

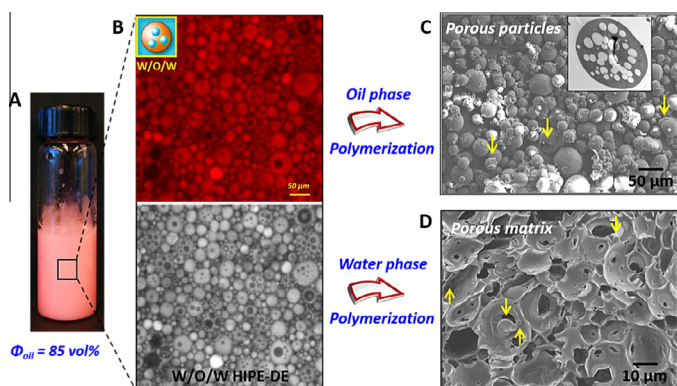


Regular Article

High internal phase emulsion with double emulsion morphology and their templated porous polymer systems

Lei Lei^a, Qi Zhang^b, Shuxian Shi^{c,*}, Shiping Zhu^{a,*}^aDepartment of Chemical Engineering, McMaster University, Hamilton L8S 4L7, Canada^bCollege of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China^cKey Laboratory of Carbon Fiber and Functional Polymers (Ministry of Education), Beijing University of Chemical Technology, Beijing 100029, China

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports synthesis of the first high internal phase emulsion (HIPE) system with double emulsion (DE) morphology (HIPE-DE). HIPE is a highly concentrated but highly stable emulsion system, which has a dispersed/internal phase fraction over 74 vol%. DE represents an emulsion system that hierarchically encapsulates two immiscible phases. The combination of HIPE and DE provides an efficient method for fabrication of complex structures. In this work, HIPE-DE having a water-in-oil-in-water (W/O/W) morphology has been prepared for the first time via a simple one-step emulsification method with poly(2-(diethylamino)ethyl methacrylate) (PDEA) microgel particles as Pickering stabilizer. An oil phase fraction up to 90 vol% was achieved by optimizing the microgel concentration in aqueous phase. The mechanism of the DE formation has been elucidated. It was found that while PDEA microgels stabilized the oil droplets in water, small amount protonated DEA monomers acted as surfactant and formed water-containing micelles inside the oil droplets. It was demonstrated that the W/O/W HIPE-DE could be precisely converted into porous polymer structures. With styrene as the oil phase in W/O/W HIPE-DE, porous polystyrene particles were obtained upon polymerization. With dissolved acrylamide as the aqueous phase and toluene as the continuous phase, porous polyacrylamide matrixes were prepared. Elevating temperature required for polymerization did not change the W/O/W HIPE-DE morphologies. This simple approach provides a versatile platform for synthesis of a variety of porous polymer systems.

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* Corresponding authors.

E-mail addresses: shisx@mail.buct.edu.cn (S. Shi), zhuship@mcmaster.ca (S. Zhu).

1. Introduction

A high internal phase emulsion (HIPE) is also known as “gel emulsion”. It is defined as an emulsion system, which contains more than 74 vol% internal/dispersed phase [1,2]. The densely packed emulsion droplets are very stable in the system. HIPE has applications in food processing, cosmetic, pharmaceutical, and petroleum industries [3–5]. The two HIPE types reported so far, either water-in-oil (W/O) or oil-in-water (O/W), can be used as template for fabrication of highly porous polymeric scaffolds in tissue engineering and for preparation of filtration membranes by adding polymerizable monomers into the continuous phase [6–8]. Both molecular and particulate surfactants (Pickering emulsion) can be employed to stabilize HIPEs. Particulate stabilizers such as colloid particles possess many advantages over conventional molecular surfactants. First, colloid particles used in Pickering emulsion can be irreversibly adsorbed onto oil-water interface due to a high level of attachment energy, resulting in stable emulsion having shelf life over months or even years [9]. Second, the size, structure, chemical composition and hydrophilicity of colloid particles can be easily pre-designed and controlled, which is important in the preparation of Pickering emulsions [10]. Furthermore, numerous functional groups can be introduced into particle surface, which provides a versatile platform for fabrication of stimuli-responsive Pickering emulsions and functionalization of the resulting materials [11–14].

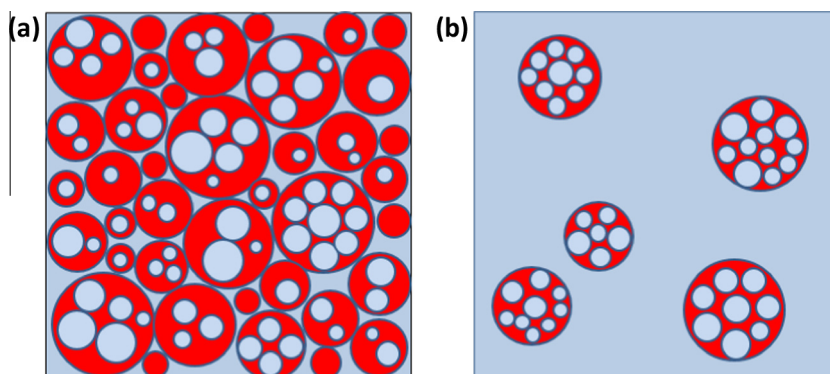
An emulsion system often suffers from catastrophic phase inversion with excessive increase in its internal phase volume fraction. Higher fraction of the internal phase has always been an objective in HIPE research [15,16]. Recently, HIPE systems having an internal phase higher than 90% have been reported by using inorganic titania or silica particle as Pickering stabilizer, while hydrophilicity of the particles must be modified prior to their use [17,18]. Organic microgels have also been used to stabilize HIPE systems. For example, Ngai et al. [16] prepared hexane-in-water (O/W) Pickering emulsion with an inner phase fraction up to 90% using poly(*N*-isopropylamide-co-methacrylic acid) (P(NIPAM-co-MAA)) microgels as the stabilizer. The HIPE was directly used as a template for preparation of porous microgel membranes by evaporating both the oil and water phases. The pore size and membrane porosity could be regulated by microgel concentration in the original Pickering emulsion.

On the other side, double emulsion (DE) represents a novel class of emulsion morphologies. It is a hierarchical multiphasic emulsion system, in which dispersed droplets of one liquid phase contain smaller droplets of another phase [19]. This fascinating and unique morphology can be of particularly useful as template for preparation of porous materials [16], fabrication of multi-compartment structures [20], and cargos for delivery of sensitive drugs [4,21].

Unfortunately, double emulsion systems are considered to be thermodynamically unstable due to flocculation, coalescence, Ostwald ripening, etc. [22]. Double emulsions are usually prepared through two-step procedures using two distinct surfactants (lipophilic and hydrophilic). For instance, a W/O emulsion is prepared first and it is then dispersed into an aqueous continuous phase to prepare the W/O/W double emulsion [23]. This approach is cumbersome and the second step emulsification may disrupt the prior emulsion droplets. Simplifying multicomponent encapsulation is of priority in the double emulsion study and one-step emulsification is most desirable.

Recently, double emulsion (DE) systems have been developed from one-step emulsification. Wang et al. reported several double emulsion systems and their corresponding resulted porous particles [24–26]. For example, polylactic acid (PLA) microspheres having interconnected chambers were generated based on a water-in-oil-in-water (W/O/W) double emulsion with 16.7 vol% oil phase fraction. The double emulsion was prepared from an oil-in-water emulsion, which consisted of polylactic acid (PLA)-containing dispersed dichloromethane phase and cetyltrimethyl ammonium bromide (CTAB)-containing continuous water phase. It was proposed that electrostatic interactions between PLA (it has carboxylic acid moiety on one chain end and hydroxyl group on the other) and CTAB (it is a cationic surfactant) led to an influx of water from the external aqueous phase to pass through the oil-water interface, thus forming small water droplets within the large oil droplets [24]. Hayward et al. [20] reported another W/O/W double emulsion (also 16.7 vol% oil phase fraction) stabilized by amphiphilic block copolymer of polystyrene-*block*-poly(*N*-isopropylacrylamide) (PS-*b*-PNIPAM). Within the primary oil droplets, salt species derived from the block copolymer formed aggregates, osmotically driving water transfer from the continuous water phase into the dispersed oil droplets and form inner water droplets, thus resulting in a W/O/W double emulsion system. Particulate stabilizers have also been employed for preparation of Pickering double emulsion systems. Lee et al. [19] reported one-step formation of W/O/W double emulsion stabilized by amphiphilic Janus particles, with styrene and acrylic acid as the respective apolar and polar regions. This double emulsion could be destabilized to release encapsulant by simply increasing pH of the continuous phase.

The combination of high internal phase emulsion (HIPE) and double emulsion (DE) is expected to result in, either HIPE constituted of DE (HIPE-DE) or DE constituted of HIPE (DE-HIPE), which may provide a powerful approach for fabrication of complex structures. As schematically illustrated in Scheme 1b. Liu et al. [27] reported a good example of DE constituted of HIPE, in which a W/O/W double emulsion was prepared via catastrophic phase



Scheme 1. Schematic illustration of (a) high internal phase emulsion constituted of double emulsion (HIPE-DE) and (b) double emulsion constituted of high internal phase emulsion (DE-HIPE).

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