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Synthesis of degradable polyHIPEs by AGET ATRP

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ABSTRACT

Conditions to synthesize a degradable polymerized high internal phase emulsion (PolyHIPE) by a controlled radical polymerization (CRP) method, atom transfer radical polymerization (ATRP), have been developed for the first time. Activators generated by electron transfer (AGET) ATRP were used to copolymerize 2-ethylhexyl methacrylate (EHMA) and bis(2-methacryloyloxyethyl) disulfide (DSDMA), a degradable cross-linker, in a HIPE system without the removal of oxygen. These conditions provided control over the polymerization and resulted in a fully degradable material. The degradation product had molecular weight $M_n = 30{,}500$, and relatively low dispersity, $M_w/M_n = 1.6$, indicating that a uniform cross-linked network was formed. Superior control over the polymerization resulted from the selection of a highly hydrophobic ATRP catalyst, $CuBr_2$ with an N,N-bis(2-pyridylmethyl)octadecylamine (BPMODA) ligand, which is preferentially located in the organic phase. Alternate conditions with a less hydrophobic catalyst, $CuBr_2$ with a 2,2′-bipyridine (bpy) ligand, result in a non-degradable polyHIPE. The $CuBr_2$/bpy catalyst predominately partitions into the aqueous phase where it exerts little control over the polymerization. The polyHIPE synthesized using a $CuBr_2$/BPMODA catalyst also exhibited a higher Young's modulus and was stiffer, due to its more uniform cross-linked network, than materials from almost identical HIPEs synthesized using a $CuBr_2$/bpy catalyst.

1. Introduction

High internal phase emulsions (HIPEs) are generally highly viscous emulsions with an internal phase from 74 vol. % up to 99 vol. % [1–3]. They are typically water in oil (w/o) emulsions, but there are also reports of oil in water (o/w) HIPEs in the literature [1–3]. HIPEs were originally reported in the 1960's and have been utilized in the cosmetic and food industries [2]. HIPEs have also been investigated because they provide a simple method for templating porous polymers [1]. Polymerized HIPEs (polyHIPEs) have macropores (voids) that are interconnected by smaller windows and pores, which lead to high porosities, up to 99%, and low densities, typically 0.10–0.15 g/cm^3 [1,4].

Due to their high porosities and low densities, polyHIPE materials have been used as materials for water and gas separation [2], carbon dioxide capture [5], catalyst support [6,7], tissue engineering scaffolds [8–13], and fire proof materials [14]. They can be functionalized in many ways [2], including grafting new polymer onto [7] or from Refs. [15,16] their surface, which broadens their utility and applications. Despite the many applications of polyHIPE materials, they suffer from low mechanical strength, and are generally not degradable. These drawbacks stem from the synthesis of polyHIPEs by conventional radical polymerization (RP) of a monomer and cross-linker in the external phase of a HIPE and limit the scope of polyHIPEs in commercial applications.

In RP cross-linking occurs at low monomer conversion even if polymer chains are highly diluted [17,18]. A large amount of intramolecular cross-linking leads to densely cross-linked domains, or microgels, formed early in the reaction [18,19]. At higher conversion these microgels are incorporated into the final network and a heterogeneous network is produced. Networks synthesized by RP have limited swelling properties and are poorly degradable due to the densely cross-linked domains and non-uniform network [17,20,21].

With the introduction of controlled radical polymerization (CPR) methods [22], such as atom transfer radical polymerization (ATRP) [23–28], more uniform cross-linked networks were synthesized [17,18,20,21]. A high concentration of polymer chains is formed early in a CRP reaction, due to fast initiation and the number of pendant cross-linkable units per chain is low. Therefore, microgel formation at low conversion is avoided and a more

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uniform network is formed under CRP conditions. Networks synthesized by CRP methods have shown superior swelling properties and a larger elastic modulus than polymer networks synthesized by RP [17,20]. Nanogels with a uniform cross-linked network were synthesized, using ATRP in inverse miniemulsion. These nanogels contained a disulfide cross-linker and were fully degradable after addition of tributylphosphine, Bu_3P, unlike similar nanogels synthesized by RP [20].

The mechanical strength of polyHIPE materials prepared by CRP methods is improved, due to the creation of a uniform network. For example when RAFT polymerization was used to copolymerize styrene and divinylbenzene by adding a RAFT agent to typical RP under HIPE conditions, the mechanical properties of the resulting polyHIPE were significantly improved [29]. The Young's modulus and crush strength both increased three-fold in comparison with the polyHIPE produced by RP, while the characteristic polyHIPE morphology was retained [29].

ATRP is a powerful and robust CRP method [23,24] that has been successfully conducted in different dispersed media, including emulsion, miniemulsion, microemulsion, dispersion, and suspension polymerizations [30]. Currently, the AGET (activators generated by electron transfer) ATRP technique is often applied to dispersed media. This procedure allows the copper catalyst to be introduced in the Cu^{II}/ligand form, which is oxidatively stable, and then reduced to the active Cu^{I}/ligand form by a reducing agent [23,30,31]. Not only can polymers with controlled molecular weights and low dispersities be synthesized by ATRP in different dispersed media, but complex architectures, such as block copolymers, star polymers, or brush polymers, can also be prepared [32,33].

AGET ATRP was previously used to synthesize polyHIPE materials [34]. 2-Ethylhexyl acrylate and divinylbenzene were copolymerized by AGET ATRP in a HIPE using $CuBr_2$ with 2,2′-bipyridine (bpy) ligand as the ATRP catalyst and ascorbic acid as the reducing agent. The primary focus of that report was to determine the type and locus of initiation under different initiating conditions, rather than development of a well-controlled AGET ATRP in a HIPE system. Despite this, it was possible to form a stable HIPE and polymerize it by AGET ATRP. The resulting polyHIPE was obtained in high yield (>90%) with void sizes between 6 and 15 μm. These results indicated that AGET ATRP could be successfully used to polymerize HIPEs.

Herein, we report the development of new AGET ATRP conditions to polymerize w/o (water in oil) HIPEs. The selection of an appropriate ATRP catalyst, the hydrophobic $CuBr_2$/BPMODA complex in this case, is crucial to obtain a well-controlled reaction and a high yield of a polyHIPE with a fully degradable structure. When alternate conditions, with a less hydrophobic catalyst ($CuBr_2$/bpy) were used, the material could not be fully degraded. Furthermore, compression testing demonstrated that the material prepared using the $CuBr_2$/bpy catalyst had a lower stiffness and yield strength than the fully degradable material synthesized using the $CuBr_2$/BPMODA catalyst.

2. Experimental section

2.1. Materials

2-Ethylhexyl methacrylate (EHMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Aldrich. Both monomer and cross-linker were passed through a basic alumina column to remove inhibitor before use. EGDMA is a non-degradable cross-linker and will be termed "CC" to reflect the carbon–carbon bonds it contributes to the polymer backbone. Bis(2-methacryloyloxyethyl) disulfide (DSDMA) [35] and N,N-bis(2-pyridylmethyl) octadecylamine (BPMODA) [36] were synthesized by previously reported procedures. DSDMA is a degradable cross-linker and will be termed "SS" to reflect the sulfur–sulfur bond it contributes to the polymer backbone. All other reagents: ethyl 2-bromoisobutyrate (EBiB), Span-80, $CuBr_2$, 2,2′-bipyridine (bpy), ascorbic acid, tetrabutylammonium bromide (TBABr), tributylphosphine (Bu_3P) and solvents, were purchased from Aldrich and used as received.

2.2. Synthesis of polyHIPEs

2.2.1. CC-BPMODA and SS-BPMODA synthesis (Table 1)

A non-degradable cross-linker (CC) and the BPMODA ligand were used in the preparation of CC-BOMODA. A degradable disulfide cross-linker (SS) and the BPMODA ligand were used in the preparation of SS-BPMODA. $CuBr_2$ was complexed with BPMODA and dissolved in the monomer at 60 °C over 1.5 h. The mixture was cooled to room temperature and surfactant (Span-80), cross-linker, and initiator (EBiB) were added. An aqueous solution of ascorbic acid and TBABr was prepared. The aqueous phase was added drop-wise to the organic phase with overhead stirring (200–300 rpm), while being chilled by an ice bath to minimize polymerization during HIPE formation. After the HIPE was formed, the same amount of a second ascorbic acid solution, identical in concentration to the solution used to form the HIPE, but not containing TBABr, was added on top of the HIPE to minimize its contact with air. The HIPE was placed in an oven for 48 h at 60 °C. The polyHIPE was removed from the oven and Soxhlet extraction was performed using deionized water for 24 h followed by methanol for an additional 24 h. The polyHIPE was dried in a fume hood until constant weight was observed.

2.2.2. SS-bpy synthesis (Table 1)

A degradable disulfide cross-linker (SS) and the bpy ligand were used to prepare SS-bpy. This polyHIPE synthesis was similar to a previously reported method [34]. Briefly, the $CuBr_2$/bpy catalyst was complexed and dissolved in a small amount of water. It was added to the organic phase with monomer, cross-linker, Span-80, and EBiB, to minimize its contact with ascorbic acid in the aqueous phase. Two identical ascorbic acid solutions were made. One solution was added to the organic phase drop-wise while overhead stirring (200–300 rpm) was applied to form a HIPE. The HIPE was kept on an ice bath throughout formation to minimize polymerization. After the HIPE was formed, the same amount of a second ascorbic acid solution, identical in concentration to the solution used to form the HIPE, was added on top of the HIPE, to reduce its contact with air. It was polymerized for 48 h at 60 °C in an oven.

Table 1
Conditions for polyHIPE synthesis using EGDMA cross-linker and BPMODA ligand for CC-BPMODA, DSDMA cross-linker and BPMODA ligand for SS-BPMODA, and DSDMA cross-linker and bpy ligand for SS-bpy.

Reagents	CC-BPMODA (wt%)	SS-BPMODA (wt%)	SS-bpy (wt%)
Organic phase			
EHMA	11.43	11.40	10.99
Cross-linker	3.42	3.71	3.56
Ligand	0.18	0.18	0.04
$CuBr_2$	0.06	0.06	0.06
EBiB	0.20	0.20	0.19
Span-80	4.00	4.00	3.87
Water	0	0	3.87[a]
Aqueous phase			
Water	80.49	80.23	77.36
Ascorbic acid	0.06	0.06	0.06
TBABr	0.16	0.16	0

[a] The catalyst was dissolved in a small amount of water and then added to the organic phase.