

Preparation of a Cross-linkable Emulsion and its Effectiveness as the Binder Resin of Water-based Printing inks Curable at Ambient Temperature ^a

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Abstract

The proposed resin system mainly comprises two components: a nano-sized emulsion and a crosslinking agent, adipic dihydrazide. The nano-emulsion was prepared through soapless emulsion polymerization of acrylic monomers in the presence of a reactive amphiphilic block copolymer, which was synthesized through living polymerization of diacetone acrylamide and acrylic acid. The nano-emulsion was narrowly distributed in size and the average diameter is around 50 nm. The nano-emulsion was very stable even at 45 wt.%. DSC analysis showed that the polymer of the emulsion had a low glass transition temperature (T_g) (about 15 °C), but the emulsion still remained stable at a wide temperature range (4-50 °C) despite the addition of the cross-linker. Emulsion films were coated with the mixture of the nano-emulsion, the cross-linker and a small amount of leveling agent by spin-coating method, and this was followed by drying at ambient temperature. SEM analysis indicated that the border of particles had disappeared and a uniform film was obtained. Investigation on dissolution behaviors of the emulsion films showed that cross-linking reaction occurred with the evaporation of water. With the drying of the film at ambient temperature, a tough and transparent cross-linked film was prepared, which had good water/solvent resistance. This self-crosslinking resin system might be used as the binder resin for water-based printing inks which can be effectively cured at ambient temperature.

Introduction

Direct ink-jet printing of polymer emulsion may be a promising method for environmentally friendly digital printing. This requires significant research and development efforts aimed at achieving a stable, narrowly distributed dispersion of nanoparticles containing the specific material in water. Acrylate polymer emulsions are widely used as coatings, paints, adhesives and so on for their good combined properties, such as chemical resistance, weathering resistance and environmental-friendly [1-3]. However, there are several disadvantages such as poor water resistance and lower mechanical strength, which have some influence on the performance of the coatings. Generally, emulsion films having better mechanical property and (or) water resistance need a higher film-forming temperature, which makes it inconvenient for practical application. There is a contradiction between processibility and properties of the emulsion films. To coordinate film-forming performance of polymer emulsion and mechanical property of the emulsion films, volatile organic compounds have been added into the emulsion to facilitate film formation. However, this brings about another problem of high VOC content [4]. A method to form films

at ambient temperature is by using low-T_g emulsion particles, but the films usually exhibit lower strength and heat resistance [5].

In this paper, we synthesized an emulsion via soapless emulsion polymerization and investigated an approach to forming uniform cross-linked films from nano-emulsion without the necessity of a heat treatment.

Experimental

Reagents and Methods

Dodecane-1-thiol, 2-bromopropanoic acid, butyl methacrylate (BMA), acrylic acid (AA), diacetoneacrylamide (DAAM), 4'-azobis (4-cyanovaleric acid) (ACVA), azodiisobutyronitrile (AIBN) and adipic dihydrazides were commercial products from Beijing Chemicals Co. BA and AA were purified by vacuum distillation before use. FTIR spectra were obtained with a Shimadzu FTIR-8400 infrared spectrophotometer. The average particle size of the emulsion was measured by transmission electron microscopy (TEM) with a H-7000 apparatus (Hitachi, Japan). Differential scanning calorimetry (DSC) was recorded on a Netzsch DSC200PC analysis apparatus. Molecular weight (relative to styrene standards) of the polymer was evaluated by gel permeation chromatography (GPC, LC-10AT). Optical micrograph was obtained on a S-4300 scanning electron microscope. Film surface hardness was measured by a QHB pencil scratch hardness tester according to GB/T6739-1996. Assessment of resistance to impact of the emulsion film was carried out according to GB1732-1979.

Synthesis of the reactive surfactant (RS)

In a 250-ml flask equipped with a mechanical stirrer and a reflux condenser was placed 10.0g of sodium hydroxide, 4.5 g of tetraethylammonium bromide, 50 ml of water and 50 ml of tetrahydrofuran. The mixture was stirred until it became clear. Dodecane-1-thiol (50.0 g) was placed in the mixture. Then, a mixture of 37.5 g of CS₂ and 36.6 g of 2-bromo-propanoic acid were added drop-wise to the above solution in such a manner that the temperature was kept at 20-25 °C, and this was followed by further stirring for 20 h at room temperature. Finally the mixture was heated at 50 °C for another 5 h. The organic layer was separated and poured into an excess amount of petroleum ether with stirring to yield a yellow precipitate. The precipitate was re-crystallized in ethanol to give 50.4 g of product. mp: 64-65 °C. FTIR (KBr, cm⁻¹): 2918, 2852, 1701, 1421, 1209, 1084, 825. ¹H NMR (400MHz,

CDCI3): 4.80-4.90 (m, 1H), 3.32-3.38 (m, 2H), 1.66-1.75(m, 2H), 1.60-1.63 (d, 3H), 1.25-1.37 (m, 18H), 0.85-0.87 (m, 3H).

The above obtained product (7.0 g), AA (7.2 g), AIBN (0.12g) and ethanol (20 ml) were charged in a 100-ml flask, which was flushed with argon for 1 h with stirring. The temperature was raised to 65 °C and kept the temperature for 6 h. Then, DAAM (12.8 g) and additional AIBN (0.15 g) and ethanol (15 ml) were added. The mixture was cooled to room temperature and poured into 200 ml of petroleum ether. The yellowish precipitate was gathered, fully washed with petroleum ether and dried in vacuo at 60 °C to afford 24.1g of final product, which is denoted as RS. FTIR (film, cm^{-1}): 3330-3400•2920, 2850, 1706, 1420, 1210, 1088, 830. Number-average molecular weight (M_n): 1350; polydispersity index (PI): 1.45.

Preparation of the poly(BMA-DAAM) emulsion

Poly(BMA-DAAM) emulsion was prepared in the presence of the reactive surfactant. 0.90 g of RS, 0.12 g of ACVA initiator, 1.0 g of DAAM and 0.15 g of NaOH was dissolved in 22 ml of water. Then 16.5 g of BMA was added and stirred. The mixture was purged with nitrogen for 1 h and kept at 65 °C for 6 h to yield a stable emulsion with the particle size of about 50 nm (Figure 1). The solid content of the emulsion was about 45 wt.%.

Preparation of the emulsion coatings

The cross-linked emulsion coatings were prepared according to the following process: 1.5 g of adipic dihydrazides water solution (5 %) and 1-2 drops of the leveling agent were mixed with 2.0 g of poly(BMA-MMA) emulsion and the mixture was stirred for 1 h. The coatings were prepared by spin casting the above solution directly on a clean aluminum plate and allowed to dry at ambient temperature. In order to further study the cross-linking reaction and its effect on the dissolution behavior, a non-crosslinked emulsion film was also made without using adipic dihydrazides. The two emulsion films were almost colorless and transparent.

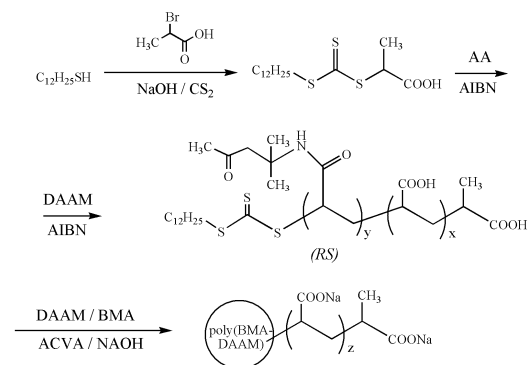
Results and Discussion

Preparation of the reactive surfactant and the emulsion

The synthetic route of the reactive surfactant and the polymer emulsion were shown in Scheme 1. AA and DAAM were polymerized in sequence to give a block oligomer (RS), which was characterized by GPC and IR. The PI value is 1.45 which is less than those observed in traditional radical polymerization (generally >2), displaying characteristics of live radical polymerization. Soapless emulsion copolymerization of BMA with DAAM was conducted in the presence of RS sodium salt. RS acted as a reactive surfactant for it participated in the polymerization process through chain transfer reaction and located at the surface of the obtained particles. As a result, the hydrophilic moiety of RS (i.e., the sodium carboxylate group) at the surface of the emulsion particles formed a stable hydrophilic shell to maintain the stability of the emulsion. In addition, as the prepared emulsion was used to prepare coatings, the hydrophilic ionic group chemically-bound to the polymer particles cannot migrate through the film and as a

result the coatings should have better water resistance and adhesion properties.

The particles were narrowly distributed in size and had an average diameter around 50 nm according to TEM (Figure 1). Glass transition temperature of the emulsion particle was measured using DSC method. The solid emulsion particle showed a glass transition at about 15 °C which was assigned to the core polymer, poly(BMA-DAAM).



Scheme 1. Synthetic route of the reactive surfactant (RS) and poly(BMA-DAAM) emulsion

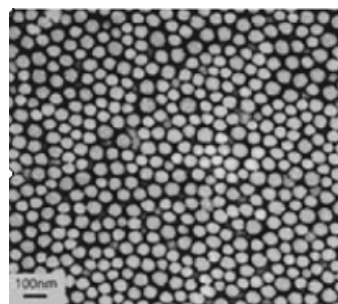


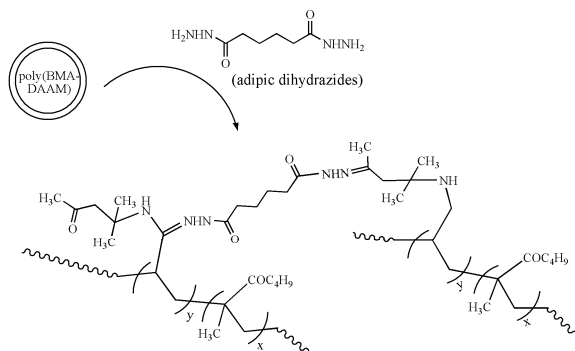
Figure 1. A TEM micrograph of the poly(BMA-DAAM) particles

Preparation of the emulsion coating

Emulsion coatings were prepared from the solution of the poly(BMA-DAAM) emulsion, adipic dihydrazides and small amount of leveling agent. The mixture made with the p(BMA-MMA) emulsion and adipic dihydrazides was stable for fairly long time (e.g., four weeks) at temperatures ranging from 4-50 °C and no precipitation was found. The dispersant was stable due to that the particles could maintain the geometry configuration, thus the adipic dihydrazide molecules was prevented from diffusing into the core of the particles to react with the carbonyl group.

It is known that good performance can only be achieved from water born dispersions after good film formation and entanglement of the polymer chains across the particle interfaces. It is clear that high Tg polymer emulsion may achieve very good properties, but high Tg will make it difficult for high levels of coalescent and good film formation. The Tg of the prepared emulsion polymer in this study (about 15 °C) is below room temperature, this is favorable for coalescent of polymer particles and film formation. However, low Tg of the emulsion polymer has a negatively affect

the performance of the film, such as mechanical properties, heat and stain resistance, etc. Hence, crosslinking reaction was used to reduce these negative effects.



Scheme 2. Crosslinking reaction of the emulsion film

In the film-forming process, the particles aggregated under the action of “capillary effect”. The morphology of the particles was broken and therefore the interface between initially separate particles will gradually fade away with the drying of the coating at room temperature, resulting in a continuous phase with uniform structure. The core polymer would diffuse from the inside to meet with adipic dihydrazides, yielding imino bonds and resulting in crosslinking structure (scheme 2).

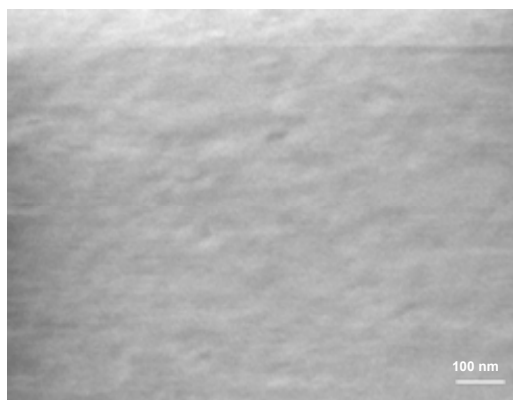


Figure 2. A TEM micrograph of the crosslinked emulsion film

Figure 2 is a phase image of a film cast from the emulsion containing the crosslinking agent, which was recorded by SEM. It can be observed that the surface of the film is uniform and smooth, and no separated particles can be observed, indicating that the film formation was efficient.

With the progress of the crosslinking process, the emulsion film became harder and more resistant to heat and solvents. As expected, the cross-linked emulsion film couldn't dissolve in water and some organic solvents such as ethanol and ethyl acetate. However, the emulsion film prepared without the addition of adipic dihydrazides still showed solubility in these organic solvents. Table 1 shows the performance of the emulsion films. It can be seen that the crosslinked film had increased surface hardness, better water resistance and solvent resistance, confirming that the crosslinking process was smoothly carried out and very beneficial

for the overall film properties. Additionally, all the emulsion films exhibited good impact resistance.

Table 1: Properties of the emulsion films

Emulsion film	surface hardness	Water resistance	Solubility in ethyl acetate	impact resistance
non-cross-linked	5B	white specks after 1h	partially soluble	no damage under 40Kg
cross-linked	B	no white specks after 12h	insoluble	no damage under 40Kg

Conclusions

Nano-sized emulsion containing functional carbonyl group was successfully prepared through soapless emulsion polymerization. Crosslinked emulsion films were made through the reaction of the emulsion with a cross-linking agent at ambient temperature. Results showed that the cross-linking process brought about performance improvement of the films.

The prepared emulsion based on self-crosslinking polymeric functional particles might be used as binders for high performance water-born inks (i.e., jet printing ink). The soapless emulsion polymerization provides good method for the design and preparation of binder resins for use in water-born inks. The crosslinking reaction makes the final ink will be highly resistant both to water and general organic solvent. However, this is commonly an issue for conventional water-borne inks. The crosslinked emulsion film provides good mechanical properties, which makes it useful for applications.

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Author Biography

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