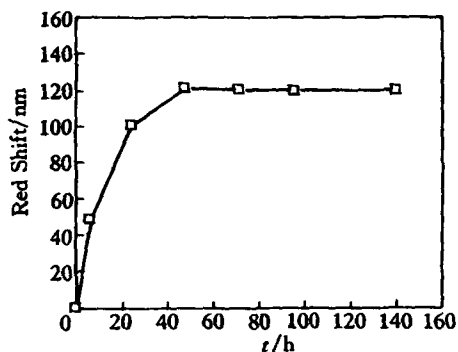
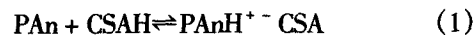


Fig. 4 The relationship between red shift of 725 nm-polaron band and time

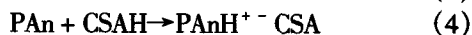
When CSAH was dropped into the solution, the absorption band at 625 nm disappeared quickly except for the absorption at 330 nm, the characteristic polaron band would appear at 725 nm rather than 800 nm when compared with in NMP. However the band at 725 nm was gradually shifting to 825 nm when the solution was kept overnight and the red shifts surprisingly amounted to 100 nm in 24 h. It demonstrates that the doping reaction of polyaniline with CSAH in DMF proceeds slowly and steadily. Fig. 4 shows the relationship between red shift of 725 nm-polaron band and time.

2.3 Discussions

Based on the different position and absorbance and shift direction of absorption band in UV-Vis spectra for these species, it is deduced that the doping reaction of polyaniline with CSAH in NMP has a kinetic advantage over the interaction of solvent with CSAH. The reaction undergoes very quickly accompanied by strong polaron band at 800 nm. But the band is shifting to shorter wavelength after the solution is kept overnight and the blue shifts about 50 nm in 24 h, which indicates that the product was thermodynamically unstable. On the contrary, the interaction (2) between basic polar solvent NMP and organic acid dopant CSAH is relatively stronger so that the equilibrium (1) between doping and dedoping shifts to the left side.



On the other hand, in the case of DMF, it is suggested that the doping reaction of polyaniline with CSAH in DMF should be kinetically disadvantageous but thermodynamic advantageous, so the emerging polaron band at 725 nm undergoes extraordinary red shift in 24 h and gradually reached stability. It shows that the doping reaction (4) proceeds slowly and steadily and the interaction of DMF with CSAH (3) is relatively weaker than that between NMP and CSAH (The electron donating number of DMF and NMP is 26.6 and 27.3^[4], respectively).



Furthermore, it also demonstrates that the interaction between NMP and CSAH is stronger than that between DMF and CSAH by FT-IR spectroscopy. The stretching vibration peak (1689 cm^{-1}) corresponding to —C=O of NMP in the mixture of NMP and CSAH whose concentration is equal to that of doping reaction is shifted to lower wavenumbers by 15 cm^{-1} , whereas the peak (1668 cm^{-1}) corresponding to —C=O of DMF in the mixture of DMF with CSAH does not undergo apparent shift.

From the view point of solubility of polyaniline in different organic solvents, NMP is a good solvent for polyaniline and polymer chain is unfolded in it, and the effective doping site of polyaniline is fully exposed, so that both the doping and dedoping reaction with CSAH are advantageous; whereas DMF is a bad solvent for polyaniline, and polymer chain is partly folded in it, thus the doping reaction proceeds slowly and the dedoping reaction is relatively difficult at the same time.

3 CONCLUSIONS

The red shift and blue shift phenomena of the UV-

Vis spectrum for polaron band were observed when polyaniline was doped with CSAH in different organic solvents. Polyaniline chain in NMP is in unfolded state so that the doping reaction is easy to proceed, but the dedoping is dominating due to the strong interaction between NMP and CSAH, while polyaniline chain in DMF is in partly folded state so that the doping reaction is kinetically disadvantageous but thermodynamic advantageous. Therefore the doping reaction of polyaniline with CSAH goes on better in DMF than in NMP.

References

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