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Hyperbranched poly(amido amine) demulsifiers with ethylenediamine/1,3-propanediamine as an initiator for oil-in-water emulsions with microdroplets

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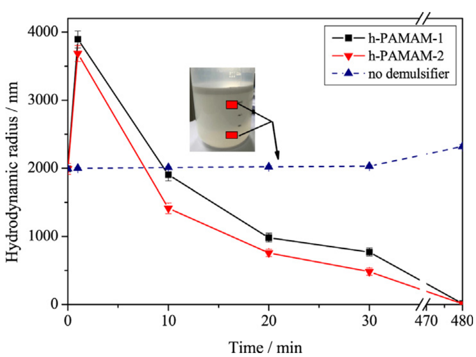
GRAPHICAL ABSTRACT



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ABSTRACT

Two kinds of hyperbranched poly(amido amine) (h-PAMAM) with abundant terminal amine groups are synthesized to break the oil-in-water (O/W) emulsions consisting of microdroplets. The demulsification performance of h-PAMAM is systematically evaluated with assistance of UV–vis spectra, micrograph, DLS and SAXS analyses. The demulsifier with 1,3-propanediamine as initiator shows a striking demulsification ability with small dosage (< 40 mg/L). The demulsification equilibrium can be obtained within 30 min, and oil removal ratio reaches to 92%, which is ascribed to the highly hyperbranched structure and the adequate molecular weight. The demulsifier molecules with hyperbranched structure easily diffuse to the oil-water interface and reveal a high interfacial activity, which causes film break and coalescence of oil droplets, and consequently leads to high oil removal ratio. The combination of UV–vis spectra, micrograph, DLS and SAXS analyses provides a new approach to monitor demulsification process and comprehend demulsification mechanism. The excellent demulsification performance of h-PAMAM shows a considerable potential applications of this hyperbranched polymer for wastewater treatment and petroleum industry.

1. Introduction

Polymer flooding extraction plays a major role in global crude oil recovery, especially in China [1]. There exist some obstinate problems, however, during the processes of oil extraction and wastewater treatment because oily wastewater usually form a kind of oil-in-water (O/W)

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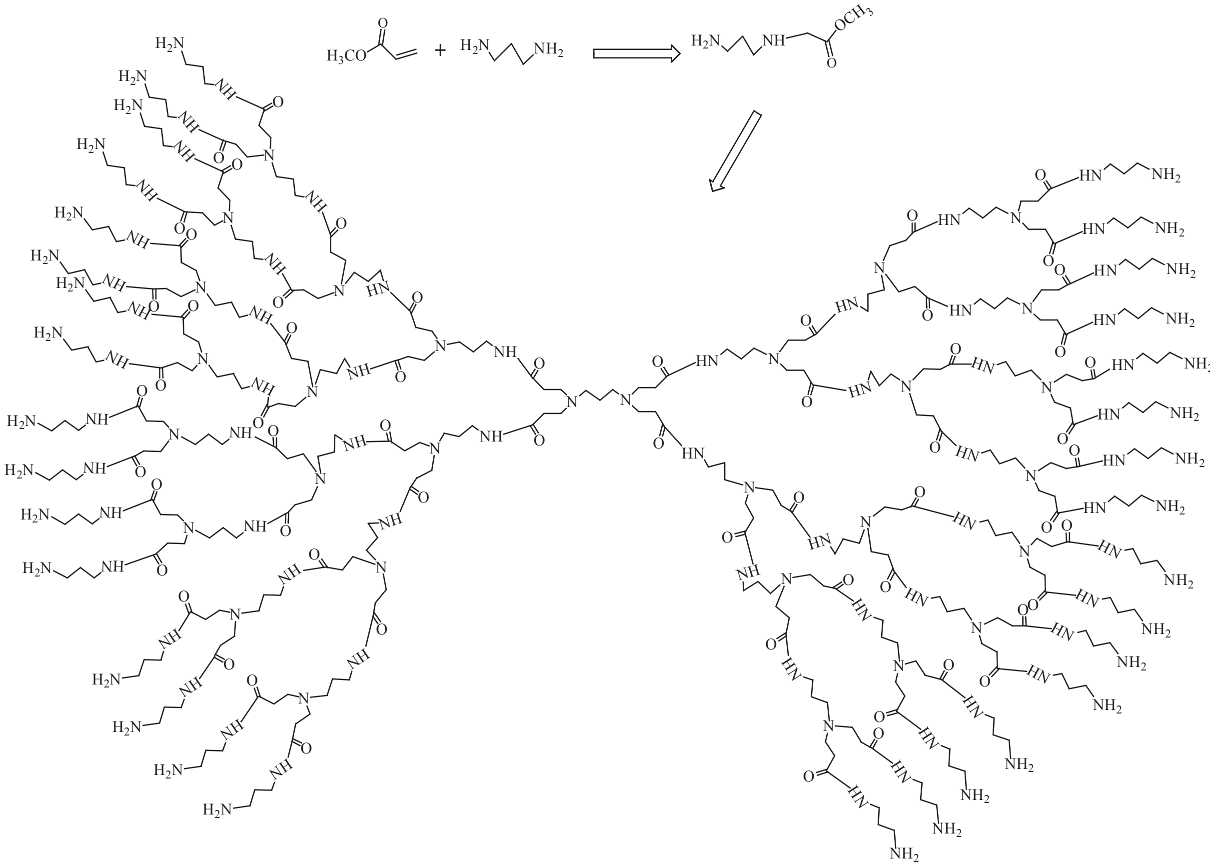

Scheme 1. Schematic representation of possible reaction process for demulsifier h-PAMAM with 1,3-propanediamine as initiator.

emulsion [2–4]. This emulsion system is composed of complex and stable liquid-liquid colloidal suspensions, and the emulsifier molecules basically gather at oil-water interface, together with the interfacially active materials defined as asphaltenes and resins from the crude oil [5–7]. The oil content in wastewater can be up to 10,000 mg/L [8], and it is hazardous to environment that the wastewater is directly discharged without proper treatment. Therefore, effective treatment methods and techniques for demulsification become urgent and imperative.

Demulsifier can drastically weaken the stability of emulsion, leading to the phase separation, and it is gradually transformed to be a practical approach to deal with the oily wastewater. In general, it can be classified into three categories: physical, chemical, and biological demulsifications [9–11]. Compared with physical or biological demulsification, chemical demulsification is widely applied to separate water from O/W emulsions by chemical demulsifiers with feasible conditions and simple operations [12–14]. Recently, biodegradable amphiphilic demulsifiers have attracted much attention because of outstanding performance, and environmentally friendly properties [15,16]. For instance, non-ionic demulsifiers based on polyethyleneimine (PEI) with various contents of ethylene oxide (EO) and propylene oxide (PO), which lead to different values of hydrophilic-lipophilic deviation (HLD), have been reported [8]. A new-type environmentally friendly Fe_3O_4@OA nanoparticles demulsifier with a single oleic acid (OA) layer coated by co-precipitation is effective for oil-water separation [17]. The effect of molecular structure on demulsification performance of the demulsifier is explored, and the results demonstrate that the branched PEO-PPO co-polymer demulsifiers have high demulsification ability. Nevertheless, when the average oil droplets size in the emulsions is smaller than 2 μm, demulsification performance of the existing demulsifiers is far from satisfactory. The researches on treatment of emulsions with such microdroplets move at a slow pace [18,19], and it is of great importance and emergency to explore new type demulsifiers to cope with the microdroplets.

Hyperbranched polymers are macromolecules of special geometric and topological features [20–23]. They can be adhered easily to oil-water interface, and may possess the potential to separate O/W emulsions. For example, methacrylated hyperbranched polyglycerol (HPG-MA) was employed as a demulsifier showing high-efficiency demulsification [18]. Though these demulsifiers display fabulous properties, they have their own limits such as relatively large dosage, and high cost. In this study, as an analogue to HPG-MA, hyperbranched polyamidoamine (h-PAMAM) is synthesized through an optimized “one-pot” method. The prepared demulsifier is employed to treat O/W emulsions with the average oil droplets size around or less than 2 μm. The demulsifier dosage, temperature, and settling time are systematically investigated to evaluate the demulsification performance. In addition, the interfacial tensions, micrographs of the emulsions with and without demulsifier, the change of oil droplet size, and the size distribution of emulsions are determined to throw light on demulsification mechanism.

2. Experimental

2.1. Chemicals

1,3-propanediamine (99%), ethylenediamine (EDA) (99%), Span 80, Tween 80, and methyl acrylate (MA) (98.5%) were purchased from Aladdin Chemical Reagent Corporation. Methanol (99.5%), *n*-hexane (97%) and ethyl ether (99.5%) were purchased from Sino-pharm Chemical Reagent Corporation. All of these chemicals were used without further purification.