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A Polymeric Dye of Aqueous Disperse Violet 17-Based Polyurethane Dispersion†

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A polymeric dye, aqueous disperse violet 17-based polyurethane dispersion (PU-DV17), was synthesized depending on a modified acetone process. The structure of PU-DV17 was confirmed by FT-IR and UV-visible analysis. Due to presence of well-known anthraquinone in PU-DV17, this polymeric dye exhibited intriguing optical behaviour in aqueous solution. The fluorescence intensity of PU-DV17 emulsion was enhanced greatly with contrast to that of DV17. It was found that the fluorescence intensity of PU-DV17 emulsion would decline along with increasing temperature between 20 ºC and 40 ºC and enhance along with increasing temperature between 40 ºC and 90 ºC. The fluorescence of PU-DV17 emulsion was very stable and was not sensitive to hydroquinone quencher.

Key Words: Polymeric dye, Aqueous polyurethane dispersion, Fluorescent polymer, Fluorescent polyurethane, Disperse violet 17.

INTRODUCTION

Polymeric dyes have attracted a great deal of attention in recent years, due to their unique properties and potential optical applications in both civil and purposes[1-4]. However, most of them were diluted by organic solvent and would severely pollute surroundings during producing and using processes[5,6]. Aqueous polyurethane dispersions possess high outstanding properties and environmental advantages, therefore the development of aqueous dye-based polyurethane dispersion is the trend in the future and have aroused much interest at present.

In recent years, polymeric dyes were investigated, mainly focused on derivatives of 1,8-naphthalimide with styrene, methylmethacrylate, acrylonitrile or vinyl[7-10]. However, polymers bearing anthraquinone structure have aroused less interest, mostly owing to the difficulty in preparing such polyanthraquinones by traditional methods. Herein, we synthesized anionic aqueous polyurethane dispersion bearing anthraquinone structures (PU-DV17) *via* a modified acetone process. Moreover, the fluorescent behaviour was studied in detail using a rejected-flow apparatus equipped with bath accessory of constant temperature.

EXPERIMENTAL

The preparation process of PU-DV17 was shown in **Scheme-I**. 2,4-Toluene diisocyanate (TDI), poly(propylene glycol) (PPG) and dimethylolpropionic acid (DMPA) according to the molar ratio first poured into the four-necked reaction kettle equipped with stirrer, thermometer and condenser under agitation. Subsequently, dibutyltin dilaurate was added into kettle by drops and then carried out at 80 ºC under N_2 atmosphere to form NCO-terminated prepolyurethane I. The NCO content was determined *via* a standard dibutylamine back titration method. Due to the high viscosity, suitable amount of acetone was added to dilute prepolyurethane I. When theoretical NCO content was reached, disperse violet 17 was charged to the kettle and reacted with prepolymer I to form prepolymer II at 100 ºC for 5 h. Subsequently, the prepolymer mixture was slowly cooled down to 30 ºC. Triethylamine (TEA) as neutralization agent was added into the reaction mixture to react with the carboxylic group in the side chain of prepolymer II. Finally, deionized water was added into the reaction mixture with agitation at high shearing rates to emulsify the solution. After removal of the acetone by rotary vacuum evaporation under reduced pressure, PU-DV17 was obtained.

RESULTS AND DISCUSSION

FT-IR spectra and UV-visible spectra: The FTIR spectra of polyurethane disperse violet 17 (PU-DV17) and disperse violet 17 (DV17) were illustrated in Fig. 1. The characteristic absorbance peaks of polyurethane were 3304 cm^{-1} [ν(NH)], 2866-2974 cm^{-1} [$\nu(CH_2)$ and $\nu(CH_3)$], 1728 cm^{-1} [ν(C=O)], 1530 cm^{-1} [δ(N-H)], 1222 cm^{-1} [ν(C-O)] and 1105 cm^{-1} [ν(C-O-C)] in the FT-IR spectrum of PU-DV17, respectively. The charac-

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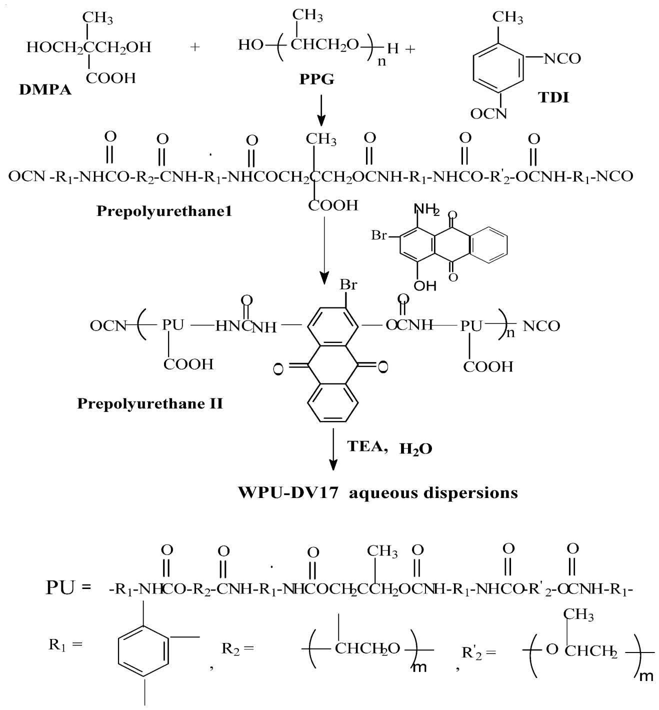
teristic absorption peaks of DV17 could be showed distinctly at 1630 cm^{-1} [ν(C=O)] in anthraquinone and 528 cm^{-1} [ν(C-Br)]. Moreover, the two characteristic peaks could also be observed in the spectrum of PU-DV17, demonstrating that the DV17 had been attached into the polyurethane chain. In addition, the absorbance peak attributed to [ν(NCO)] at around 2275 cm^{-1} disappeared, which indicated a complete reaction.

PU-DV17 film and DV17 were dissolved in DMF. The UV-VIS spectrum of PU-DV17 showed two absorption bands associated with the anthraquinone unit at the same frequency as DV17, namely at 534, 564 nm, which further confirms that DV17 has been attached into the polyurethane chain.



Scheme-I: Synthesis and structure formula of PU-DV17

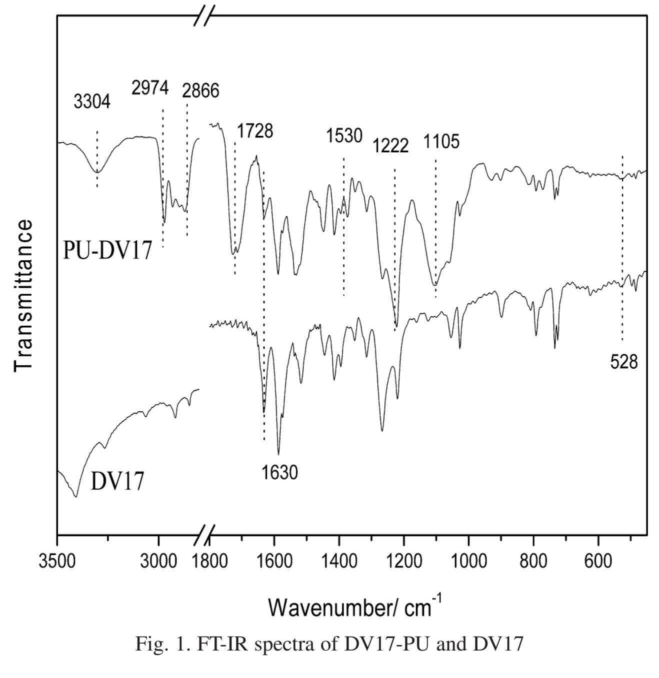


Fig. 1. FT-IR spectra of DV17-PU and DV17

Fluorescence of PU-DV17: Fluorescence spectroscopy was used to investigate the emission spectra of PU-DV17 dispersions and DV17 in DMF (Fig. 2). Compared with DV17 in DMF, the emission maximum of PU-DV17 was significantly hypsochromic shift about 13 nm. The fluorescence intensity of PU-DV17 was much higher than that of DV17 at the same DV17 contents. DV17 could display very faint fluorescence emission. In fact, DV17 displays almost no fluorescence emission. Different from the "concentrational self-quenching effect" caused by concentrational factor, such fluorescence quenching is called "structural self-quenching effect."[11] This phenomenon would also be attributed to the exciplex formation between electron-donating amino group and electron-accepting carbon-oxygen double bond inter-molecular.

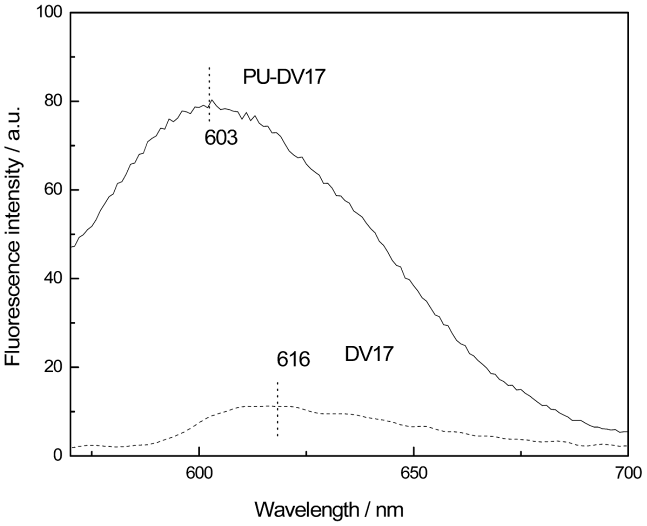


Fig. 2. Fluorescence spectra of WPU-DV17 and DV17 in DMF

The fluorescence intensity of PU-DV17 was greatly enhanced comparing with that of DV17, which was mainly ascribed to the following three factors: First, DV17 was fixed to the polyurethane chains, which hindered the formation of exciplex among DV17. Furthermore, the intramolecular rotation and vibration of DV17 were restricted, which had a large contribution to the radiative transition process[12]. Secondly, PU-DV17 formed emulsions with electrical double surface layers due to the ionization of acidic groups, leading to augmented light absorption area[3,13]. Thirdly, DV17 inside PU-DV17 was inside electrical double layer, thus the mobility of DV17 was decreased and DV17 was shielded from possible quencher.

Generally speaking, fluorescent intensity would gradually decline in solution along with increasing temperature. However, Fig. 3 indicted that fluorescent intensities of PU-DV17 would decline along with increasing temperature between 20 ºC and 40 ºC and enhance along with increasing temperature between 40 ºC and 90 ºC, which is an abnormal phenomena against the general fluorescent materials. The fluorescent intensities would decline between 20 ºC and 40 ºC, mainly attributed to the effect of energy transform in PU-DV17. Fluorescent intensity would enhance along with increasing temperature between 40 ºC and 90 ºC, which was attributed to two factors: First, DV17 was attached into polyurethane chains, leading to changed fluorophore structure, so as to energy between S_1 and T_1 was lessened in fluorophore. Transition of $T_1 \rightarrow S_1$ may engender along with reverse process of $S_1 \rightarrow T_1$, due to thermal activation. Secondly, hydrogen bond was decreased in PU-DV17 along with increasing temperature.

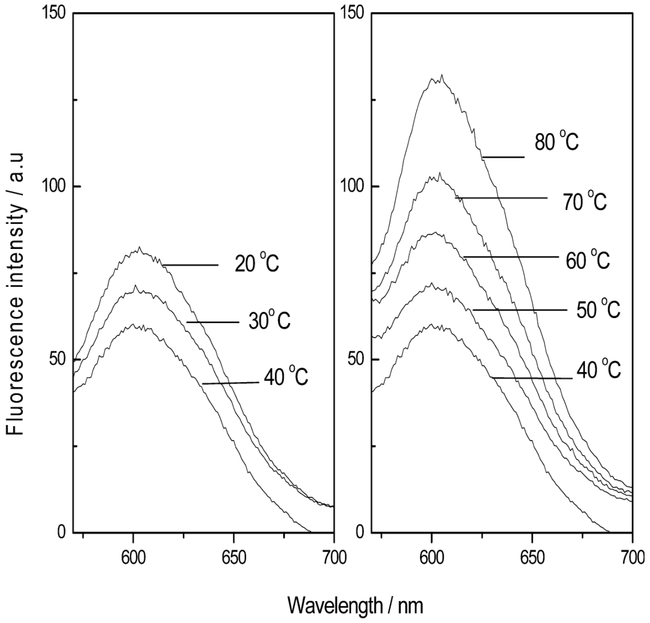


Fig. 3. Fluorescence spectra of PU-DV17 at different temperature

The fluorescence of PU-DV17 was stable during storage. Hardly any difference of fluorescence spectra was observed after 30 days. On the other hand, after some quenchers (for example:pyridine) were added into PU-DV17, fluorescence decreased only a little. The fluorescence of the PU-DV17 can be regularly quenched by adding the diphenylamine. Quencher constant K_{SV} is 6.7 by calculation according to the Stern-Volmer equation. Generally speaking, the fluorescence of PU-DV17 is not sensitive to quencher.

Conclusion

The polymeric dye of PU-DV17 was prepared by a modified acetone process. Comparing with DV17, obvious hypsochromic shift of PU-DV17 was observed in the fluorescence spectra. The fluorescence intensity of PU-DV17 was prominently enhanced comparing with that of DV17. It was ascribed to hinder the formation of exciplex among DV17 and augment light absorption area of DV17 segments. Fluorescent intensity would decline between 20 ºC and 40 ºC, mainly attributed to the effect of energy transform in PU-DV17. Fluorescent intensity of PU-DV17 would enhance along with increasing temperature between 40 ºC and 90 ºC, ascribed to transition of $S_1 \rightarrow T_1$ and decreased hydrogen bond in PU-DV17 along with increasing temperature. The fluorescence of PU-DV17 is not sensitive to quencher.

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