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4'-*p*-*N*,*N*-Bis(2-hydroxyethyl)benzyl-3,3':6',2''-Terpyridine에 기초한 형광성 수분산 우레탄의 합성과 특성연구

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Synthesis and Characterization of Fluorescent Waterborne Polyurethane Based on 4'-*p*-*N*,*N*-Bis(2-hydroxyethyl)benzyl-3,3':6',2''-Terpyridine

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Abstract: Cationic waterborne polyurethane fluorescent material based on 4'-*p*-*N*,*N*-bis(2-hydroxyethyl)benzyl-3,3':6',2''-terpyridine (TPPDA-CWPU) was synthesized. The structure was characterized by FTIR and UV-vis spectroscopy. The content of TPPDA in the fluorescent polyurethane was 6.3×10^{-4} mg/mg and the grafting ratio was 33.87%. The number-averaged and weight-average molecular weights of TPPDA-CWPU were about 16060 and 27131 $g\cdot mol^{-1}$, respectively. The maximum absorption wavelength of TPPDA-CWPU was blue shifted ca. 6 nm compared to TPPDA. TPPDA-CWPU showed different fluorescence properties under different solid content. Compared with 20% solid content, the fluorescence intensity of 1% solid content increased by ten times. The quantum yield of TPPDA-CWPU was 0.3, which was four times higher than that of TPPDA. Moreover, TPPDA-CWPU was sensitive to acidic condition and there was the phenomenon of fluorescence quenching in the case of strong acidic conditions. It is believed that more applications will be possible in the pH-responsive polymer.

Keywords: fluorescence, 4'-*p*-*N*,*N*-bis(2-hydroxyethyl)benzyl-3,3':6',2''-terpyridine, waterborne polyurethane, cationic.

Introduction

Fluorescent materials are widely used in the fields of biological imaging and medical diagnosis such as nucleic acid determination, protein analysis, biological macromolecules and so on.[1-3] The synthesis and application of functional fluorescent polymers are getting more and more attention of scientific researchers. Among them, designing appropriate fluorescent molecules are used to modify the polymer structure to achieve functional polymers, which is one of the most direct and simple way.[4-6] Waterborne polyurethane (WPU) has emerged as one of the most flourishing and attractive research areas owing to its unique physical and chemical properties such as adjustable mechanical properties, excellent abrasion resistance, environmental friendliness and good biocompatibility.[7-13] As a result, these WPU modified by fluorescence can simultaneously realize coloring and function to meet the requirements of the modern printing and dyeing industry in order to achieve energy saving, environmental protection and green chemistry.[14-16] Fluorescent poly(styrene-*co*-maleimide) (SMI) was prepared by poly(styrene-*co*-maleic anhydride) (SMA) which was modified by 4-amino-*N*-(2,4-dimethylphenyl)-1,8-naphthalimide.[17] Another group synthesized a cationic waterborne polyurethane covalently bonded anthraquinone dye chromophore which was via incorporating micromolecule disperse Red 91 into the polyurethane skeleton.[18] Few studies were reported in the literature on cationic WPU with the fluorescent molecules of triple pyridine introduced into polymer chain.

Herein, we chose the fluorescent monomer: 4'-*p*-*N*,*N*-bis(2-hydroxyethyl)benzyl-3,3':6',2''-terpyridine (TPPDA) as a chain extender to access the WPU hard segment, the luminescent

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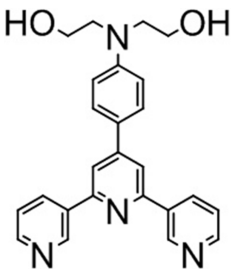
properties of the fluorescent monomer were combined with the water dispersion and the polymer properties of WPU to obtain a kind of polymer fluorescent material which could be dispersed in water.[19-22] WPU was chosen as the carrier of TPPDA for its excellent properties such as superior performance, extensive application, excellent dispersion in water, and structure that could be modified well, which made TPPDA-CWPU a more promising application potential. In this article, it was explored the structural characterization of TPPDA-CWPU by FTIR and UV-vis. The concentration of TPPDA in TPPDA-CWPU was measured. The molecular weight and quantum yield of TPPDA-CWPU were obtained. In addition, there was obvious influence of different dispersion concentration on the fluorescence intensity of TPPDA-CWPU.

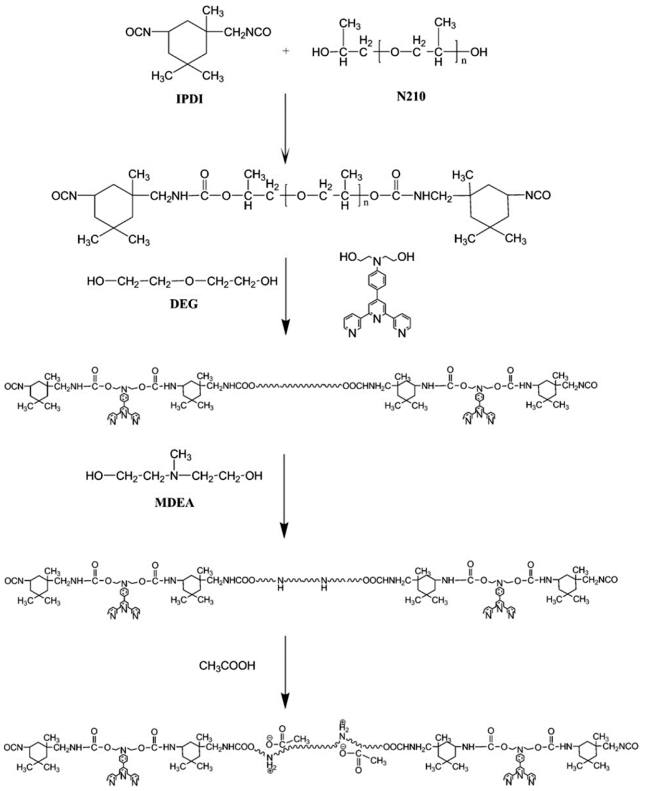
Experimental

Materials. Polyoxypropylene diol (N210, Mn=1000) was purchased from Sinopec(Shanghai), the trace water in N210 was removed under reduced pressure at 110 ºC before used. The other reagents were used as received. Isophorone diisocyanate (IPDI) was purchased from Bayer. *N*-methyldiethanolamine (MDEA) was bought from Aladdin (Shanghai). Diethylene glycol (DEG), acetic acid (HAc), acetone (Ac) and dimethyl formamide (DMF) were received from China Medicine, Shanghai Chemical Reagent Corporation. The dibutyltin dilautrate (DBTDL) and stannous octoate were supplied by Bayer AG. The structure of TPPDA is shown in Scheme 1. TPPDA was provided by professor Tian Yupeng of Anhui University. TPPDA-CWPU was synthesized according to Scheme 2.

Synthesis of TPPDA-CWPU. The synthesis of TPPDA-CWPU was carried out in a 250 mL four-neck flask equipped with mechanical stirrer, thermometer, nitrogenous inlet and reflux condenser with a $CaCl_2$ drying tube. Under dry nitrogen protection, in four-neck flask with 33.33 g IPDI, 30.07 g N210,



Scheme 1. Chemical structure of TPPDA.



Scheme 2. Synthetic route of TPPDA-CWPU.

stir slowly and heated to 90±2 ºC, constant temperature reaction 2.5 h. Then, cooling the reaction system to 45~50 ºC, 0.15 g TPPDA dissolved by 1.5 mL DMF was added into the system. Simultaneously, 9.25 g DEG as chain extender, 10 mL acetone, stannous octoate and DBTDL (0.1 wt% respectively) as catalysts were poured into the reaction system to further react with the isocyanate group (NCO) at 80±2 ºC for additional 2.5 h. Cooling the reaction system to 38~42 ºC, MDEA (3.91 g) dissolved in anhydrous acetone (10 mL) was then dropwise added to react with this prepolymer for chain extending at 56~60 ºC together with 10 mL Ac for 2 h. Some acetone is added to dilute and decrease the viscosity of the reaction system so as to ensure completion of the reaction. Afterwards, 4.03 g ethanol was added and reaction for 1 h to obtain ethanol-terminated polyurethane, cooling the system below 40 ºC and neutralized by 2.82 mL HAc about 2 min. Last, the ethanol-terminated polyurethane was dissolved in water (300 g) followed by dispersion at 1000 r/min speed conditions to give a polyurethane emulsion. Removing acetone by distillation under reduced pressure to obtain TPPDA-CWPU, and its solid content was adjusted to 20%.

Measurements. Samples should be purified by dialysis to

eliminate the unreactive TPPDA completely before test. The FTIR spectra of the dried fluorescent polyurethane films were conducted on a Nexus 870 FTIR spectrometer in the 2 cm^{-1} resolution mode, measurements which using attenuated total reflectance were carried out within the wavelength range of 4000~500 cm^{-1} and the number of scanning is 32. Concentration measure by using UV-3600 double beam UV-vis spectroscopy and the wavelength ranged of 275~500 nm. The molecular weight of TPPDA-CWPU was measured by gel permeation chromatography (GPC) (Waters 1515 Isocratic HPLC, USA) with eluent tetrahydrofuran (THF) at 35 ºC. The molecular weight spectrogram was then recorded in 190-800 nm scanning wavelength and 0-20 $cm^3 \cdot min^{-1}$ flow rate. UV-vis spectroscopic studies were carried out with an Agilent 8453 diode array spectrometer, which background correction was made using a DMF/water mixture (1/99 v/v) blank. And solution samples were prepared using a DMF/water mixture (1/99 v/v) as the solvent. The wavelength was ranged from 200 to 450 nm with a medium speed scanning. The fluorescence spectra of TPPDA-CWPU were measured on F-7000 FL luminescence spectrometer at excitation of the maximum absorption wavelength, both the excitation slit width and emission slit width were 5 nm, the excitation voltage was 500 mV. All emission spectra were carried out in 1-cm quartz cuvettes. Quantum yield test was measured by full function steady-state transient fluorescence spectrometer (FLSP920) from the Edinburgh Instrument Co., UK.

Results and Discussion

Structural Characterization. The structure of TPPDA, CWPU and TPPDA-CWPU was characterized by FTIR in the wavenumber range of 4000~500 cm^{-1}. As shown in Figure 1, the typical absorptions at 3300, 1700 and 1236 cm^{-1} were assigned to the stretching band of N-H, -C=O and C-O in the urethane group. There was no peak at 2270 cm^{-1}, indicating that the isocyanate was completely involved in the reaction. Because TPPDA was trace in polyurethane film, there was no obvious peak in infrared spectra. A broad and strong band appeared at 3650~3150 cm^{-1}, which indicated the form of intramolecular or intermolecular hydrogen bond in the TPPDA.

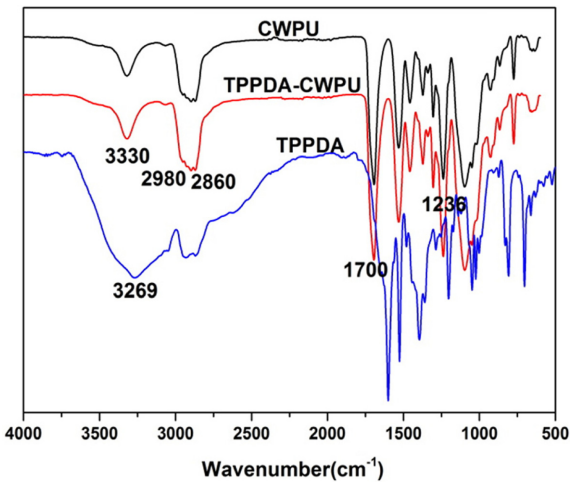


Figure 1. FTIR spectra of TPPDA, CWPU and TPPDA-CWPU.

Concentration Measure of Fluorescent Polyurethane Containing TPPDA. In this paper, the concentration of TPPDA in TPPDA-CWPU was measured by UV-vis spectra. At first, a series of TPPDA solutions with different concentrations were prepared in DMF, and then the standard curve was obtained. Figure 2(a) showed the UV-vis absorption curve at TPPDA with different concentrations. The relationship

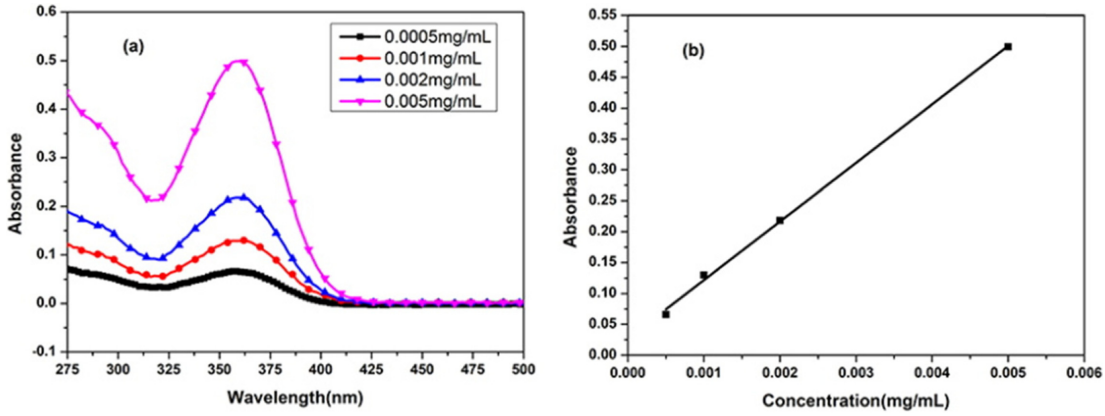


Figure 2. (a) UV-vis spectra of TPPDA with different concentrations in DMF (▼) 0.005 mg/mL, (▲) 0.002 mg/mL, (●) 0.001 mg/mL, (■) 0.0005 mg/mL; (b) The fitting curve of the maximum absorbance peak value *versus* the TPPDA concentration.

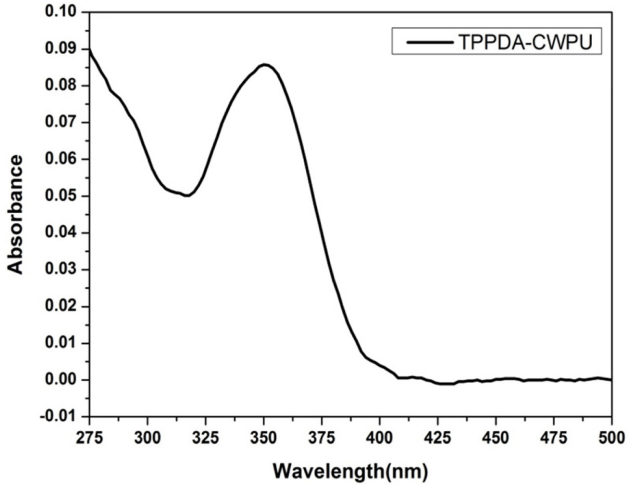


Figure 3. UV-vis absorbance spectrum of TPPDA-CWPU in DMF with 1 mg/mL.

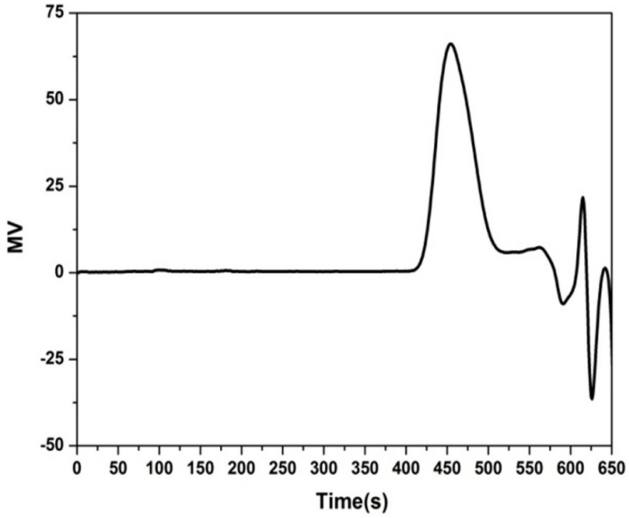


Figure 4. Molecular weight of TPPDA-CWPU.

between the maximum absorbance peak value and the TPPDA concentration was shown in Figure 2(b). It can be calculated from the fitting curve equation of the maximum absorbance peak value and TPPDA concentration for y=0.0269+94.78906x from Figure 2(b). The polymer TPPDA-CWPU was prepared in a solution of 1 mg/mL with the same solvent and the maximum absorption peak value was obtained by UV-vis absorption spectroscopy (Figure 3). Then the highest peak value of the TPPDA-CWPU sample was brought into the fitting curve equation, and the concentration of TPPDA in the sample was 6.3×10^{-4} mg/mL. Therefore, the content of TPPDA in the TPPDA-CWPU film was 6.3×10^{-4} mg/mg, the addition amount was 1.86×10^{-3} mg/mg, and the grafting ratio was 33.87%.

Molecular Weight. One of the important factors that influence the fluorescent properties of the fluorescent polyurethane was the molecular weight. Therefore, it was important to examin the molecular weight of TPPDA-CWPU. As seen in Figure 4 and Table 1, the number-averaged molecular weight (M_n) and weight-average molecular weight (M_w) of TPPDA-CWPU were about 16060 and 27131 g·mol^{-1}, respectively. And the polydispersity index was 1.69, showing relatively narrow molecular weight distribution of the fluorescent aqueous polyurethane TPPDA-CWPU.

UV-vis Spectra. As displayed in Figure 5, UV-vis of TPPDA-CWPU was recorded in a DMF/water mixture (1/99 v/v). The corresponding monomolecular TPPDA in DMF/water mixture (1/99 v/v) was also measured. The peak wavelength of TPPDA was 360 nm, while TPPDA-CWPU was 354 nm, showing ca. 6 nm hypsochromic effect. This phenomenon is partly resulted from the disappearance of intermolecular hydrogen bond in the TPPDA. And the carbonyl

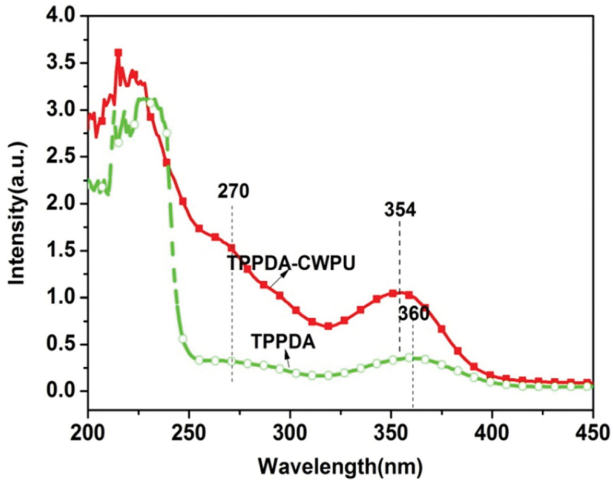


Figure 5. UV-vis spectra of TPPDA and TPPDA-CWPU in the same solvent of DMF/water mixture (1/99 v/v).

Table 1. Molecular Weight of TPPDA-CWPU

Distribution	M_p (Daltons)	M_n (Daltons)	M_w (Daltons)	M_z (Daltons)	M_z+1	M_v	PD
TPPDA-CWPU	26804	16060	27131	40585	54066	25318	1.68935

group in the urethane bond as an electron-withdrawing group causes an inductive effect toward TPPDA. This effect decreased the degree of electron delocalization in the polyurethane chains. As a result, more energy for π(tpy) → π*(tpy) intramolecular charge transfer (ICT) transition with p(bishydroxylamino) → π(Ar) CT character is needed. It was found that the absorption peaks of 250~290 nm attributed to the B band absorption of benzene. B band absorption was enhanced significantly, which indicated the effect on benzene absorption peak of TPPDA that accessed to polyurethane chains. The decreasing absorption of TPPDA with a red shift was due to the aggregation caused quenching (ACQ) effect.[19]

Influence of Different Dispersion Concentrations on the Fluorescence Performance of TPPDA-CWPU. As can be shown in Figure 6, the fluorescence intensity of different concentrations was explored. The fluorescence emission intensity of TPPDA-CWPU increased with the decrease of the dispersion concentration. It showed that fluorescence emission intensity reached maximum in the solid content of 1%. The fluorescence intensity of TPPDA-CWPU decreased with solid content increased. This may be due to the interaction that reinforced as the solid content increased between the fluorescence molecules and solvent molecules, which resulted in energy loss. Simultaneously, it was also found that the maximum emission wavelength of TPPDA-CWPU had a weak red shift which is due to the aggregation caused quenching (ACQ). The fluorescence emission intensity decreased when the solid content was less than 1%, which owing to the disappearing of ACQ effect.

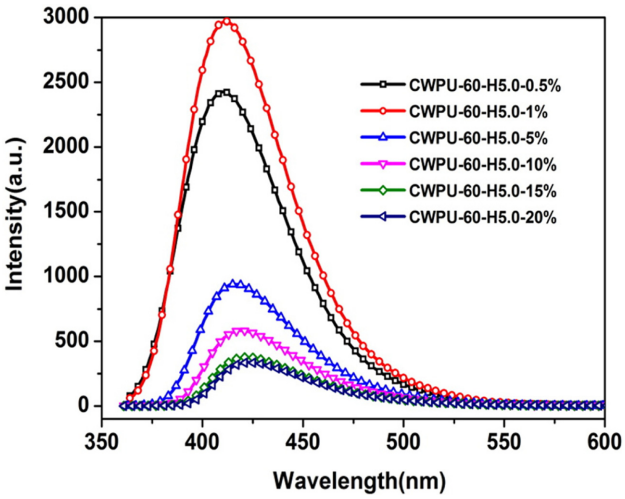


Figure 6. Influence of different dispersion concentration on the fluorescence performance of TPPDA-CWPU.

Fluorescence Quantum Yield. It is known that fluorescence quantum yield is important parameter of fluorescent material. The fluorescence quantum yield is the ratio between the number of photons emitted by the fluorescent substance and the number of photons absorbed by the excited light. The fluorescence quantum yield of TPPDA and TPPDA-CWPU in DMF/water mixture (1/99 v/v) were calculated using the equation:

$$\Phi_S = \Phi_r\left(\frac{A_r \eta_s^2 D_s}{A_s \eta_r^2 D_r}\right) \quad (1)$$

where Φ_S is the fluorescence quantum yield of the sample to be measured, Φ_r is the fluorescence quantum yield of reference samples, A_r is the absorbance of the maximum absorption peak of reference sample measured by UV-vis absorption spectroscopy, A_s is the absorbance of the maximum absorption peak of unknown sample measured by UV-vis absorption spectroscopy, η_s is the refractive index of unknown sample, η_r is the refractive index of reference sample, D_s is the integral area of fluorescence emission peak of unknown sample, D_r is the integral area of fluorescence emission peak of reference sample. The reference sample of this experiment was the blank reference ratio of solvent to each sample, and the measured result was absolute value. The quantum yields of TPPDA and TPPDA-CWPU were 0.07 and 0.3, respectively. The quantum yield of TPPDA-CWPU was four times higher than that of TPPDA, which suggested that the fluorescence performance of TPPDA-CWPU was better than TPPDA. This maybe due to the presence of TPPDA which can not be dispersed well in DMF/water mixture (1/99 v/v). And there were fluorescence aggregation quenching phenomenon, which led to lower fluorescence quantum yield. When TPPDA was connected to the waterborne polyurethane chain to form TPPDA-CWPU, it could disperse well in water and avoid the phenomenon of fluorescence quenching, so the fluorescence performance was improved.

pH Sensitivity. In this paper, the pH sensitivity about TPPDA-CWPU has been tested. Cationic waterborne polyurethane has electric double layer structure which can exist stably under certain acidic conditions, but it will be demulsification under alkaline conditions. Adjusting the solid content of the emulsion to 1%, the fluorescence spectra of TPPDA-CWPU with different pH were shown in Figure 7. In the diagram, with the decrease of the pH value, the fluorescence emission intensity decreased gradually. When the pH value

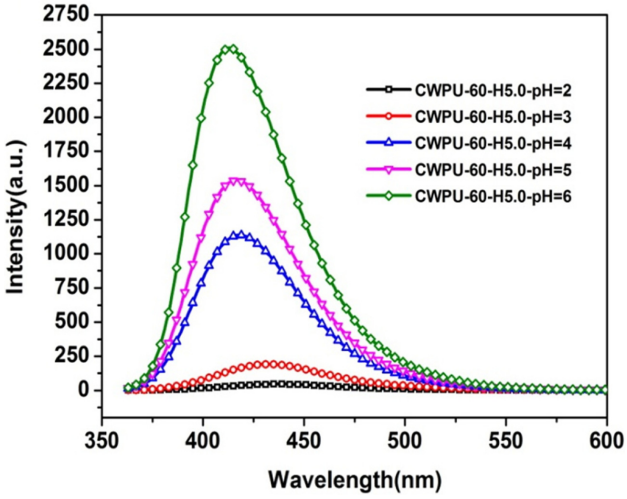


Figure 7. Fluorescence spectra of TPPDA-CWPU at different pHs.

was 3, the fluorescence emission intensity decreased obviously and the pH value was 2, there was almost no fluorescence emission. It shows that TPPDA-CWPU has a greater sensitivity to the changes of pH, which propose that intramolecular charge transfer and solvation in aqueous solutions may be the mechanism of the fluorescence weakening under strongly acidic conditions. Through the above analysis, the TPPDA-CWPU has a pH response effect, and can be used as a fluorescent probe.

Influence of Ionic Type on the Fluorescence Performances of FWPU. The fluorescence properties of FWPU with different ionic types were tested. From Figure 8, anionic and cationic FWPU showed different fluorescence emission intensity. In the 20% solid content, anionic type > cationic type > TPPDA, and relative to TPPDA, the maximum excitation wavelength were blue shifted 60 and 48 nm respectively. While in the 1% solid content, it was the cationic type > anionic type > TPPDA, they were all blue shift of around 60 nm compared with TPPDA. These results showed that the effect of ionic type on the fluorescence properties of FWPU was large, which was caused by different ionic properties of WPU in aqueous solution.

Conclusions

In summary, we have prepared TPPDA-CWPU with fluorescent monomer TPPDA in the polyurethane skeleton. The concentration of TPPDA-CWPU containing TPPDA was 6.3×10^{-4} mg/mg, the addition amount was 1.86×10^{-3} mg/mg, so the grafting ratio was 33.87%. The M_n and M_w of TPPDA-CWPU were about 16060 and 27131 g·mol^{-1}, respectively. It turned out that the fluorescence emission intensity of TPPDA could be improved by introduction of polyurethane chains. The fluorescence emission intensity of TPPDA-CWPU increased with the dispersion concentration decreased and the fluorescence emission intensity reached maximum when the solid content was 1%. The quantum yield of TPPDA-CWPU (0.3) was four times higher than that of TPPDA (0.07). CWPU was very sensitive to acid, the fluorescence emission intensity decreased with decreasing pH values. Afterwards, we explored the influence of ion type on the fluorescence performance of FWPU. Anionic and cationic FWPU showed different fluorescence emission intensity. In the 20% solid content, anionic type > cationic type > TPPDA; While in the 1% solid content, it was cationic type > anionic type > TPPDA. Finally, the cationic FWPU with enhanced fluorescence emission intensity

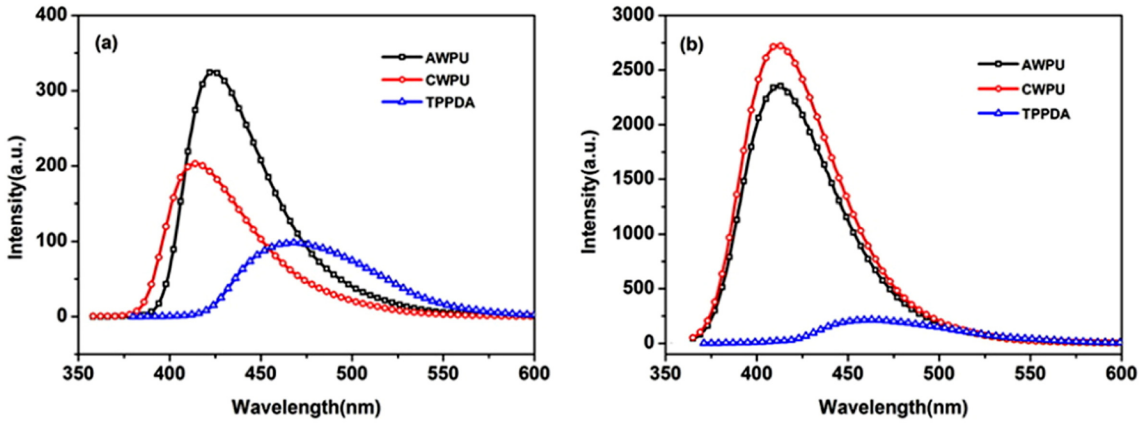


Figure 8. Influence of waterborne polyurethane ion type on the fluorescence performance of FWPU (a) solid content is 20%; (b) solid content is 1%.

and high sensitivity to acidic conditions offers promising applications in biomedicine.

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