Progress in Organic Coatings 99 (2016) 386–392

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

The effect of β-cyclodextrin on formation of poly (styrene-butyl acrylate) latexes and their film performance

Peixin He[a], Panpan Yi[a], Hang Liu[a], Mingji Su[a], Yuhong Zhang[a,*], Zhiguo Wang[a], Yulin Li[a,b,**]

[a] Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Ministry of Education, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, PR China
[b] CQM—Centro de Química da Madeira, MMRG, Universidade da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal

ARTICLE INFO

Article history:
Received 15 October 2015
Received in revised form 9 May 2016
Accepted 26 June 2016
Available online 15 July 2016

Keywords:
β-Cyclodextrin
Emulsion polymerization
Nanolatexes
Latex film performance

ABSTRACT

P(St-BA)/β-CD nanoparticle latexes (nanolatexes) were prepared via emulsion polymerization of styrene (St) and butyl acrylate (BA) in the presence of β-cyclodextrin (β-CD) using a small amount of sodium dodecyl sulfate (SDS) below its critical micelle concentration. The average particle sizes of the nanolatexes can be well controlled from 85 to 185 nm by varying the content of β-CD from 0.4 to 2.0 wt%. The nanolatexes exhibit a highest monomer conversion and optimal stability upon addition of 1.2 wt% of β-CD. Interestingly, unlike conventional surfactant, the addition of β-CD cannot cause observable change in surface tension of the emulsion. The films obtained from P (St-BA)/β-CD latexes have a dense structure with a smoother surface compared to the P (St-BA) latex film in the absence of β-CD. Furthermore, the films in the presence of β-CD present better water resistance and higher tensile strength, probably because β-CD is able to form inclusion complexes with both soft BA component and SDS, which can enhance the rigidity of BA and prevent SDS movement to the outer surface of the resulting films.

1. Introduction

The increasing pollution problems caused by our modern industry and living style drive researcher's attentions to develop eco-friendly materials [1]. In the field of coatings industry, the big amount of volatile organic compounds (VOC) coming from solvent based coatings (SBC) make our preferable selection of water-borne coatings (WBC), which is often involved in a lower VOC content [2]. As a kind of coating materials, water-borne suspensions should be endowed with some hydrophilicity to maintain sufficient colloidal stability during storage, which may compromise their mechanical property and the resistance to penetration from water and other solvents after formation of films [2–4]. The contradictory requirements motivate us to explore a new technology to fabricate WBC with good combinative properties, such as better colloidal stability, film formability, mechanical properties, gloss, scratch/water resistance, etc [5].

Polystyrene (PSt) has been widely used for preparation of polymeric latexes for coatings applications so far by virtue of its offering of good hardness, strength, adhesion and water resistance to the latex films. On the other hand, pure PSt latexes had poor film-formability, cohesiveness and flexibility. Recently, emulsion polymerization has become an interesting approach to fabricate polymer-based latexes with well-controlled size and structure [6–9]. To overcome these disadvantages, miniemulsion copolymerization of St with other acrylate monomers has been widely adopted to prepare polymeric latexes for formation of coating films with better combinative performance [10,11]. For instance, Armes' group developed an organic surfactant-free emulsion polymerization method to prepare poly (styrene-co-n-butyl acrylate)/silica (P (St-BA)/SiO_2) latexes with ability to form a transparent film with improved flame retardancy. The incorporation of soft butyl acrylate (BA) composition can be used to improve the film formability as well as its toughness [11]. However, the single employment of SiO_2 nanoparticles as an inorganic surfactant tends to induce a flocculation, instead of formation of individual nanoparticles, especially for the system with increased BA content [12]. A systematic research has been investigated by our group in the past decade to

* Corresponding author.
** Corresponding author at: Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Ministry of Education, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, PR China.
E-mail addresses: zhangyuhong@hubu.edu.cn (Y. Zhang), yulinli@uma.pt (Y. Li).

http://dx.doi.org/10.1016/j.porgcoat.2016.06.017
0300-9440/

develop PSt-based latexes via emulsion polymerization [10,13–15]. Our most recent study indicate that the employment of a nonionic polyethylene glycol surfactant, less toxic than cationic one [9,16], can benefit formation of P (St-BA)/SiO_2 latexes with enhanced colloidal stability. Although these latexes had good film formability and film resistance to strong acidic/basic erosion, the latexes preparation process is still involved in organic solvent, which aid to dissolve a hydrophobic initiator, 2-azobis (isobutyronitrile) (AIBN) [10].

Herein, in this study, we proposed an effective approach to development of P(St-BA) latexes with controlled nanosizes by emulsifying hydrophobic St and BA monomers in aqueous solution containing sodium dodecyl sulfate (SDS) as anionic surfactant. Water soluble initiator, potassium persulfate (KPS), was selected to replace the previous AIBN hydrophobic initiator for avoidance of any organic solvent. To further enhance the interactions between the surfactant and P (St-BA) latexes matrix, β-cyclodextrins (β-CD) (a kind of cyclic oligomer consisting of 7 glucopyranose units of 1, 4 α-linked glucose), which has an ability to form host-guest complexes with both BA composition and SDS surfactant [17–19], was incorporated. The effects of β-CD on the size, surface charge, and colloidal stability of P (St-BA) latexes were systematically investigated. The resulting latex films were studied concerning their mechanical property, water absorption ability, and smoothness. It was found that the employment of β-CD can reduce the dosage of emulsifier to be used and at the same time improve the stability of the formed latexes. Furthermore, the presence of β-CD can be employed to adjust the size and surface charges of P (St-BA) latexes and improve the physical properties of the latex films, including tensile strength, water resistance and smoothness. The above merits of these systems make them promising for WBC applications.

2. Experimental

2.1. Materials

Styrene (St), butyl acrylate (BA) and sodium dodecyl sulfate (SDS) were bought from Tianjin Chemical Regent Co. Ltd., China. β-cyclodextrin (β-CD) was obtained from the Yinhe Chemical Company, Wuhan, China. Potassium persulfate (KPS) was obtained from Chemical Reagent Company, Shanghai, China. Both β-CD and KPS were recrystallized before use. Sodium Bicarbonate ($NaHCO_3$) was purchased from Rainbow Chemical plant, Shanghai, China.

2.2. Preparation of P (St -BA)/β-CD latex nanoparticles and latex film

The P (St-BA) latexes were prepared in the presence of β-CD with a small amount of SDS according to the feed ratios shown in Table 1. The emulsion polymerization was carried out in a 250 mL four-necked flask with a reflux condenser, stirring, nitrogen gas inlet, thermometer and dropping funnels. Firstly, β-CD and $NaHCO_3$ were dissolved in deionized water (45 mL) and then added to the flask under stirring at 70 °C for 1 h. The entire system was degassed with nitrogen gas. 20 wt% of the St and BA mixture monomers was added slowly into the flask through a dropping funnel for 1 h. All the SDS solution (10 mL, 0.18 g SDS) was poured into the reactor in one-time. Then the KPS solution (15 mL, 0.18 g KPS) was dripped slowly into the flask at 80 °C. And the rest of the mixture monomers and KPS solution were added dropwise into the flask sequentially in 3 h. Finally, the reaction mixture was kept at 80 °C for additional 4 h to complete the polymerization. As to the conventional emulsion polymerization, it was carried out under the same conditions as mentioned above except that the β-CD was replaced by the same amount of SDS.

Table 1
Recipes for preparation of P (St-BA)/β-CD nanolatexes.

No.	St (g)	BA (g)	CD (g)	SDS (g)
1	15	15	0.12	0.18
2	15	15	0.24	0.18
3	15	15	0.36	0.18
4	15	15	0.48	0.18
5	15	15	0.60	0.18
6	18	12	0.36	0.18
7	21	9	0.36	0.18
8	15	15	0	0.30
9	15	15	0	0.42
10	15	15	0	0.54
11	15	15	0	0.66
12	15	15	0	0.78
13	18	12	0	0.54
14	21	9	0	0.54

Fixed chemical amount: KPS: 0.18 g; $NaHCO_3$: 0.06 g; H_2O: 70 g.

A certain amount of each of the P (St-BA)/β-CD latexes was casted onto on a clear glass plate, followed by natural evaporation under room temperature to get latex films. As comparison, pure P (St-BA) film was prepared in a similar process. The latex films were dried at 50 °C for 16 h to obtain a solid film with a final thickness of about 0.75 mm.

2.3. Characterization

2.3.1. Characterization of P (St-BA)/β-CD latexes

2.3.1.1. Determination of coagulum percentage and monomer conversion. To check the homogeneity of the latex suspension, the precipitate was collected after polymerization, followed by drying at 60 °C in an oven. Coagulum percentage (CP) was calculated according to the following equation:

$$CP(wt\%) = \frac{W_1}{W_2} \times 100\% \quad (1)$$

where *CP* is the coagulum percentage, W_1 and W_2 are the dry weight of the coagulum and weight of total monomers, respectively.

The monomer conversion (MC) was determined by gravimetric analysis and given by Eq. (2), as follows

$$MC\,(wt\%) = \frac{S * W - W_3}{W_2} \times 100\% \quad (2)$$

where *MC* is the monomer conversion, *S* is the solid content (the percentage of the remaining portion of the emulsion or coating after drying). *W* is the weight of total materials added to the system, W_3 is the weight of total nonvolatile components (β-CD, SDS, KPS and $NaHCO_3$) in the system.

2.3.1.2. Z-Average particle size, particle disperse index (PDI) and zeta potential measurements. The *Z*-average particle size, the particle disperse index (PDI) and *Zeta potential* of the obtained latexes were measured by a Zetasizer (Malvern Nano S, UK). Each sample was measured thrice.

2.3.1.3. TEM observation. The morphology of the latex particles was observed by a Transmission Electron Microscope (TEM FEI tecnai G20, FEI Corp., USA). For preparation of TEM samples, the latexes were diluted under ultrasonication for 10 min, followed by dropping onto carbon-coated copper grid to be air-dried.

2.3.1.4. Surface tension measurement. A certain amount of emulsion was poured into the beaker. Surface tension experiments were carried out on a KRÜSS Processor Tensiometer (K-12, Germany) via plate method at 25 °C.