Chinese Chemical Letters Vol. 15, No. 5, pp 515-517, 2004
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Characterization of a Novel Aqueous Dispersion Poly[urethane-(disperse blue 14)-urethane] Dye

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Abstract: A novel polymeric dye of aqueous dispersion poly[urethane-(disperse blue 14)-urethane] was synthesized based on poly(propylene glycol) (PPG), 2, 4-tolylene diisocyanate (TDI), dimethylol propionic acid (DMPA), disperse blue 14 and triethylamine (TEA) depending on a modified acetone process. Fourier transform infrared spectroscopy (FTIR) was used to identify the structure of the polymeric dye, indicating an obvious carbonyl stretching absorption in disperse blue 14. The polymer was also characterized by the analysis of DSC, TGA, WAXD and UV-Vis spectroscopy.

Keywords: Aqueous dispersion, poly[urethane-(disperse blue 14)-urethane], polymeric dye.

Polymeric dyes, such as polyester dye, polyurethane dye and polystyrene dye, have been reported in recent years[1~4]. Most of them are organic solvent soluble polymeric dye and will severely pollute environment during producing and using processes[2, 3]. Comparing with similar materials obtained from organic media, waterborne polymeric dyes prepared from aqueous dispersions have superior properties[5~7]. In general, the reaction between –NCO and active hydrogen in the matrix of small molecular organic dye is utilized to incorporate dyes into polymer chain. Neutralization agent is used to form aqueous dispersions. Hues of these dyes are not only fresh but also immortally fadeless. In this letter, we report the synthesis of a novel polymeric dye of aqueous dispersion poly[urethane-(disperse blue 14)-urethane] (PU-DB14) from PPG, DMPA, TDI, TEA and disperse blue 14 as shown in **Scheme 1**.

PPG, DMPA and TDI were first added to the reactor according to a suitable mole ratio. The prepolymerization of polyurethane was carried out at 90°C under N_2 atmosphere for 3 h. NCO-terminated prepolyurethane **1** was synthesized. The content of –NCO was determined by the standard dibutylamine titration method. In order to dilute prepolymer **1**, suitable amount of acetone was added based on the modified acetone process. Then disperse blue 14 was reacted with prepolymer **1** to form polymeric dye **2** at 50°C for 5 h. As neutralization agent, TEA was added into the reaction mixture to react with the carboxylic group in the side chain of polymeric dye **2**

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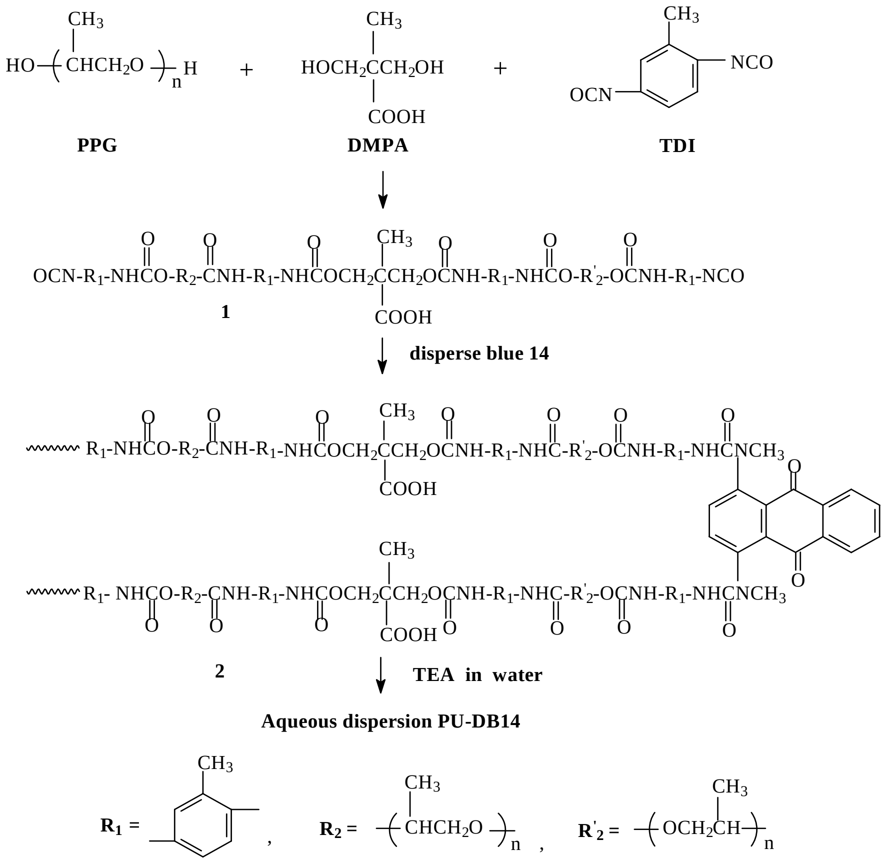
Scheme 1



at 30-40°C for 1 h. Finally, deionized water was added into the reaction mixture. High speed stirring was used to emulsify the solution. Aqueous disperse PU-DB14 was obtained after removal of acetone from the emulsion by rotary vacuum evaporation.

Film was prepared for further characterization by casting the aqueous dispersions on leveled PTFE surface and drying at room temperature for 5 days, and then in a vacuum system at 50°C for 2 days.

The structure of PU-DB14 was confirmed by FTIR. The spectra showed the N-H stretching at 3299 cm^{-1} (hydrogen-bonded) and the C-O-C stretching attributed to the ether oxygen of PPG at 1102 cm^{-1}. The absorption for the urethane carbonyl group was at 1727 cm^{-1}, while the absorption for the C=O in anthraquinone of disperse blue 14 was at 1596 cm^{-1}. Because of conjugating between C=O and benzene ring, the absorption of C=O in anthraquinone shifted to lower wavenumber, compared with the carbonyl group in urethane. In addition, the C-N stretching was observed at 1227 cm^{-1}, and $-CH_2$, $-CH_3$ stretching at 2969, 2929 cm^{-1} (symmetry).

DSC analysis showed that PU-DB14 has only a single glass transition temperature of 55°C. This confirmed that the product was a copolymer but not a mixture of prepolymer and organic monomer dye. The soft segment and hard segment in PU-DB14 were compatible. TGA measurement indicated a two-stage degradation for the polymeric dye. The first-stage degradation related to the hard segments started at about 255°C, and the second-stage related to the soft segments at about 360°C. A wide peak ($2\theta \approx 19°$) in WAXD spectrum implied the film of polymeric dye was amorphous.

UV-Vis spectra showed three absorptions at 555, 600 and 650 nm, respectively, assigned to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition of anthraquinone chromophore for the chloroform solution of disperse blue 14 and PU-DB14, which further confirmed that disperse blue 14 had been bonded to the prepolyurethane. But there was another peak only appeared at 510 nm of polymer spectrum, indicating a new absorption for PU-DB14. In addition, UV-Vis spectra of the aqueous dispersion PU-DB14 also showed a new absorption at 760 nm. The absorption peak weakened with the decrease of molecular weight of aqueous dispersions. The origination for this absorption is still under investigation.

Acknowledgments

Financial support from the National Natural Science Foundation of China (No. 50273035) is acknowledged.

References

1. I. Grabchev, *Dyes and Pigments*, **1998,** *38*(4), 219.
2. K. Singh, S. Singh, J. A. Taylor, *Dyes and Pigments*, **2002,** *54***(**3), 189.
3. J. Y. Lee, E. J. Park, *J. Macromol. Sci-Pure Appl. Chem.*, **2001,** *A38*(9), 973.
4. T. Konstantinova, P. Meallier, Hr. Konstantinov, D. Staneva, *Polym. Degrad. Stab.,* **1995,** *48*, 161.
5. B. Vogt-Birnbrich, *Prog. Org. Coat.*, **1996,** *29*, 31.
6. T. Buruiana, E. C. Buruiana, A. Airinei, I. Grecu, *Eur. Polym. J.*, **2001,** *37*, 343.
7. K. L. Noble, *Prog. Org. Coat.*, **1997,** *32*, 131.

Received 6 May, 2003