

UV-Vis Spectra of *N, N'*-Bis(4'-Aminophenyl)-1,4-quinonenediimine Doped with $H_4SiW_{12}O_{40}$

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Abstract: We have synthesized aniline oligomer composites by using heteropoly acid ($H_4SiW_{12}O_{40}$) as a dopant. The doping and dedoping processes of the aniline oligomer composites were investigated with the aid of UV-Vis spectra. The bands of the aniline oligomer at 572 nm weakened or disappeared, and the bands at 268, 412, and 771 nm appeared, after the aniline oligomer was doped. When the solution of the aniline oligomer doped with $H_4SiW_{12}O_{40}$ was kept at lower values of pH, the aniline oligomer could not be dedoped by dilution. The turning point of doping and dedoping occurred at pH 5.5. The band at 771 nm shifted towards longer wavelengths when the aniline oligomer composites were synthesized using acetone as the solvent. This observation indicates that the molecular chain became stretched. In addition, we also investigated the change of the electronic absorption spectra of the composites with respect to the time laid up.

Keywords: heteropoly acid, aniline oligomer with three units, UV-Vis spectra, doping, dedoping.

Introduction

Polyaniline (Pan) is well known for its good environmental stability and high conductivity.^{1,2} It is different from other conjugated conducting polymers in doping property. Treatment with an appropriate protonic acid can make Pan to be doped via protonation without changing the number of π -electrons by exposure to an appropriate protonic acid through protonation in aqueous solution.^{3,4} Recently, the studies on the synthesis, characterization, processibility, and application of Pan has gotten widespread development,⁵⁻¹⁰ and has become increasingly important. The interaction between molecule chains of Pan increases with increasing the doping percentage, resulting in insolubility in many solvents. It is the insolubility that makes it difficult to process the doped materials and limits the investigation of doping structure, conducting principle, and applications of the materials. Recently, the investigation about aniline oligomer has attached considerable interest.¹¹⁻¹⁴ Compared with Pan, the basic structure unit of aniline oligomer in molecule is similar. And aniline oligomer has a good solubility in many organic solvents. Therefore the study on the structure of aniline oligomer will be profitable for the investigation of the doping structure and doping process of Pan.

Inorganic metal oxide cluster anions, a class of inorganic

compounds, are believed to have extensive prospects of application in synthetic chemistry, analytic chemistry, biology, medicine, and materials science.¹⁵⁻¹⁷ In this paper, a series of aniline oligomer composites were synthesized by using $H_4SiW_{12}O_{40}$ as a dopant. The UV-Vis spectra of these aniline oligomer composites were studied. The effect of concentration, time, and pH on doping and dedoping of the aniline oligomers were investigated.

Experimental

Synthesis. *N, N'*-bis(4'-aminophenyl)-1,4-quinonenediimine was prepared according to reference (11). It was examined with IR and 1H NMR spectroscopy. All reagents were of analytical grade. The aniline used was distilled twice under vacuum. $H_4SiW_{12}O_{40}$ was dried under vacuum at 60°C for 24 h.

$H_4SiW_{12}O_{40}$ was dissolved in 25 mL of distilled water, then 0.5 g (1.74 mmol) *N, N'*-bis(4'-aminophenyl)-1,4-quinonenediimine was added to the solution, the reaction mixture was kept at room temperature for 48 h with continuous stirring. The precipitate formed was filtered, washed thoroughly with distilled water, and dried under vacuum at 40°C for 48 h. The quantity of $H_4SiW_{12}O_{40}$ is 10.00, 5.00, 2.50, 1.25 and 0.60 g, respectively.

$H_4SiW_{12}O_{40}$ was dissolved in 10 mL of acetone, then 0.5 g (1.74 mmol) *N, N'*-bis(4'-aminophenyl)-1,4-quinonenediimine was added to the solution with continuous stirring. Precipitate

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Table I. Results of Elemental Analysis

Empirical Formula ^a	C	H	N	W
$(C_{18}N_4H_{16})(SiW_{12})^{a_{0.64}}$	10.18	0.87	2.64	66.52
$(C_{18}N_4H_{16})(SiW_{12})^{a_{0.47}}$	13.16	0.97	3.41	63.19
$(C_{18}N_4H_{16})(SiW_{12})^{a_{0.37}}$	15.97	1.29	4.14	60.33
$(C_{18}N_4H_{16})(SiW_{12})^{a_{0.19}}$	25.88	2.01	6.71	50.20
$(C_{18}N_4H_{16})(SiW_{12})^{a_{0.11}}$	35.72	2.72	9.26	40.13
$(C_{18}N_4H_{16})(SiW_{12})^{b_{0.38}}$	17.05	1.70	4.79	58.42
$(C_{18}N_4H_{16})(SiW_{12})^{b_{0.35}}$	16.07	1.77	4.00	58.14
$(C_{18}N_4H_{16})(SiW_{12})^{b_{0.32}}$	16.93	1.86	3.94	55.39
$(C_{18}N_4H_{16})(SiW_{12})^{b_{0.21}}$	21.91	2.12	5.75	49.59

^awater method. ^bacetone method.

formed immediately. The mixture was kept at room temperature for 4 h with continuous stirring. The precipitate was filtered and washed with acetone and distilled water, respectively. The powder was dried under vacuum at 40 °C for 48 h. The quantity of $H_4SiW_{12}O_{40}$ is 10.00, 5.00, 2.50 and 1.25 g, respectively. The chemical analysis data of the oligomer composites were shown in Table I.

Measurement Instruments. PE2400 CHN element analyzer was used for elemental analysis. Tungsten was analyzed by 8-hydroxy-quinoline tannin acid-methylviolet gravimetry. The UV-Vis absorption spectra were obtained with Beckman-DU8B UV spectrophotometer.

Results and Discussion

Electronic absorption spectra of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine showed two absorption bands. The absorption with maxima at 330 nm was assigned to the $\pi-\pi^*$ transition of the benzenoid moiety ($[C_6H_4NH]$). The second band at the 572 nm was due to the $\pi_b-\pi_q^*$ transition of the quinone and benzene group ($[C_6H_4-N=C_6H_4N]$).¹⁸ They were the typical electronic absorption bands of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine base. Compared with the absorption of Pan at 620 nm, the absorption of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine shifted to lower wavelength. i.e. 572 nm. This situation was conformable to the short molecular chain of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine.¹⁴ After the aniline oligomer with three amine units was doped with $H_4SiW_{12}O_{40}$, a strong band at 268 nm appeared (see Figure 1). In order to investigate the band at 268 nm, $H_4SiW_{12}O_{40}$ was dissolved in *N,N'*-dimethylformamide (DMF). The band at 268 nm appeared also in the UV spectra of DMF solution of $H_4SiW_{12}O_{40}$. So we deduced that the band at 268 nm was the characteristic band of heteropoly acid. The band at 572 nm weakened or even disappeared, at the same time, the bands at 412 and 771 nm appeared due to the presence of polaron.¹⁹ These indicated

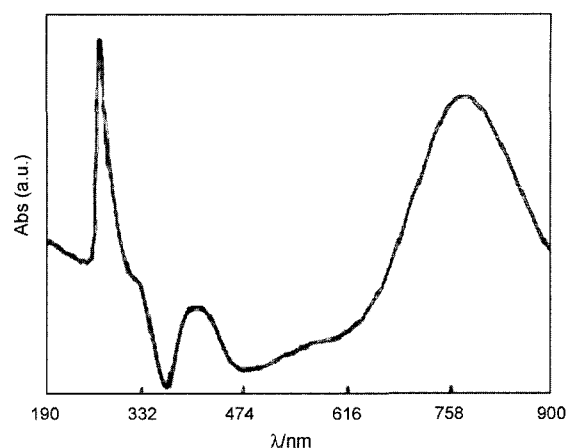


Figure 1. UV-Vis spectra of aniline oligomer doped with $H_4SiW_{12}O_{40}$.

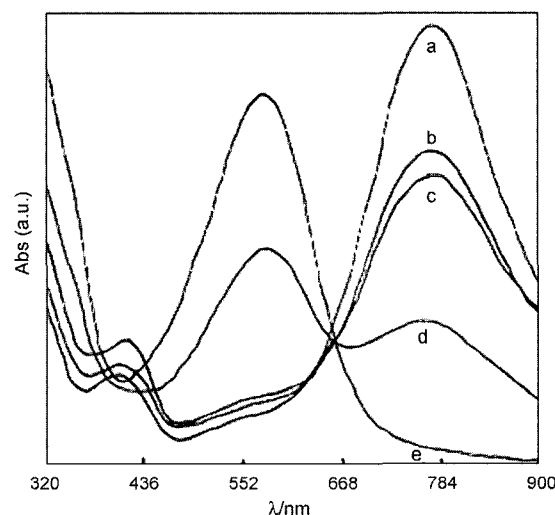


Figure 2. UV-Vis spectra of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine doped with $H_4SiW_{12}O_{40}$: (a) $(C_{18}N_4H_{16})(SiW_{12})^{a_{0.64}}$; (b) $(C_{18}N_4H_{16})(SiW_{12})^{a_{0.47}}$; (c) $(C_{18}N_4H_{16})(SiW_{12})^{a_{0.37}}$; (d) $(C_{18}N_4H_{16})(SiW_{12})^{a_{0.19}}$; (e) $(C_{18}N_4H_{16})(SiW_{12})^{a_{0.11}}$.

that the oligomer had been doped with proton of the heteropoly acid.

Effect of Doping Amount. All doped oligomers were dissolved in DMF with a concentration of 0.18 mg/mL. Figure 2 showed the UV-Vis spectra of the oligomers. As seen in Figure 2, the intensity of the absorption bands at 771 and 412 nm increased with increasing the doping amount. The bigger the doping amount was, the bigger the intensity gap between 771 and 412 nm was. The oligomer doped with a small amount of $H_4SiW_{12}O_{40}$, such as sample "e" was dedoped easily. Therefore, the UV-Vis spectra of "e" showed the characteristic spectra of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine base. This indicated that the sample "e" had been dedoped in this concentration. Obviously, in the

same condition, the bigger the doping ratio was, the more difficult the dedoping of the oligomer composite was.

Effect of pH. Figure 3 showed the change of UV-Vis spectra of the oligomers with the change of the pH of solution. The pH was adjusted by $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and 25% aqueous ammonia solution, respectively, and controlled by pHs-2 acidity measurer. There were two absorption bands at 330 and 572 nm in pH=6. They are characteristic bands of N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine base. This indicated that N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine was not doped at pH=6. The bands at 412 and 771 nm appeared at pH \leq 5.5, and the intensity of the bands increased with decreasing the pH of the solution. This indicated that N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine base had been doped in the lower pH. The pH value of 5.5 was the turning point from doping to dedoping. The doping of N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine was reversible and rapid. Obviously, the concentration of H^+ was the most important factor on doping and dedoping of the oligomers.

Effect of Solution Concentration. $(\text{C}_{18}\text{N}_4\text{H}_{16})(\text{SiW}_{12})_{0.64}$ was dissolved in DMF. The concentration of the solution was 0.18 mg/mL. The solution was diluted with DMF to 0.12, 0.09 and 0.07 mg/mL, respectively. The color of the solution changed from green to light green, blue-green and blue, respectively. Figure 4 showed the UV-Vis spectra of the solutions. The UV-Vis spectra of original concentration solution showed three absorption bands, which were typical absorption bands of doped N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine, at ca. 330, 412 and 771 nm, respectively. But the intensity of the bands at 412 and 771 nm decreased, and that at 572 nm increased gradually with diluting the solution. The bands at 412 and 771 nm disappeared completely when the solution concentration was 0.07 mg/mL. The UV-Vis spectra of this solution showed typical absorption spectra of N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine

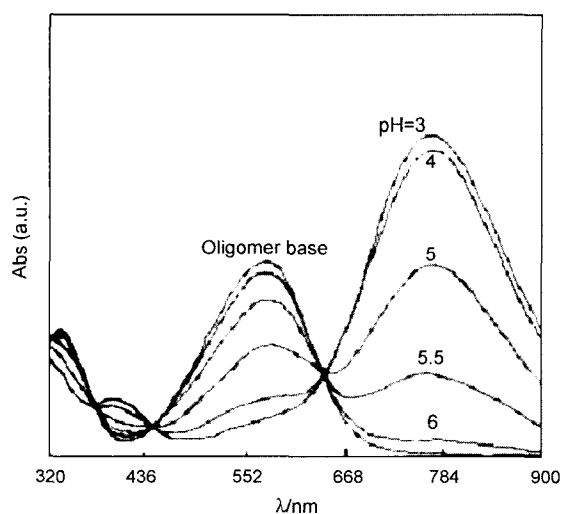


Figure 3. UV-Vis spectra of aniline oligomer dispersion vs. pH value.

base. This indicated that the dilution causes dedoping of the oligomer composites.

When the pH of the solution was kept lower than 3 in dilution, we could find that the bands at 412 and 771 nm decreased gradually with increasing diluting. This indicated the concentration of N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine doped with $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ decreased. However, the band at 572 nm had not appeared in the course of diluting. This fact could be explained by two hypotheses. One was that the oligomer had not been dedoped in the course of diluting. Another was that the oligomer had been dedoped in the diluting course, and the disappearance of the band at 572 nm was due to too lower of the concentration of the oligomer. In order to study the reason, 25% aqueous ammonia solution was added to the diluted solution. The band at 572 nm appeared (see Figure 5 curve a). This suggested that N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine doped with $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was not dedoped when the pH had been kept to lower, and that the concentration of H^+ was the decisive factor for the reversibility of doping and dedoping.

Effect of Time. The solutions, which were diluted to 0.12, 0.09 and 0.07 mg/mL, were laid up for 12, 48 and 96 h, respectively. The UV-Vis spectra showed that the solution of original concentration dedoped after it was laid up for 96 h. The solution diluted to 0.5 times dedoped after it was laid up for 48 h. The solution diluted to 1 and 1.5 times dedoped after they were laid up for 12 h. These indicated that the doped N,N' -bis(4'-aminophenyl)-1,4-quinonenediimine dedoped with increasing time of laying up. But the dedoping times of different concentration solutions were different, the higher the concentration of solution was, the longer its dedoping time was.

Effect of Solvent. UV-Vis spectra of the oligomers, which were synthesized by using water and acetone as solvent,

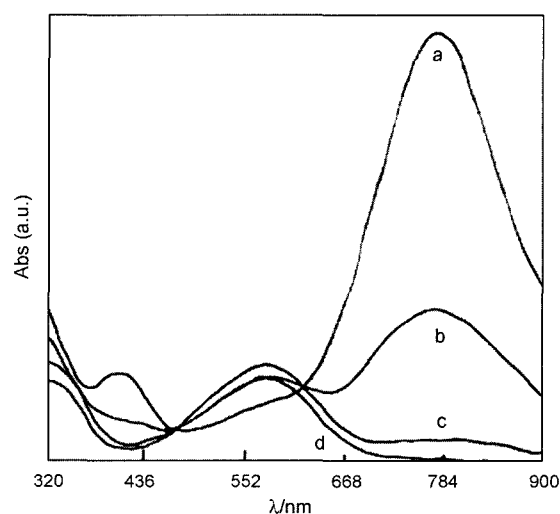


Figure 4. UV-Vis spectra of different concentration $(\text{C}_{18}\text{N}_4\text{H}_{16})(\text{SiW}_{12})_{0.64}$ in DMF: (a) 0.18 mg/mL; (b) diluted to 0.5 times; (c) diluted to 1 times; (d) diluted to 1.5 times.

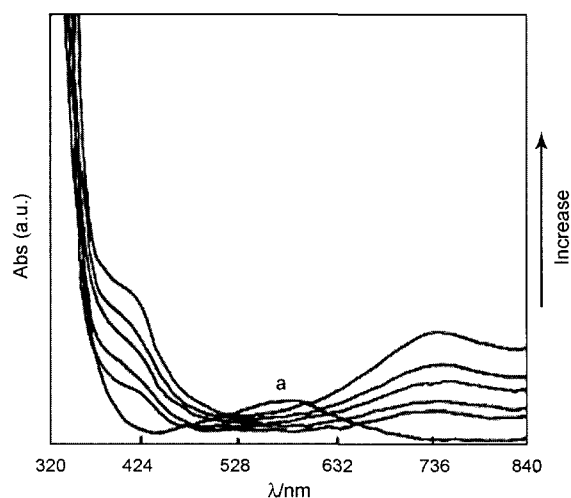


Figure 5. UV-Vis spectra of $(C_{18}N_4H_{16})(SiW_{12})_{0.64}$ diluted by DMF in $pH < 3$.

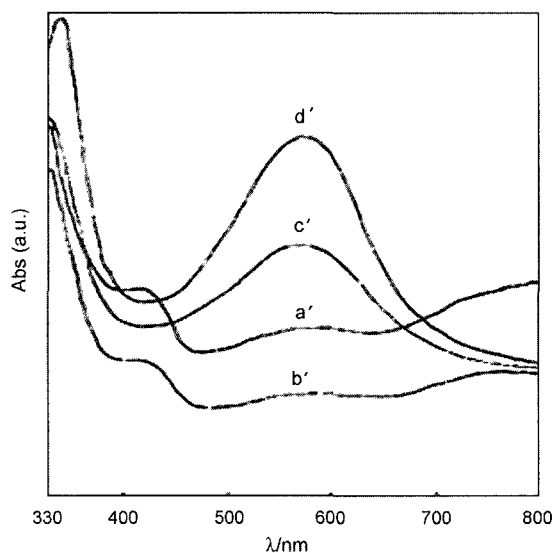


Figure 6. UV-Vis spectra of *N,N'*-bis(4'-aminophenyl)-1,4-quinonenediimine doped with $H_4SiW_{12}O_{40}$ using acetone as solvent: (a') $(C_{18}N_4H_{16})(SiW_{12})_{0.38}^b$; (b') $(C_{18}N_4H_{16})(SiW_{12})_{0.35}^b$; (c') $(C_{18}N_4H_{16})(SiW_{12})_{0.32}^b$; (d') $(C_{18}N_4H_{16})(SiW_{12})_{0.21}^b$.

respectively, were similar. However, the intensity of the band at 771 nm was weaker in the case of acetone as solvent than water at the same doping amount. At the same time, the band at ca. 771 nm seemed to shift to long wavelength for the oligomer composite synthesized by using acetone as solvent (see Figure 6). The fact indicated that molecular chain was stretched in acetone solvent.¹⁹

Conclusions

Aniline oligomer composites were synthesized by using

heteropoly acid ($H_4SiW_{12}O_{40}$) as dopant. A strong band at 268 nm, which was the characteristic band of heteropoly acid, appeared in the UV-Vis spectra of the aniline oligomer doped with heteropoly acid. At the same time, the characteristic bands at 412 and 771 nm appeared due to the polaron of doped aniline oligomer appeared. The higher the doping amount was, the more difficult the dedoping of the oligomer composite was in DMF. The pH of 5.5 was the turning point from doping to dedoping. The doped oligomer would not dedoped when the solution was kept at lower pH. Compared with the spectrum of doped oligomer obtained in water solvent, the band at ca. 771 nm in the spectrum of doped oligomer obtained shifted to long wavelength in acetone solvent. This indicated that molecular chain was stretched in acetone solvent.

References

- (1) E. M. Genies, A. Boyle, and M. Lapkowschi, *Synth. Met.*, **36**, 136 (1990).
- (2) J. Gong, X. J. Cui, Z. W. Xie, S. G. Wang, and L. Y. Qu, *Synth. Met.*, **129**, 187 (2002).
- (3) J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986).
- (4) J. Gong, X. J. Cui, Z. W. Xie, and L. Y. Qu, *Chin. Chem. Lett.*, **13**, 123 (2002).
- (5) A. G. MacDiarmid, J. C. Chiang, A. F. Ritcher, and A. J. Epstein, *Synth. Met.*, **18**, 285 (1987).
- (6) C. M. Carllin, L. J. Kapley, and A. J. Bard, *J. Electrochem. Soc.*, **132**, 353 (1985).
- (7) F. S. Wang and L. X. Wang, *Science of China*, **9** (1989).
- (8) M. Morita, K. Komaguchi, and H. Tsutsumi, *Electrochim Acta*, **37**, 1093 (1992).
- (9) M. Lira-Cantu and P. Gomea-Romoro, *Chem. Mater.*, **10**, 698 (1998).
- (10) S. H. Lee, J. W. Yoon, and M. H. Suh, *Macromol. Res.*, **10**, 282 (2002).
- (11) Y. Wei, C. C. Yang, and T. Z. Ding, *Tetrahedron Lett.*, **37**, 731 (1996).
- (12) Y. Wei, C. C. Yang, C. Wei, and G. Z. Feng, *Synth. Met.*, **84**, 289 (1997).
- (13) J. Gong, J. H. Yang, X. J. Cui, Z. M. Su, and L. Y. Qu, *Chin. Chem. Lett.*, **13**, 266 (2002).
- (14) J. Gong, J. H. Yang, X. J. Cui, S. G. Wang, Z. M. Su, and L. Y. Qu, *Synth. Met.*, **129**, 15 (2002).
- (15) M. T. Pope and A. Muller, *Polyoxometalates: from Platonic Solids to Anti-retroviral Activity*, Kluwer Academic Publishers, Netherlands, 1994.
- (16) J. Gong, Z. M. Su, Z. M. Dai, R. S. Wang, and L. Y. Qu, *Synth. Met.*, **101**, 751 (1999).
- (17) J. Gong, R. N. Hua, Z. W. Xie, S. G. Wang, and L. Y. Qu, *Polymer J.*, **33**, 377 (2001).
- (18) J. M. Wilbur, T. C. Sandreczki, I. M. Brown, D. J. Leopold, and S. Mohite, *Synth. Met.*, **82**, 175 (1996).
- (19) Z. J. Xiu, Z. N. Qi, and F. S. Wang, *Acta Polym. Sinica*, **4**, 445 (1997).