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Synthesis of cationic binder through surfactant-free emulsion polymerization for textile pigment applications

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ABSTRACT

The cationic P(DMDAAC-BA-MMA-HEA) copolymer latex was prepared with diallyldimethylammonium chloride, butyl acrylate, methylmethacrylate and hydroxyethyl acrylate as monomers via surfactant-free emulsion polymerization. The structures and morphologies of the latex were confirmed by Fourier transform infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM). The utilization performance of the cationic latex as a binder for pigment dyeing of cotton fabrics was investigated. FT-IR showed that the polymer was prepared successfully. TEM micrograph revealed that the hybrid latex particles were uniform spheres with the diameter ranged from 500 to 600 nm. Cotton fabric dyed with the cationic binder demonstrated 3–4 grade dry and wet rubbing fastness and 4 grade soaping fastness, which were comparable with commercial binders. Moreover, the binder can be used safely in pigment dyeing to give the dyed fabric improved hand feel and excellent elongation at break. It could be said that an efficient way to produce a binder with good performance was developed by the use of cationic emulsifier-free emulsion polymerization.

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1. Introduction

Pigment dyeing is a technical innovation in low energy consumption and emission reduction in dyeing industry. Pigment is a kind of water-soluble dyestuff without affinity and reactivity to fiber, and is adhered to fiber by a thin binder film formed on the fabric. Therefore, performance of the binder greatly affects the quality of the dyed fabric, and plays an important role in the application and development of coating dyeing [1–4].

The binder for pigment dyeing is generally prepared by emulsion polymerization. Nevertheless, traditional emulsion polymerization tends to cause low emulsion purity. The emulsifier existing in the binder exerts a negative impact on color fastness and the hand feel of the dyed fabric. Surfactant-free emulsion polymerization refers to the emulsion polymerization that does not contain or only contains a little emulsifier (the concentration is less than critical micelle concentration CMC). It is a well-known method for preparing latex particles with a clean surface, which can overcome the

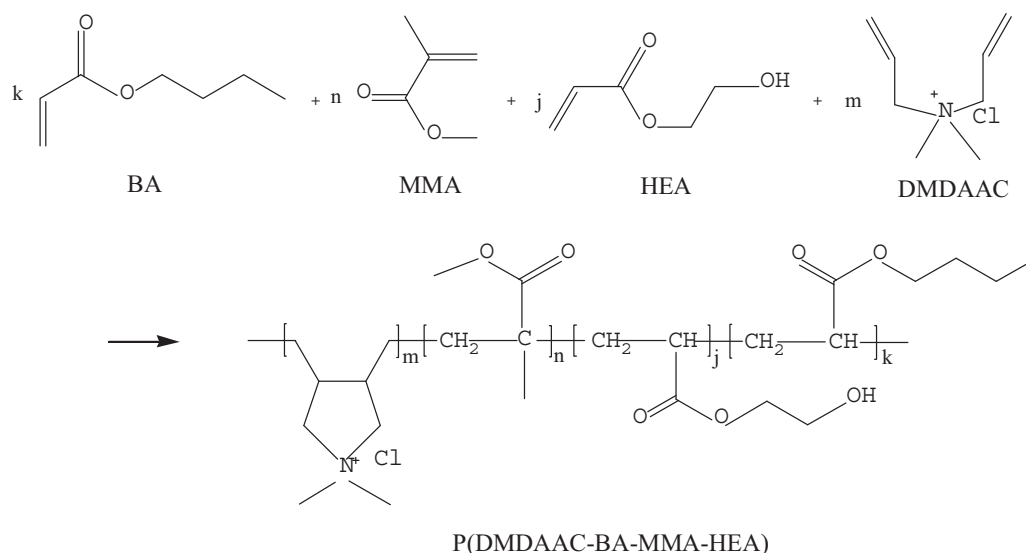
product defects that the residual emulsifier brings about. Because of the incomparable advantages in comparison with traditional emulsion polymerization, surfactant-free emulsion polymerization is widely used in the fields of biology, medicine, and chemical industry [5–9].

The binders used for pigment dyeing are mostly negatively charged and have the same charge as the surface of the cotton fabric and the pigment particles. Therefore, they are only suitable for the light color coating of the low pigment pickup as a result of the rejection of the same charge. Cationic binders have attracted much attention from academic areas because of their affinity for fabric [10,11]. Ji and her co-workers [12] reported the synthesis of a cationic acrylate binder with cetyltrimethylammonium bromide and XL-50 as emulsifiers by emulsion polymerization. The cationic binder was better than the conventional anion binder in terms of calcium ion stability, wet rubbing fastness, color fastness to washing and hand feel.

There is lots of work in the preparation of cationic latex [13–18] and surfactant-free emulsion. However, a small number of publications deal with cationic binders prepared by direct surfactant-free emulsion polymerization method. Diallyldimethylammonium chloride (DMDAAC) is a cationic quaternary ammonium salt with two unsaturated double bonds, and is widely applied in water soluble cationic polymer because of its non-toxicity,

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**Scheme 1.** Polymerization mechanism of P(DMDAAC-BA-MMA-HEA).

high density positive charge and low cost [19–22]. Surfactant-free emulsion polymerization can be achieved not only because of the oligomer with certain surface activity generated in the polymerization process with DMDAAC as monomers but also because of the weak surface activity of DMDAAC itself. Bai et al. [23] prepared a series of styrene-acrylic cationic emulsions with styrene, acrylamide and diallyldimethylammonium chloride as monomers under emulsifier-free condition. They showed that the latex had the advantages of high solid content, good water-resistance and favorable stability.

Accordingly, this study aims to develop a binder that can improve color fastness and hand feel of the dyed fabric. Stable surfactant-free latex using DMDAAC, vinyl monomers and crosslinking monomers was prepared. The effect of Hydroxyethyl acrylate (HEA) crosslinking monomers on the properties of the latex was studied. In addition, the application performance was investigated when the latex was used in pigment dyeing.

2. Materials and methods

2.1. Materials

N-butyl acrylate (BA) was supplied by Tianjin Hongyan Reagent Corporation (China). Methyl methacrylate (MMA) was obtained from Tianjin Fuchen Chemical Reagent Plant (China). Diallyl dimethyl ammonium chloride (DMDAAC) was provided by Shandong Luyue Chemical Corporation (China). Hydroxyethyl acrylate (HEA) was purchased from Tianjin Chemical Reagent No 6 Plant (China). Potassium persulfate (KPS) was provided by Tianjin Zhiyuan Chemical Reagent Corporation (China). Deionized water was used throughout the experiments. All reagents were of analytical grade and used as received.

2.2. Preparation of cationic latex

The surfactant-free emulsion polymerizations were carried out in a 250 mL three-necked glass flask fitted with a reflux condenser, a crescent Teflon mechanical stirrer and feeding inlets. Firstly, a mixture of HEA, DMDAAC and deionized water was added to the reactor, heated to 65 °C under stirring. Then an aqueous solution of KPS (0.09 g, 1.8 wt%) was introduced into the flask and the reaction lasted for 0.5 h. After that, the temperature was increased to 85 °C. Once the temperature was reached, the residual monomers

of BA and MMA and an aqueous solution of KPS (0.18 g, 0.39 wt%) were simultaneously dropped into the reactor in 90 min. The reaction mixture was kept at 85 °C for 4 h. Finally, the emulsion was cooled to room temperature while being stirred. The polymerization mechanism is shown in Scheme 1.

2.3. Determination of latex

2.3.1. Gel rate

The coagula from the latex, the reactor and the stirrer were collected and washed with distilled water. They were dried in an oven at 105 °C to constant weight. The gel rate was determined by the following Eq. (1):

$$\text{Gel rate(\%)} = \frac{W_c}{W_m} \times 100\% \quad (1)$$

where W_c is the constant weight of the coagula (g), and W_m is the weight of all monomers used (g).

2.3.2. Conversion

A total of 1–2 g latex was put into a weighing bottle that was of constant weight, and then 1 or 2 drops of 2% hydroquinone solution were added for polymerization retardation. The weighing bottle was dried in an oven at 105 °C until constant weight was obtained. The conversion of the latex was calculated by the following Eq. (2):

$$\text{Conversion(\%)} = \frac{m_1 - m_0 w}{m_0 w_d} \times 100\% \quad (2)$$

where m_0 is the sample weight (g), m_1 is the constant weight of the sample after being dried (g), w is the mass percentage of non-volatile compositions and w_d is the mass percentage of total monomers.

2.3.3. Rotating viscosity

An American BROOKFIELD DV-II+ programmable control rotating viscometer was used to determine the rotating viscosity of the latex. The constant temperature of water-bath was set at 25 °C after the level of the viscometer was calibrated. Then the power switch was turned on to get into the operation interface. After auto zero correction according to the prompts, the rotating viscosity of the sample was tested on the viscometer at the speed of 100 rpm with No. 18 rotor.

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