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Influence of asymmetric ratio of amphiphilic diblock copolymers on one-step formation and stability of multiple emulsions

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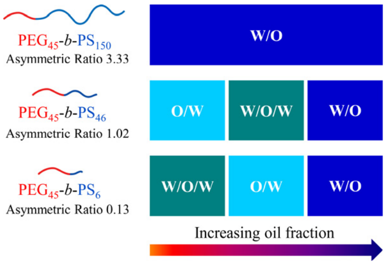
HIGHLIGHTS

- Multiple emulsions with long-term stability can be formed in one-step phase inversion process by using synthesized block copolymer as the stabilizer.
- The correlation between the nature of the block copolymer including the hydrophilic-to-hydrophobic segment ratio on multiple emulsion formation and stability has been examined.
- This study provides a valuable guidance toward the catastrophic phase inversion and the preparation of stable multiple emulsions using classical block copolymers as stabilizers.

GRAPHICAL ABSTRACT

The asymmetric ratio, namely the ratio of block length between PS and PEG of diblock copolymer, has a dramatic influence on the catastrophic phase inversion as well as the type and stability of the resulting emulsions.



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ABSTRACT

Multiple emulsions have attracted significant interests for fundamental study and practical applications. However, the preparation of stable multiple emulsions is difficult in general because the emulsification often involves a two-step process as well as two kinds of surfactants are needed to stabilize the two thermodynamically unstable interfaces. Recently, we described a one-step inversion approach for fabricating multiple emulsions with long-term stability by using a precisely defined amphiphilic copolymer, poly(ethylene glycol)-*b*-polystyrene (PEG-*b*-PS), as sole surfactant. Herein we examine the correlation of the nature of this block copolymer with its emulsification performance in more details. Our result shows that the asymmetric ratio, namely the ratio of block length between PS and PEG of the synthesized diblock copolymer, has a great influence on the catastrophic phase inversion as well as the type and stability of the resulting emulsions. The symmetric block copolymer with the asymmetric value close to 1 can lead to stable multiple emulsions because they might have the highest surface covering density not only at the oil-in-water (O/W) normal emulsion interface, but also at the water-in-oil (W/O) inverse emulsion interface. For highly asymmetric block copolymer like PEG_{45}-*b*-PS_{150}, only W/O emulsion is obtained as the longer PS block will increase the hydrophobicity of the polymer and then it will be preferentially wetted by oil. However, for asymmetric PEG_{45}-*b*-PS_{6} block copolymer with shorter PS block, it leads to very different catastrophic phase inversion depending on whether the micelles are formed in the aqueous phase.

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1. Introduction

Phase inversion in non-ionic surfactant-oil-water system from oil-in-water (O/W) to water-in-oil (W/O) emulsion or vice versa has been studied for many decades because it often occurs in food processing and many industrial applications [1–3]. Transitional inversion is induced by changing parameters such as temperature, pH and electrolyte concentration which affect the hydrophilic-lipophilic balance (HLB) of the system. While catastrophic inversion is typically induced by increasing the fraction of the dispersed phase and has the characteristics of a catastrophe, meaning a sudden change in behavior of the system as a result of the inversion between the dispersed phase and the continuous phase. Brooks and Richmond were the first to develop a mapping procedure linking the phase inversion boundaries with non-ionic surfactant-oil-water phase behavior, instead of classical three-component systems on triangular diagrams [3]. Generally, the dynamic emulsion inversion is quite dependent on the experimental protocols [4–6].

Catastrophic inversion method is important in many industrial processes, particularly when the oil phase is viscous [7], and the conventional stirring process is quite inefficient in creating small droplets [8–10]. In addition, an evolution through the formation of multiple emulsions is often detected in the abnormal-to-normal inversion path [11–13]. However, the produced multiple emulsions of both the water-in-oil-in-water (W/O/W) and the oil-in-water-in-oil (O/W/O) before the catastrophic inversion are often termed as temporary or abnormal emulsions because they are extremely unstable. It has been stated that the intervening film between the colliding abnormal emulsion drops behaves as if surfactant is absent [14,15]. Only recently, some reports have shown that stable multiple emulsions can be produced with surfactant blends as a result of the simultaneous occurrence of catastrophic and transitional phase inversions, but the stability of these emulsions is limited due to rapid surfactant migration between the phases [15–18]. Multiple emulsions of both the W/O/W and the O/W/O have potential applications in various fields, including pharmaceutics, cosmetics, and food industries [19]. In addition, they are widely used as templates for the preparation of microcapsules to carry both polar and non-polar cargos for improved synergistic delivery [20–23], or as microreactors for chemical reactions [24]. These promising applications, however, have so far been impeded by the difficulties in making stable simple formulations.

The emulsion type is usually determined by the nature of the used surfactants [8]. The most studied surfactants involved in catastrophic inversion are small molecules or solid particles [25–27]. Hanson et al. are the first to obtain long-term stability W/O/W multiple emulsions in a one-step process by using single-component, synthetic amphiphilic diblock copolypeptide surfactants with polydimethylsiloxane as oil phase [28]. Then, Guenoun et al. showed responsive multiple emulsions prepared in a catastrophic inversion processing using a responsive diblock copolymer and demonstrated the encapsulation and release of active molecules at will by both temperature and pH triggers [29].

Recently, we report a one-step phase inversion process to produce W/O/W multiple emulsions stabilized solely by a synthetic diblock copolymer, poly(ethylene glycol)-*b*-polystyrene (PEG-*b*-PS). The prepared multiple emulsions are very stable and exhibit no significant structural change during a storage period of six months. This remarkable stability stems from the fact that our synthesized block copolymers are effectively adsorbed at the interfaces with the lipophilic PS blocks extended on the oil side, and the hydrophilic PEG block extended on the water side, allowing the efficient emulsion stabilization through the steric repulsion mechanism. In addition, we demonstrate that they could be a versatile platform for precise encapsulation of incompatible actives [30]. In the present study, we examine the correlation of the nature of block copolymers with their emulsification performance in more details. In particular, the following effects of asymmetric ratio of PEG-*b*-PS diblock copolymer on multiple emulsion formation, morphology and kinetic stability are investigated. Our results show that the asymmetric ratio of the diblock copolymer has a dramatic influence on the catastrophic phase inversion and the stability of the resulting emulsions. In this paper, the details of the experiments and the analysis of the obtained emulsions will be discussed.

2. Experiments

2.1. Materials

2-Bromoisobutyryl bromide (98%, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine (99%, Aldrich, PMDETA), *p*-toluenesulfonyl chloride (>99%, Sigma–Aldrich), pyrene (>99%, Sigma–Aldrich), and toluene (99%, Sigma) were used as received. Copper (I) bromide (98%, Aldrich) was purified with glacial acetic acid and washed with absolute ethanol, then vacuum dried and stored under argon [31]. Triethylamine (Fisher Scientific, AR) was refluxed with *p*-toluenesulfonyl chloride for 12 h before distilled over CaH_2. Styrene (>99%, 10–15 ppm 4-*tert*-butylcatechol inhibitor, Sigma–Aldrich) was dried over finely grounded CaH_2 for 1 day and then fractionally distilled. Poly(ethylene glycol) monomethyl ether (Fluka, AR, MPEG-OH, $M_n = 2000$ g/mol) was dissolved in tetrahydrofuran (THF) and precipitated in diethyl ether to obtain polymer powder before it was vacuum dried. THF was distilled over sodium benzophenone ketyl.

2.2. Synthesis of PEG-b-PS diblock copolymers

The block copolymers, poly(ethylene glycol)-*b*-polystyrene (PEG-*b*-PS), with varying asymmetric ratios (e.g., length ratios of PS block to PEG block) used to control the formation of emulsions were synthesized by atom-transfer radical polymerization (ATRP) using α-(2-bromoisobutyrylate)-ω-methyl PEG-2000 as macroinitiator [32]. α-(2-bromoisobutyrylate)-ω-methyl PEG-2000 macroinitiator was synthesized following the literature method [33]. The polymers were subsequently dried and analyzed by ^{1}H NMR and size exclusion chromatography (SEC). The asymmetric ratio in the synthesized PEG_m-*b*-PS_n diblock copolymers was determined by ^{1}H NMR from the ratio of methylene group of the PEG block and aromatic group of the PS block. Table 1 summarizes the characteristics of the three synthesized block copolymers used in this study.

2.3. Emulsion preparation and characterization

The emulsions stabilized by the diblock copolymers with varying asymmetric ratios were prepared by homogenizing a specific internal fraction of toluene and D.I. water using an Ultra Turrax T10 homogenizer (10 mm head) operating at 13,500 rpm for 2 min. The total emulsion volume was kept as 4 mL for all samples. The copolymers were dissolved in toluene before emulsification and trace amount of fluorescent dye was added for confocal imaging. The oil phase was labeled by perylene. 408 nm laser was used to excite the fluorescent molecules. An oil immersion objective (60×, NA = 1.49) was used to view the samples. The emulsions were placed on the cover slides and a series of *x*/*y* layers were scanned.

2.4. Interfacial tension measurement

Interfacial tension was measured by Dataphysics OCA20LHT-TEC700-HTFC1500 using a pendant drop method. D.I. water was loaded into a syringe and injected into an optical quartz cuvette