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Regular Article

Alizarin Yellow R (AYR) as compatible stabilizer for miniemulsion polymerization

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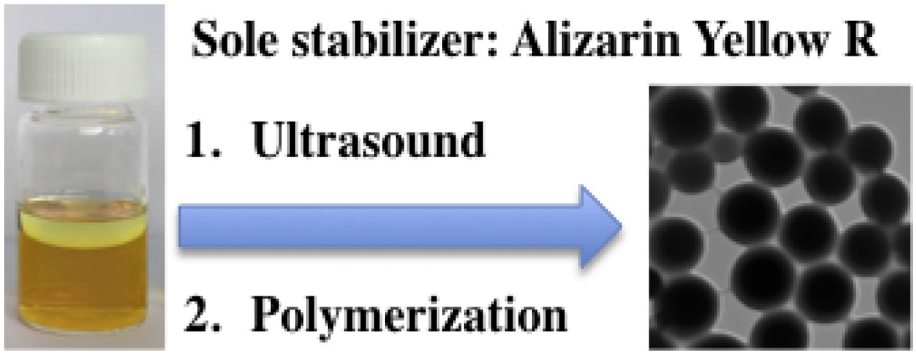
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Many solid particles have been used in Pickering stabilized (mini)emulsions. Stabilizing "particles" can be also formed in situ e.g. by aggregation of dye molecules as reported recently. Among the dyes sodium 2-hydroxy-5-[(E)-(4-nitrophenyl)diazenyl]benzoate (Alizarin Yellow R, (AYR)) is one of the best stabilizers. It is assumed to act as sole stabilizer also in heterophase polymerizations and offers a great potential for applications.

Experiments: Aqueous solutions of AYR in varying concentrations (0.3, 0.5, 1.0, 1.5, 2.0 mg/mL (dye/water)) were employed as continuous phase in direct miniemulsions. The oil phase comprised ethenylbenzene (styrene) and hexadecane. The effects of AYR concentration and ultrasonication time on size and distribution of the droplets were investigated. The miniemulsions were polymerized with a water-soluble azo-initiator (2,2′-azobis[n-(2-carboxyethyl)-2-methylpropionamidine] n-hydrate, VA-057) and conversion and kinetics were determined.

Findings: The AYR is successfully employed as stabilizer in Pickering-like miniemulsion polymerizations of styrene. The higher the AYR concentrations the more stable the miniemulsions, the smaller the droplet sizes and the narrower the distributions are, ranging from ca. 450 to 180 nm and 0.38 to 0.15, respectively. The nucleation mechanism of the polymer particles could be revealed by the number ratio of

Abbreviations: AYR, 2-hydroxy-5-[(E)-(4-nitrophenyl)diazenyl]benzoate (Alizarin Yellow R); VA-057, 2,2′-azobis[n-(2-carboxyethyl)-2-methylpropionamidine] n-hydrate; SDS, sodium dodecylsulfate; KPS, potassium persulfate; St, ethenylbenzene (styrene); HD, hexadecane; SC, solid content; DLS, dynamic light scattering; TEM, transmission electron microscopy; SEM, scanning electron microscopy; PDI, polydispersity index.

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droplets and particles and follows droplet nucleation. This is confirmed by polymerization kinetics, which is in accordance with classical miniemulsion polymerization, too.

1. Introduction

Emulsion and miniemulsion polymerization are frequently employed techniques for the commercial production of polymers, especially for solvent based products, such as cosmetics, coatings, and adhesives [1–16]. In (mini)emulsion polymerization, the emulsifier (surfactant, stabilizer) plays a crucial role to stabilize dispersions of the two mutually insoluble phases (i.e. water and oil). However, conventional emulsifiers like sodium dodecylsulfate (SDS) can have a negative effect on film forming properties owing to their migration to the surface. It is costly to remove the emulsifier from the latex. Therefore, many efforts have been undertaken to eliminate the disadvantages of emulsifiers [1–4]. For example, in soap-free emulsion polymerization, which uses potassium persulfate (KPS) or hydrophilic/ionic comonomers as emulsifier, colloidal stability is generated in the process of polymerization. Another type of stabilization mechanism in heterophase polymerizations is Pickering-like stabilization using solid particles instead of classical emulsifiers [17–37].

There are many reports concerning the type of stabilizing solid particles and mechanism of colloidal stabilization [11–16]. Effective solid particles include $CaCO_3$, $BaSO_4$, montmorillonite, laponite, clay, SiO_2, and so on. The particles' size, content and surface hydrophobicity exhibit great influence on the formation, size, stability and other properties of the droplets [17–29]. The relation between droplet size and mass content of the solid particles can be estimated by the following equation:

$$D_{droplet} = 6M_{oil}/(\rho_{oil}\alpha_{solid}M_{solid}) \quad (1)$$

where ρ_{oil} is the oil density, α_{solid} the interfacial area covered per mass of the solid particles and M_{oil}/M_{solid} the mass ratio of oil to solid particles. If a low content of solid particles is used, a small interfacial area will be stabilized; as a result, large droplets are obtained. On the contrary, small droplets can be prepared by a large amount of solid particles. There are also plenty of reports on new solid stabilizers, such as mixtures of zinc oxide nanoparticles and polymerizable surfactants [38], combinations of nanocrystals and surfactants [39], dually labeled Pickering-type stabilizers [40], and macro-RAFT diblock copolymers as sole stabilizers [41].

Although many solid particles have been used in Pickering stabilized (mini)emulsions, only very recently we have reported on "particles" (aggregates) which were formed as emulsion stabilizer in situ [42]. There, the aggregates of many different water-soluble dyes like sodium 2-hydroxy-5-[(E)-(4-nitrophenyl)diazenyl]benzoate (Alizarin Yellow R, AYR) can act as Pickering-like stabilizers for miniemulsions. In the present contribution we report on the use of such miniemulsions of ethenylbenzene (styrene, St) in water for polymerization with AYR as stabilizer. The influence of ultrasonication time and dye concentration on the diameter and size distribution of the droplets are discussed. The morphology of the initial droplets and final latex particles were investigated by electron microscopy. The polymerization kinetics is investigated and a nucleation mechanism is suggested.

2. Materials and methods

2.1. Materials

St (Merck, 99%) was purified by passing through an Al_2O_3-filled column and was kept in the refrigerator before use. Alizarin Yellow R (AYR, Merck), hexadecane (HD, TCI) and 2,2′-azobis[n-(2-carboxyethyl)-2-methylpropionamidine] n-hydrate (VA-057, 98%, Wako pure chemical industries Ltd.) were used as received. Milli-Q grade water was used in all processes.

2.2. St Pickering-like miniemulsion polymerization

AYR was dissolved in water (0.3, 0.5, 1.0, 1.5, 2.0 mg/mL (dye/water)) with a pH of 6.0. For the Pickering miniemulsion polymerization of St, a typical recipe was as follows: The oil phase was prepared by dissolving 80 mg of HD in 2.00 g of St and mixed with the water phase (8.00 g of AYR solution) by stirring for 3 min. Then, the crude emulsion was sonified by ultrasound for a certain time (Branson digital sonifier W450, 70% amplitude, ½″ tip) under ice cooling. After sonication and standing for a fixed time, 70 mg of VA-057 was added to the miniemulsion. Then the miniemulsion was transferred to a 20 mL screw cap bottle, which was flushed with argon. The closed bottle was placed in an oil bath, which was pre-heated to 70 °C and equipped with a magnetic stirrer. All polymerizations were continued for 180 min. The detailed recipe of the miniemulsions is given in Table 1.

2.3. Characterization

2.3.1. St conversion measurements

The conversion of St was calculated from the solid content (SC). The SC was determined with a Moisture Analyzer (Sartorius MA150).

Table 1
Formulation and stability of the miniemulsions stabilized by AYR.

run	AYR-dye concentration (mg/mL)	HD (mg)	Ultrasonication time (min)[a]	Dispersion stability
1	1.0	80	0.5	Yes
2	1.0	80	1	Yes
3	1.0	80	2	Yes
4	1.0	80	3	Yes
5	1.0	80	4	Yes
6	1.0	80	8	Yes
7	0.3	80	4	Yes
8	0.5	80	4	Yes
9	1.5	80	4	Yes
10	2.0	80	4	Yes
11	1.0	0	4	No
12	0.3	80	4	Yes

[a] standing time between sonication and polymerization was 0 for all samples except for runs 11 and 12 with 24 h.