

## Amphiphilic copolymer stabilized core–shell structural casein-based emulsion



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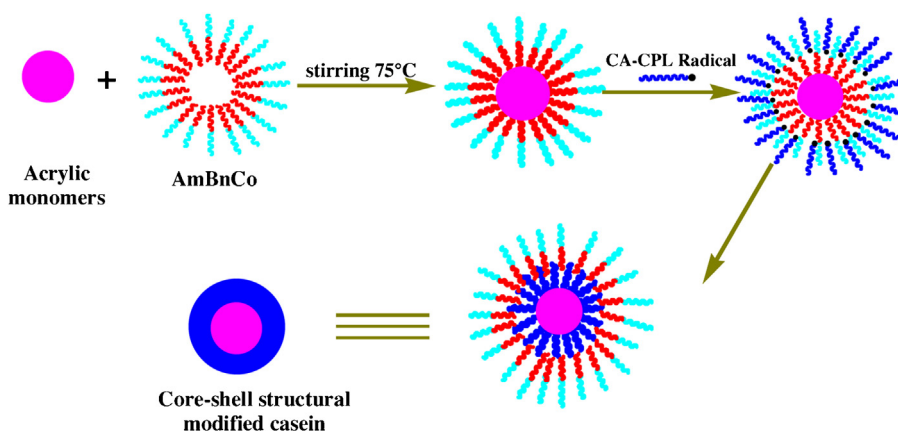
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### HIGHLIGHTS

- Self-made amphiphilic copolymer was used as stabilizing agent in emulsifier-free polymerization.
- Core–shell structural nano-sized casein-based emulsion for film former was successfully prepared.
- Presence of 1.0 wt% of AmBnCo gives superior emulsion stability.

### GRAPHICAL ABSTRACT

Core–shell structural casein-based emulsion for film former was successfully prepared via emulsifier-free emulsion polymerization stabilized by self-made amphiphilic copolymers.



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### ABSTRACT

Casein-based emulsion for film former was innovatively prepared via emulsifier-free emulsion polymerization by employing self-made amphiphilic copolymers ( $A_mB_nC_o$ ) as the stabilizer. Structure of  $A_mB_nC_o$  was confirmed by  $^1H$  NMR spectrometry. Stability of the as-prepared emulsion in different concentrations of  $A_mB_nC_o$  was evaluated by measuring their droplet size, microstructure and viscosity. The results indicated that the obtained particles were 40–50 nm in size with uniform size distribution, and exhibited obvious core–shell structure. The emulsion containing 1.0 wt% of  $A_mB_nC_o$  presented superior storage stability.

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## 1. Introduction

Biodegradable polymers have received considerable attention over the past decade due to the decline of available fossil resources and the increasing preference for environmentally friendly

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products [1–4]. The current generation of bio-based polymers is produced primarily from renewable resources, such as sugar canes, starches, and proteins; such materials for packaging, adhesives, coatings, and biomedical applications can be produced with less overall energy consumption than their petrochemical counterparts and tend to be less toxic to the environment [3,4].

Casein is a naturally occurring macromolecule that accounts for approximately 80% of the protein content in cow's milk; it is a phosphoprotein that can be separated into various electrophoretic fractions, such as  $\alpha_s$ -casein,  $\kappa$ -casein,  $\beta$ -casein, and  $\gamma$ -casein in which each constituent differs in primary, secondary, and tertiary structure, amino acid composition, and molecular weight (19–24 kDa) [5–7]. Due to its random coil conformation with a high degree of molecular flexibility and large number of polar groups, casein shows good film-forming properties. This makes it an excellent candidate for numerous applications such as paper coatings, adhesives, and food packagings [5–7]. However, like other protein-based materials, casein possesses two major drawbacks: limited mechanical strength and water sensitivity, which might restrict its practical applications [5]. Chemical modification of the casein structure or physical blending with other materials, including plasticizers [5–7], cross-linkers [7], waxes [8], and other polymers [9] have been attempted to correct its deficiencies.

Emulsion polymerization has been a technique to modify casein structure. However, the conventional emulsion polymerization will greatly influence the purification and performance of the products. Moreover, the environmental pollution coming from the usage of emulsifier is also a severity. In this case, the emulsifier-free emulsion polymerization has attracted much attention in recent years. Soap-free emulsion polymerization refers to the polymerization process that completely without emulsifier or only with trace of emulsifier (concentration less than the critical micelle concentration). Compared with conventional emulsion polymerization, it may provide the following advantages [10,11]: no emulsifier migration during film formation, monodisperse particle size distribution, and excellent shear stability. Up to now, following methods have been adopted to obtain such emulsifier-free polymer latexes from hydrophobic monomers: (1) polymerization by using of ionic group-containing initiators [12–16]; (2) polymerization in the presence of amphiphilic polymer or oligomer; (3) copolymerization with hydrophilic monomers [11,17,18]; (4) copolymerization with ionic hydrophilic monomers [19,20]. Among them, amphiphilic polymers with both hydrophilic and hydrophobic components have been broadly used as surfactants due to the different solubility of varied components. In this case, an amphiphilic copolymer chain tends to adsorb on the liquid–liquid interface stabilizing it by reducing its interfacial tension [21–27]. Relative to small molecule amphiphiles, polymeric amphiphiles can bring about interfacial assemblies with enhanced dynamic stability [28]. As one kind of amphiphilic polymers, random amphiphilic polymers can be easily prepared and applied in many industrial fields such as emulsifiers, dispersants, and surfactants.

Up to now, several studies have been done regarding modified casein emulsion in our research group [29–33]. Modified casein emulsion has been endowed with improved mechanical properties and water resistance. However, storage stability of the obtained emulsion remains to be improved. The aim of this paper is to prepare amphiphilic copolymers without any purification steps and apply them as surfactants during casein modification. Effects of emulsifier concentration on emulsion stability were investigated by measuring particle size distribution, microstructure, and viscosity so as to determine the range of experimental conditions. The as-prepared amphiphilic copolymers could be used to enhance emulsion stability by interfacial adsorption, as described in Scheme 1. This knowledge can be used to design and fabricate of water-based binder with novel properties.

## 2. Experimental

### 2.1. Materials

Casein (CA) was purchased from Zhejiang Huatian Co., Ltd. Triethanolamine was obtained from Tianjin Fengchuan Chemical Reagent Co., Ltd. Caprolactam (CPL,  $\geq 85\%$ ) was supplied by Shanghai Guoyao Chemical Reagent Co., Ltd. Methyl methacrylate (MMA,  $\geq 99\%$ ) was bought from Tianjin Kemiou Chemical Reagent Factory. Vinyl acetate (VAC,  $\geq 99.5\%$ ) and acrylamide (AM,  $\geq 98\%$ ) were supplied by Tianjin Fuchen Chemical Reagent Factory. Butyl acrylate (BA,  $\geq 99\%$ ) and ammonium persulfate (APS,  $\geq 98\%$ ) were purchased from Tianjin Hongyan Reagent Factory. Kalium persulfate (KPS,  $\geq 99.5\%$ ) and sodium bisulphite ( $\text{NaHSO}_3$ ,  $\geq 58.5\%$ ) were supplied by Tianjin No. 3 Chemical Reagent Factory. Ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) was bought from Xi'an Sanpu Chemical Reagent Co., Ltd. Thickener (BJ90) was supplied by Nanjing Baiju Technology Co., Ltd. All the chemicals used were of analytically pure grades and applied without any further purification.

### 2.2. Synthesis of amphiphilic copolymers

A 250 mL three-necked round-bottom flask was equipped with a reflux condenser, a thermometer, and a magnetic stirring bar. The reactor flask, charged with deionized water (60 g), VAC (3.94 g), BA (3.84 g), and AM (0.575 g) was immersed in a water bath at  $60^\circ\text{C}$  and was stirred at 300 rpm for 20 min. After the reaction mixture was heated up to  $85^\circ\text{C}$ , the initiator solution was prepared by dissolving KPS (0.24 g) and  $\text{NaHSO}_3$  (0.0735 g) in 5 g aqueous solution. Then the initiator solution was dropwise added to the system at the speed of two drops per second. Amphiphilic copolymers were obtained after stirring for 1.5 h and cooling down to room temperature.

### 2.3. Preparation of core-shell structural modified casein emulsion

The polymerization was conducted as follows. Casein, 4.20 g, was added to 1.05 g of triethanolamine dissolved in 110 mL of distilled deionized water in a 250 mL three necked round-bottom flask fitted with a digital electric stirrer, a reflux condenser, a thermometer, and a constant pressure dropping funnel. This solution was kept stirring for 2 h under  $65^\circ\text{C}$ . After the reaction mixture was heated up to  $75^\circ\text{C}$ , 1.8 g of caprolactam dissolved in 18 mL of distilled deionized water was drop wise added to the system at the speed of two drops per second and then stirred for 2 h. Then BA (0.793 g), MMA (4.415 g), VAC (0.793 g) were added to the flask. The reaction was kept at the remaining temperature for 0.5 h. Thereafter, the polymerization was started with 18 g aqueous solution of APS (0.180 g) added at the speed of two drops per second and then stirred for 0.5 h. The reaction was kept at  $75^\circ\text{C}$  for 1.5 h after feeding amphiphilic copolymers in various concentrations (1.0–5.0 wt%). Modified casein emulsion was obtained after cooling down to room temperature.

### 2.4. Characterization

#### 2.4.1. Critical micelle concentration (CMC) analysis

Critical micelle concentration (CMC) analysis was performed on DCAT21 instrument (manufactured by sartorius Co., Ltd., Germany) after the amphiphilic copolymers was diluted into 1 g/L concentration by deionized water.

#### 2.4.2. $^1\text{H}$ NMR analysis

$^1\text{H}$  NMR (400 MHz) spectrum was acquired in  $\text{CDCl}_3$  using a Varian Infinity-plus-400 spectrometer (manufactured by Varian Co., Ltd., USA) at  $25^\circ\text{C}$ . The sample for tests was purified in a vacuum

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