Research Article

Silvia T. Huerta-Marcial and Josué D. Mota-Morales*

Tailoring the morphology of poly(high internal phase emulsions) synthesized by using deep eutectic solvents

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Abstract: High internal phase emulsions (HIPEs) are among complex biphasic fluids that expand on the traditional emulsion compositions, for instance, for the preparation of macroporous polymers by emulsion templating. The use of deep eutectic solvents (DESs) as the nonaqueous internal phase of HIPEs allows expanding the conditions at which polymerizations are typically carried out in aqueous HIPEs. Herein, the properties of polystyrene macroporous polymers were studied by polymerizing DES-in-oil HIPEs using choline chloride-based DESs as the internal phase. The effect of DESs' composition – with amide, alcohol, and carboxylic acid as hydrogen bond donors – and the homogenization method used for the HIPE preparation – vortexing versus high-speed homogenizer – was studied. The stability and droplet size of HIPE precursor, as well as the macroporous structure and the mechanical properties of the synthesized polyHIPEs, are discussed.

Keywords: HIPE, polyHIPE, DES, StDVB, choline chloride

1 Introduction

Porous polymers are a unique class of materials worth for their high porosities, lightweight, low densities, and high specific surface area. Some conventional methods used to produce porous polymers include foaming (1,2), the use of super critical fluids (3,4), thermally induced phased separation (5,6), and emulsion templating (7–11).

Among these methods, emulsion templating provides a versatile alternative for producing interconnected macroporous polymers. The method consists of polymerizing the continuous phase surrounding the internal one followed by the extraction of the dispersed phase, which results in a replica of the droplets in the emulsion precursor. The resulting foam materials have cavities of the diameter of the emulsion droplets with smaller interconnecting pore voids, thus creating an open porous morphology (12). For these porous materials, characteristic pore size ranges from a few nanometers to hundreds of micrometers depending on the nature of the colloidal system employed (emulsions, microemulsions, or solid particles) (13). Considering that the emulsion takes the shape of its container, it is possible to obtain different forms of these materials, e.g., films, monoliths, beads, and rods. Porous polymers are used in a wide variety of applications (13) in the fields of supported catalysis (14), tissue engineering (15–17), chromatography (7,18), microfluidics, water purification (10,19), etc.

High internal phase emulsions (HIPEs) are particularly interesting for the synthesis of interconnected porous polymers because the droplets that constitute the emulsion are in the range of micrometers (20). At the same time, small voids and texture in the inner surface can be introduced during polymerization to yield hierarchical materials. HIPEs are highly viscous emulsions containing more than 74% volume fraction of dispersed phase within a minor continuous phase (21) and are typically stabilized by the addition of surfactants. Above this critical value, polyhedral arrangements are observed because spherical droplets exceed their physical packing limit and deform (22). The polymerization of HIPEs can be carried out by using a variety of polymerization mechanisms to solidify the continuous phase. Subsequent extraction of the internal phase results in an interconnected porous scaffold, namely a polyHIPE (7–9,23–26).

The typical synthetic routes used to produce macroporous polymers via HIPEs require the use of aqueous solutions as one of the phases (either dispersed or

* **Corresponding author: Josué D. Mota-Morales**, Departamento de Nanotecnología, Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Querétaro, QRO 76230, Mexico, e-mail: jmota@fata.unam.mx, mota_josue@hotmail.com
Silvia T. Huerta-Marcial: Departamento de Nanotecnología, Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Querétaro, QRO 76230, Mexico

continuous) in the emulsions. Water-in-oil (w/o) HIPEs are the most common type, which consist of an aqueous electrolyte solution as the internal phase, dispersed in a continuous phase containing the monomer and cross-linker, initiator, and emulsifier. The emulsifier can be surfactants (7,9,10,14), particles (27), or a combination of both (15). For example, Wong et al. (23) prepared highly interconnected porous materials by polymerizing HIPEs. The emulsions consisted of styrene (St)/divinylbenzene (DVB) stabilized by the Hypermer 2296 surfactant in an aqueous internal phase (80 vol%) containing calcium chloride dihydrate. They found that hierarchical poly-HIPE can be obtained by varying the surfactant concentration.

On the other hand, the growing environmental awareness has led to the search for greener solvents that help reduce the dependency on organic solvents for polymer production. In this regard, several solvents featuring green characteristic have emerged over the last decade; for instance, ionic liquids (ILs), low-transition temperature mixtures, biomass-derived renewable solvents, among others, each suitable for specific applications. In this context, deep eutectic solvents (DESs) have emerged as an alternative to common solvents due to their easy preparation and compositional plasticity (28–31). The term deep eutectic solvent (DES) was first reported by Abbott et al. (28) to describe a eutectic mixture of two or more components that is possible through hydrogen bond interactions between hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). These mixtures exhibit melting point lower than that of the individual component (28,29). DESs have shown similar physicochemical properties to traditional ILs. Examples include high chemical and thermal inertness, low volatility, nonflammability, and the ability to dissolve a wide range of solutes (26). Unlike their IL parents, where the composition is rigorously restricted to electro-neutrality cation–anion and all their components are charged, DES properties can be customized not only by changing the nature of their HBA and HBD components but also by adjusting their molar ratio close to the eutectic point (32–35). Due to this set of characteristics, DESs are currently used in multiple applications beyond solvents and can be considered by themselves as a versatile and new class of functional materials.

For instance, in the specific case of polymerizations, DESs can play the role of both solvents and monomers, expanding the conditions at which polymerizations are normally carried out in both water and organic solvents. DES functioning as an inert solvent, i.e., being the media

where the reaction takes place without participating in the polymerization, has served for both heterogeneous and homogeneous polymerizations (36). In the case of heterogeneous polymerizations, Mota-Morales et al. demonstrated in a seminal report, the viability of choline chloride (ChCl)/urea (U) DES to produce nonaqueous HIPEs. For this, DESs were mixed with methyl methacrylate (MMA), lauryl acrylate, and stearyl methacrylate, with the aid of glycol dipolyhydroxystearate ABA triblock copolymer (cithrol) as a surfactant and the crosslinkers, ethylene glycol dimethacrylate (EGDMA) if methacrylates or 1,4-butanediol diacrylate if acrylates (24,37). They found that the MMA monomer supplies the most attracting features, producing polyHIPEs with thermal stability (above 220°C), high degree of porosity, and consistent droplet diameter to pore diameter (6–16 μm).

Pérez-García et al. further demonstrated the validity of the DES-in-oil HIPE approach for the synthesis of polyHIPEs made of St and crosslinked with DVB stabilized with the nonionic surfactant Span 60 (sorbitan stearate) upon free-radical polymerization. The enhanced stability of the HIPEs, even under vacuum, was ascribed to several factors, being the high viscosity of the DES and a salting out effect of DES on the surfactant critical micellar concentration, the most important. Droplet size did not change significantly during polymerization, and the structure of the monoliths produced was an approximate replica of the precursor emulsion.

From the fundamental viewpoint, DESs allow studying the effect of nonaqueous polar internal phases of increased viscosity, along with the well-established parameters for HIPE stability that include internal phase volume fraction, surfactant concentration, phase polarity, interfacial tension, and temperature. Furthermore, DESs can provide an enhanced polymerization environment within the HIPEs for the creation of hierarchically porous polymers in a sustainable manner.

Based on the work of Pérez-García et al. (25), in this work, polystyrene macroporous polymers were studied by polymerizing DES-in-oil HIPEs using ChCl-based DESs as the internal phase. Four different HBDs were used to prepare DESs, with functional groups such as amides (U), trifunctional alcohol (glycerol, Gly) and diol (ethylene glycol, EGly), and carboxylic acid (oxalic acid). Oxalic acid dihydrate–choline chloride (OAc–ChCl) DES represents a new internal phase for nonaqueous styrenic HIPEs. The effect of both DESs' composition and the homogenization method used for HIPE preparation on their stability and droplet size and the porous structure and the mechanical properties of the synthesized

polyHIPEs is discussed. Finally, it is corroborated that due to their high viscosity and polarity, DESs stand as an attractive alternative class of internal phase for the nonaqueous synthesis of styrenic macroporous polymers.

2 Materials and methods

St 99%, DVB of technical grade 80%, 2,2'-azobis(2-methylpropionitrile) (AIBN) 97%, U 98%, ChCl 98%, Gly 99.5%, EGly 99.8%, oxalic acid dihydrate (OAc) 99%, and Span 60 (sorbitan stearate) were purchased from Sigma-Aldrich. ChCl was oven-dried at 90°C for 12 h to remove all moisture in the salt. The rest of the reagents were used as received without any further purification.

The continuous phase (20 vol%) was prepared by dissolving 1.0 wt% AIBN (thermal initiator) with respect to the total amount of monomers and surfactant mixture. The composition of the monomers was 10:1 molar ratio of St/DVB, respectively. The concentration of surfactant Span 60 (emulsifier) used was 20 wt% with respect to the total amount of monomers. The internal nonaqueous DES phase (80 vol%) was prepared by mixing ChCl separately with U, Gly, EGly (in a 1:2 molar ratio), or OAc (in a 1:1 molar ratio) and heated at 60°C until a clear-viscous-homogeneous liquid was obtained. HIPEs were prepared by mixing both phases in a 16 mL borosilicate glass vial and homogenized with a high-speed homogenizer in two different ways: (1) using an IKA T10 basic Ultra-Turrax® (provided with a 5 mm extension arm diameter) at 11,000 rpm for 1.5 min followed by vortexing at 3,200 rpm for 0.5 min or (2) using an IKA T18 digital Ultra-Turrax® (10 mm extension arm diameter) at 11,000 rpm for 1.5 min. All the obtained HIPEs were labeled using the acronym HIPE followed by the HBD in the DES and the number of the homogenizer used. The obtained HIPEs with different internal phases were polymerized in an oven at 60°C for 24 h. After polymerization was completed, the internal phase and surfactant were removed by Soxhlet extraction with ethanol for 16 h. The resulting monoliths were dried at room temperature until constant weight was reached. Dried monolith conversion was determined gravimetrically. PolyHIPEs were labeled according to their precursor emulsion replacing HIPE acronym by polyHIPE.

The microstructures of DES-based emulsions were studied using confocal microscopy (Laser Scanning Zeiss LSM880/Axion Observer 7). The monomer phase was marked with rhodamine B (Sigma-Aldrich) as a fluorescent marker to determine the droplet size. The morphologies of

all polyHIPE monoliths were investigated by scanning electron microscopy (SEM; JEOL JSM-6060 LV) with an accelerating voltage of 15 kV. Samples were platinum coated for 240 s in an inert argon atmosphere at 1×10^{-2} mbar (Sputter Coater EMS 550). The average droplet size, pore, and pore window diameters were calculated in sets of 100 using Image J analysis software.

The monoliths' mechanical properties were evaluated according to ASTM D 1621 using a testing machine Zwick/Roell Z005 model equipped with a 5 kN load cell at 2 mm min^{-1} compression rate. Samples were measured in triplicates by compressing to 75% of their initial height and their elastic modulus was determined from the initial linear slope obtained from the stress-strain plot. The stress at yield was recorded to show the compression strength of monoliths.

3 Results and discussion

3.1 Stability and droplet size characterization of DES-in-oil HIPEs

The stability and droplet size of HIPEs are governed by several parameters including internal phase volume fraction, the surfactant nature and its concentration, phase polarity, interfacial tension, and temperature (7,8,23).

In this study St-based HIPEs were prepared, in which the similarity of chemical structures of the monomer St and the crosslinker DVB that formed the continuous phase gives rise to polyHIPEs with homogeneous physical properties, e.g., without segregation of polymers. The HIPEs were stabilized through addition of Span 60 nonionic surfactant that has a hydrophilic/lipophilic balance (HLB) of 4.7 and corresponds to low HLB value (between 2 and 6) (26). The surfactant concentration used was chosen according to the previous results obtained by Pérez-García et al. (25), in which the optimal concentration to enhance the stability of St/DVB/surfactant/DES HIPEs was 20 wt%.

In HIPE systems, in general, it is well established that coalescence and Ostwald ripening mechanisms are characterized by an increase in droplet size of the emulsions that can disrupt the drop stability (38,39). However, through surfactant addition, effective electrostatic repulsion can be established to prevent coalescence and Ostwald ripening which are driven by dispersed phase diffusion. Additionally, these phenomena can be prevented by the inclusion of a highly viscous internal phase (40).

The high viscosity of the internal phase reduces drastically the Ostwald ripening effect, therefore preventing the collapse of the continuous phase's thin walls and the HIPEs from breaking.

Herein, four HBDs with different functional groups, namely, amide (U), trifunctional alcohol (Gly), diol (EGly), and carboxylic acid (OAc), were chosen to prepare the dispersed phase by mixing them with ChCl in different molar ratios. The stability and droplet size of the HIPEs and the pore size and mechanical properties of the resulting polyHIPEs were then evaluated. It is important to mention that previous investigations reported the preparation of DES-in-oil HIPEs by mixing both phases by vortexing. To provide a more general protocol for the preparation of HIPE, in this work, HIPEs were prepared by mixing both phases with high-speed homogenizers, IKA T10 basic Ultra-Turrax® and IKA T18 digital Ultra-Turrax®, both at 11,000 rpm. The impact of the preparation method, vortexing only versus homogenizer, on the stability and droplet size of the prepared HIPEs, in addition to the morphology and the mechanical properties of the synthesized polyHIPEs, is described subsequently.

The obtained HIPEs had a white aspect, presented a high apparent viscosity in the order of HIPE-U > HIPE-Gly > HIPE-OAc > HIPE-EGly, that is, in agreement with the viscosity reported for the corresponding DES (750, 259, 126,¹ 37 cP, 25°C, respectively, (41)). Visual observation of HIPEs showed that emulsions prepared with DESs with a viscosity greater than 200 cP (HIPE-U10, U18, Gly10, and Gly18) did not show phase separation in a period of 3 days at room temperature. On the other hand, for emulsions prepared with a viscosity below 150 cP (HIPE-OAc10, OAc18, EGly10, and EGly18) the phase separation was observed in a period greater than 12 h at RT. These results are comparable to the previous ones using vortex stirring as the mechanical source for emulsion preparation (25). A summary of these results is shown in Table 1.

Carranza et al. (24) were the first to propose that the relatively high viscosity of DESs enhances the HIPE stability similar to that of ILs. ILs decrease the cloud point of nonionic surfactants equivalent to adding salt to the dispersed phase on water-in-oil emulsions (42,43). Pérez-García et al. (25) later corroborated this observation on St HIPEs using U–ChCl, Gly–ChCl, and EGly–ChCl DES as internal phases. These investigations demonstrated that both St and MMA HIPE-based DESs

showed good stability at both room temperature and 60°C.

Confocal microscopy was carried out in HIPEs to determine the morphology, droplet size, and phase arrangements of these emulsions in more detail. In the case of HIPE-U and HIPE-Gly, it was observed that a structure consisted of closely packed polyhedral and polydispersed droplets separated by a thin film of continuous phase (ca. $0.8 \pm 0.6 \mu\text{m}$), which is characteristic of HIPEs. A representative confocal micrograph of these HIPEs is shown in Figure 1. Evidence of packed polyhedral arrangements in HIPEs had been reported with different techniques such as deconvolution fluorescence microscopy (25), optical microscopy (37), and confocal microscopy (26). Fluorescent images of HIPE-OAc and HIPE-EGly with rhodamine B dissolved in the continuous phase could not be acquired due to the low stability of the emulsion during confocal observations; phase separation in these emulsions was observed probably due to heating of the samples during the observation.

3.2 Determination of the stability, morphology, and mechanical properties of polyHIPEs obtained from DES-in-oil HIPEs

After polymerization of DES-in-oil HIPEs and the subsequent extraction of the internal phase, polyHIPEs were obtained. The visual aspect of these polyHIPEs was the first characteristic considered to establish their stability. The polymers obtained from stable emulsions with a highly viscous internal phase (internal phase viscosity > 100 cP), polyHIPE-U10, U18, Gly10, Gly18, OAc10, and OAc18, took the form of the container where polymerization was carried out. They appeared as a white monolith, light (bulk density ca. $0.15\text{--}0.19 \text{ g cm}^{-3}$, Table 2), with a texture similar to a chalk (dry and dusty). On the other hand, HIPE-EGly10 and EGly18 (internal phase viscosity ca. 37 cP (41)) exhibited the creaming effect, i.e., the migration of the continuous phase to the top of the container, and the polyHIPEs formed crumbled. The stability of the resulting polyHIPEs is summarized in Table 1.

For the polyHIPEs synthesized, conversion was determined gravimetrically and, as expected, conversions were found to be high (90–95%). Similar results had been reported for polymer monoliths obtained from

¹ Value obtained in this work.

Table 1: Stability of HIPEs and polyHIPEs by visual observation and pore size and pore throat size of polyHIPEs

HIPE	Stability	PolyHIPE	PolyHIPE pore size (μm)	PolyHIPE pore throat (μm)
HIPE-U10	>3 days	Good	4.50 ± 0.13	0.79 ± 0.3
HIPE-Gly10	>3 days	Good	5.36 ± 1.12	1.43 ± 0.43
HIPE-OAc10	>12 h	Good	5.32 ± 1.51	1.81 ± 0.66
HIPE-EGly10	>12 h	Crumbled	—	—
HIPE-U18	>3 days	Good	1.8 ± 0.44	0.55 ± 0.17
HIPE-Gly18	>3 days	Good	6.64 ± 1.4	1.3 ± 0.4
HIPE-OAc18	>12 h	Good	1.39 ± 0.37	—
HIPE-EGly18	>12 h	Crumbled	—	—
HIPE-U ^a	<3 days	Good	3 ± 0.8	0.87 ± 0.2
HIPE-Gly ^a	<1 days	Good	8 ± 3.2	2.07 ± 1.3
HIPE-EGly ^a	<5 h	Fragile	—	—

^aValues reported by Pérez-García et al. (25).

Figure 1: Confocal micrograph of HIPE-Gly10. Monomers (continuous phase) were marked with fluorescent dye rhodamine B.

DES-in-oil emulsions, using different monomers such as MMA, lauryl acrylate, stearyl methacrylate, and St/DVB as continuous phases and DES U-ChCl and Gly-ChCl as internal phases, all prepared by vortex stirring. In these

studies, high conversions had been ascribed to the type of internal phase, which promotes an environment where polymerization is only carried out in the continuous phase of the HIPE and acts as a template to obtain interconnected macroporous materials (24–26). Another important aspect in the synthesis of these polymer monoliths is that they were prepared using a simple method of homogenization such as vortexing with a maximum of 3,200 rpm; while in the present work, high-power homogenizers were used with a 3.5-fold speed (11,000 rpm), and high conversions were maintained. These results show that high conversions are obtained regardless of the different forms of homogenization of emulsion precursors such as vortex stirring and high-power homogenizers. It is essential to note that polymerization was carried out without the use of inert atmosphere as it is usual for free radical polymerizations.

An accepted method to analyze the emulsion stability during polymerization is by comparison of the size of the HIPE droplet to that of the polyHIPE pore, where no change in the size or minor differences

Table 2: Density and mechanical properties of polyHIPEs

PolyHIPE	ρ_b (g cm^{-3})	Elastic modulus (MPa)	Crush strength (MPa)
PolyHIPE-U10	0.16	13.0 ± 2.1	0.88
PolyHIPE-Gly10	0.17	16.83 ± 4.7	0.80
PolyHIPE-OAc10	0.19	25.7 ± 3.8	1.80
PolyHIPE-U18	0.15	8.7 ± 0.6	0.95
PolyHIPE-Gly18	0.18	14.9 ± 3.0	1.34
PolyHIPE-OAc18	0.15	15.3 ± 1.5	0.82
PolyHIPE-U ^a	0.17	7.29	0.87
PolyHIPE-Gly ^a	0.23	21.57	1.86

^aValues reported by Pérez-García et al. (25).

indicates good stability. Figure 2 shows SEM images of polyHIPE monoliths. Looking carefully into the structure of styrenic polyHIPE monoliths, it is observed that those prepared with the IKA T10® homogenizer present the typical structure of a macroporous polymer which consists of an interconnected pore network connected by spherical pore throats that are about a quarter the size of the pore diameter. The average pore diameter of polyHIPE-U10 showed little relative change to its precursor emulsion (3.9 to 4.5 μm). When compared to its parent HIPE, polyHIPE-Gly10 showed an increased average pore diameter from 3.3 to 5.4 μm possibly due to Ostwald ripening. PolyHIPE-OAc10 could not be compared to its precursor emulsion as noted above; however, it showed a stable and homogeneous structure with an average pore size of 5.3 μm . Coalescence can be avoided with the use of high viscosity internal phases (40),

consequently the polyHIPE pore was related directly to its precursor emulsion and its size was $\text{polyHIPE-U10} < \text{polyHIPE-OAc10} < \text{polyHIPE-Gly10}$. The droplet size of HIPE and the pore size of polyHIPE are summarized in Table 1.

PolyHIPE monoliths prepared with the IKA T18® homogenizer presented a series of characteristics such as phase inversion, decrease in average pore size, coalescence, and even the absence of an interconnected three-dimensional network characteristic of porous polymers for polyHIPE-OAc18. This last one presents a highly concentrated two-dimensional network, which was associated with the high mixing speed and the increase in the extension arm diameter of the homogenizer, that could have caused the reorganization of the continuous/internal phases of the emulsion, along with the arrangement of the surfactant between the phases.

Figure 2: SEM micrographs at $\times 2,000$ magnification of St/DVB polyHIPEs post-DES extraction: (a) polyHIPE-U10, (b) polyHIPE-Gly10, (c) polyHIPE-OAc10, (d) polyHIPE-U18, (e) polyHIPE-Gly18, and (f) polyHIPE-OAc18.

The coalescence effect can be seen more clearly in Figure S1 for polyHIPE-Gly18. The porous structure of polyHIPE-EGly10 and EGly18 collapsed (Figure S2) due to the low stability of HIPEs during polymerization and for this reason the rest of the characterization was not carried out in these samples.

Figure 3 represents the relationship of the pore size of polyHIPE-U, polyHIPE-Gly, and polyHIPE-OAc with the drop size of their precursor emulsions; together with a comparison with the values reported by Pérez-García et al. (25) where vortex stirring was used as the homogenization method. Figure S3 shows a representation of Figure 3 including error bars. As described above, a relatively minor change ($0.7\text{ }\mu\text{m}$) was observed for polyHIPE-U10 with respect to its precursor HIPE-U10; similar results were reported by Pérez-García et al. for this system with a change of $1\text{ }\mu\text{m}$ between the HIPE and its polyHIPE. In the case of polyHIPE-Gly10, the change was approximately $2\text{ }\mu\text{m}$ with respect to HIPE-Gly10, which is equal to that reported by Pérez-García et al. However, the sizes of both the drop and the pore in this study were smaller than that reported by Pérez-García et al., due to the effect of the mixing force that in this case was greater and caused the formation of smaller polyhedral droplets compared to those formed by vortexing. For polyHIPE-OAc data could not be obtained as was described before.

Figure 3: Drop size of HIPE (black points) and pore size of polyHIPE (blue points) using IKA T10 Ultra-Turrax® (circles) and IKA T18 Ultra-Turrax® (triangles), to homogenize. Squares represent data taken from Pérez-García et al. (25).

A wide range of monomers have been used for the preparation of polyHIPE monoliths with a variety of average pore sizes. HIPEs prepared with glycidyl methacrylate

(GMA)/EGDMA monomers produced monoliths with a porosity range of 40–500 nm (7), whereas their variant GMA/EGDMA/MMA had a porosity increase to 720 nm (10); HIPEs of MMA/EDGMA generated porous monoliths of 1.4–38.2 μm using two stirring methods (9) (e.g., standard overhead stirrer at 500 rpm for 180 min and high-speed stirring at 25,000 rpm for 10 min); St/DVB, MMA/EDGMA, and SMA/EDGMA monomers functionalized with multi-walled carbon nanotubes (37) had average pore sizes between 5 and 20 μm .

The morphology of the porous polyHIPEs plays a significant role in the mechanical properties which are fundamental for their final application. Compression analyses of polyHIPEs-U10, U18, Gly10, Gly18, OAc10, and OAc18 were carried out to evaluate the influence of the methods used to homogenize (IKA T10® homogenizer at 11,000 rpm for 1.5 min followed by vortexing at 3,200 rpm for 0.5 min, and IKA T18® at 11,000 rpm for 1.5 min) the emulsions on both the elastic modulus and crush strength. The elastic modulus was determined from the slope of the initial linear elastic region in the stress–strain curve, and the crush strength was obtained as the maximum compressive strength value at the end of the initial elastic region. The results are reported in Table 2. It seems that the pore throat size is related to the magnitude of the elastic modulus, both variables follow the same trend as polyHIPE – U18 < U10 < Gly18 < Gly10 < OAc10 (Figure 4), discarding to polyHIPE-OAc18 which did not present pore throat. In the same context, it can be observed that the values of the polyHIPEs homogenized with IKA T10 had higher values than their

Figure 4: Pore throat size (black points) and elastic modulus (blue points) for polyHIPEs using: IKA T10 Ultra-Turrax® (circles) and IKA T18 Ultra-Turrax® (triangles), to homogenize. Squares represent data taken from Pérez-García et al. (25).

counterparts homogenized with IKA T18, which indicates that the diameter of the homogenizer had an important influence on both the morphology and the mechanical properties of the synthesized polyHIPE monoliths. Comparing the values of the elastic module with respect to those obtained by Pérez-García et al. (25), a small increase in the module value is observed for polyHIPE-U and a decrease in the module value for polyHIPE-Gly. These changes in the magnitude of the respective modules are likely due to the small changes in the pore size of the resulting polyHIPEs, which indicates that the mixing protocol has a profound impact on the morphology of the material (44). Figure S4 shows a representation of Figure 4 including error bars. Finally, the crush strength had values in the range of 0.80 to 1.80 for the complete group of polyHIPEs synthesized and that are similar to those reported for this kind of systems (Table 2).

4 Conclusions

In this work, it is demonstrated that the use of a carboxylic acid as HBD of DES represents a suitable internal phase for nonaqueous HIPEs along with other functional groups assayed before such as amides and alcohols, thus expanding the range of DES with different chemical structure, polarity, and viscosity for the synthesis of DES-in-oil HIPEs. Furthermore, the use of high-speed homogenizers was proposed to establish a more general protocol for the preparation of nonaqueous HIPEs. The stability and droplet size of HIPEs were affected by DESs' viscosity and the diameter of the high-speed homogenizer. It was found that the polymerization of stable emulsions with a highly viscous internal phase (internal phase viscosity > 100 cP) results in an interconnected macroporous polyHIPE. Moreover, in this study, the sizes of both the drop of the HIPEs and the pore of the resulting polyHIPEs were smaller than those already reported when using a simple method of homogenization such as vortexing. This is due to the effect of the mixing force that in this case was greater and caused the formation of smaller polyhedral droplets. Conversions of monomers were higher than 90% using high power homogenizers. Furthermore, we have also demonstrated that the pore throat size is related to the magnitude of the elastic modulus, both follow the same trend as polyHIPE – U18 < U10 < Gly18 < Gly10 < OAc10 and these properties also are affected by the diameter of the homogenizer. Thus, the porous structure can be

easily modified by both the constituents of the internal phase and the mixing protocol used for HIPE preparation.

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