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Review

Preparation of polystyrene latex particles from radiation induced miniemulsion polymerization using Y-like branched emulsifiers as the sole stabilizer

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Abstract

A series of Y-like branched emulsifiers: 12-butyryloxy-9-octadecenoic acid (BOA), 12-hexanoyloxy-9-octadecenoic acid (HOA), 12-isobutyryloxy-9-octadecenoic acid (IBOA), 12-benzoyloxy-9-octadecenoic acid (BzOA) were synthesized and characterized by FT-IR and ^{1}H NMR spectra. Monodispersed polystyrene latexes were prepared by ^{60}Co-γ ray radiation induced miniemulsion polymerization with the use of the Y-like branched emulsifiers at room temperature. The influences of different branch group in Y-like branched emulsifiers on the particle size, the surface coverage with carboxylic groups, and the surface tension of the latexes were investigated, which may show some interesting information on the probable mechanism underlying in the miniemulsion polymerization system. Kinetics analysis shows that there is no constant rate stage which seems to indicate a droplet nucleation mechanism. Transmission electron microscopy (TEM) and laser particle and zeta potential analyzer (LPZPA) were used to observe the polystyrene latex particles and original droplets, respectively. Preservation of the original particle size and distribution throughout polymerization underlines the predominance of droplet nucleation. The high efficiency of these Y-like branched emulsifiers in miniemulsion polymerization suggests that the emulsifiers act not only as the surfactants, but also as the so-called "cosurfactant".

Keywords: Y-like branched emulsifiers; γ Rays radiation; Miniemulsion polymerization; Polystyrene

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Contents

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1. Introduction

Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50–500 nm prepared by shearing a system containing oil, water, a surfactant, and a so-called "cosurfactant" [1]. The characteristic and significant features of miniemulsions: (a) to perform the polymerization under preservation of droplet size, distribution and composition; and (b) to use surfactants in a very efficient manner, have accounted for their growing scientific and technical interest. The stability of a miniemulsion system is basically dictated by (1) the suppression of Ostwald ripening [2] which controlled by an osmotic pressure in the droplets afforded by the hydrophobe; and (2) minimizing coalescence enabled by a sufficient surface coverage by surfactants. Miniemulsion formulations, even when they are critically stabilized, [2] promote droplet nucleation mechanism [3] and thus afford an 1:1 copying of droplets to particles [4] as established by a combination of SANS, surface tension measurements, and conductometry [5].

The roles of the hydrophobes and the surfactants used in miniemulsions have been well elaborated in literature. The formation of a stable miniemulsion depends on the choice of hydrophobe. To cite a few, e.g. cetyl alcohol, hexadecane, [3,6,7] dodecyl mercaptan, [8] reactive alkyl methacrylates, [9] redissolved polystyrene [10–12] can be used as the "cosurfactant". These materials slow down the diffusion of monomer molecules from the smaller droplets to the larger droplets. This diffusion (Ostwald ripening) is inherent in all emulsion systems because the smaller droplets have higher vapor pressures than the larger droplets, as the result small droplets tend to disappear with time by diffusion into the larger droplets, unless the Ostwald ripening is suppressed by the so-called 'cosurfactant'.

A systematic study on surfactants drawn from nonionic, cationic, and anionic series has revealed their very good efficiency in miniemulsions which can reduce the rate of coalescence [13]. Low surface coverage of the droplets afforded by a model surfactant like sodium dodecyl sulfate (SDS) have been found to effectively control the collision process. The equilibrium concentration of the surfactant required to form critically stabilized miniemulsions has been found to be well below the CMC, and this rules out the existence of micelles in the system. The much higher surface tensions of the polymerized latexes in comparison to the equilibrium surface tension values of respective surfactants further substantiates the absence of surfactant micelles in the systems and hence rules out the micellar or homogeneous nucleation process.

Recently, it was shown that amphiphilic comblike polymers containing long alkyl side chains can act both as a surfactant and – although located at the interface – as an osmotic agent [14,15].

Now another question raises: whether a Y-like amphiphilic emulsifier, consisting of a long (18C) and a moderate length (4–7C) side hydrophobic chain similar to a hydrophobe and a polar functional site being capable of adsorbing at the oil/water interface, could be an alternative and ideal choice in this special heterophase polymerization system?

In this work, Y-like branched emulsifiers with different side chains (butyryl, isobutyryl, hexanoyl, benzoyl) were synthesized by the esterification of 12-hydroxy-9-octadecenoic acid (OOA) with different carboxylic acids, and then it was investigated whether such emulsifiers are really able to replace the hydrophobe and the surfactant at the same time. The following issues will be addressed in this paper:

1. First, we synthesized a series of Y-like branched emulsifiers, and characterized them with IR, ^1H NMR spectra. Then, we investigated the scope for the effective use of the synthesized Y-like branched emulsifiers in miniemulsions involving styrene as the monomer and subsequent in polymerization induced by γ ray.
2. The influences of the synthesized emulsifiers with different branched groups on the surface coverage of the droplets in miniemulsion, the ultimate particle size and size distribution in the resulted latexes were analyzed by the particle size determination and surface tension measurements.
3. Kinetics analysis was made to deduce the reaction mechanisms in the miniemulsion systems.

2. Experimental

2.1. Materials

Styrene (Shanghai Chemical Reagents Co.) was distilled under vacuum before use. Castor oil was of chemical grade and used as received. Toluene was of analytical grade and used as received. *iso*-butyric acid, *n*-hexanoic acid, *n*-butyric acid, benzoic acid were of chemical grade and used as received. Other agents were all of analytical grade and used without further purification. Double-distilled and deionized (DDI) water was used.

2.2. Preparation of 12-hydroxy-9-octadecenoic acid

The OOA was prepared firstly as shown in Scheme 1. Hundred milliliters castor oil and 15 g NaOH/100 ml H_2O were added into a 500 ml round bottom three-necked flask equipped with a mechanical stirrer and a condenser. The mixture was stirred and heated to 100 °C to react for 4 h, the mixture became transparent. Then cooled to 50 °C, 50 wt.% H_2SO_4 was dripped into the mixture with stirring by a mechanical stirrer until the pH value reached 1–2. Then the mixture was transferred into a separating funnel, keeping it still for 6 h, after that separated out the water layer. The oil layer was washed with the same volume saturated sodium chloride solution at 60 °C three times. At last, dried the oil layer in 10 kPa at 80 °C. The purified sample was red brown semitransparent and was used for the characterization by FT-IR and ^1H NMR spectra as shown in Fig. 1. We can see that the absorption peak at 1744 cm^{-1} (ester group of castor oil) was disappeared after reaction, at the same time, the absorption peak at 1711 cm^{-1} (carboxylic group of OOA) appeared.

^1H NMR (300 MHz, δ, ppm, $CDCl_3$): δ 0.89 (t, 3H, $-CH_3$), 1.28 (m, 20H, $-CH_2-$), 1.44 (m, 2H, $-CH_2-$), 1.62 (m, 2H, $-CH_2-$), 2.03 (m, 2H, $-CH_2-$), 2.23 (m, 2H, $-CH_2-$), 2.32