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Deep-eutectic solvents as support in the nonaqueous synthesis of macroporous poly(HIPEs)

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This study demonstrates the formation and polymerization of high internal phase emulsions (HIPEs) with (meth)acrylic monomers as continuous phase and urea-choline chloride deep-eutectic solvent as a favorable nonaqueous internal phase. After recovering of DES, resultant poly(HIPEs) showed interconnected macroporosity which can be tuned by varying the experimental conditions.

Emerging challenges in sustainable development and an increasing demand for functional materials have spurred contemporary research to design bioinspired systems. Nature provides a perfect balance between function and sophistication of adaptable hybrids. In this context, emulsion-templated materials, using high internal phase emulsions (HIPEs), have been used to confer hierarchical architectures to porous materials.¹

HIPEs are highly viscous emulsions in which the internal volume fraction accounts for more than 74% dispersed within a minor continuous phase.² The introduction of a polymerizable continuous phase and subsequent extraction of the internal phase allows the synthesis of functional architectures with a unique hierarchical pore distribution. The resulting poly(HIPEs) consist of spherical cavities normally having a similar diameter to the original HIPE and can be interconnected by secondary pores. Furthermore, tertiary porosity may be introduced by inducing phase separation during polymerization through the addition of non-polymerizable materials to the continuous phase.^{3,4} Much effort has gone in developing versatile means of emulsion templating including the application of supercritical fluids^{5,6} and ionic liquids (IL)⁷ as internal phases, and the use of amphiphilic colloidal particles in place of surfactants.^{8,9} However, only a handful of works outline nonaqueous preparation of poly(HIPEs). Ordered porous ceramics by using oil-in-formamide emulsions¹⁰ and self-assembly of colloidal systems in ethanol¹¹ are some examples. Cameron and Sherrington¹² introduced the non-aqueous synthesis of poly(HIPEs) using N,N'-dimethyl acetamide and dimethyl sulfoxide as internal phases; while Hariri et al.¹³ devised polymerizable oil-in-oil HIPEs. Most recently, Shirshova and coworkers^{14,15} have demonstrated the use of an ionic liquid as an internal phase for poly(HIPE) synthesis. Water-free synthesis

expands on the available polymerization mechanisms otherwise impossible due to water sensitivity or evaporation.

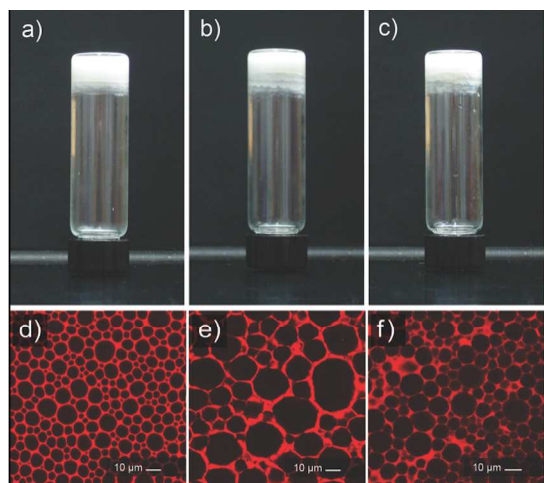
First documented by Abbott et al.,^{16,17} deep-eutectic solvents (DESs) are a new generation of green solvents comprised of a eutectic mixture formed through the association of hydrogen-bond donors and ammonium or phosphonium salts. DESs can be easily prepared by heating a mixture of two or more components, many of which are natural molecules or their structural derivatives (e.g. citric acid; choline chloride).¹⁸ Some of the most notable features of DES include their low cost, biocompatibility, negligible vapor pressure, high thermal and chemical stabilities, and their ability to dissolve both ionic and organic solutes. HIPEs containing DESs can broaden the available range of polymerization temperatures for potential applications as analytical chromatographic adsorbents,¹⁹ nanocomposites,²⁰ scaffolds for tissue engineering²¹ and other bioinspired materials.^{22,23} In addition, DESs provide an alternative green tool in the creation of hierarchically porous materials through enhanced polymerization of HIPEs in a nonaqueous or *in vacuo* environments. To this end, we propose DESs as an alternative internal phase for the nonaqueous synthesis of porous polymer solids.

Herein three different acrylic monomers, methyl methacrylate (MMA), lauryl acrylate (LA) and stearyl methacrylate (SMA), were chosen based on their chain length, C₁, C₁₂, and C₁₈ respectively; and their type acrylate or methacrylate. To ensure homogeneity in the physical properties of resulting poly(HIPEs), monomers were crosslinked with a similar type of crosslinker EGDMA, in the case of methacrylates, or BDA, in the case of acrylates. A small group of ChCl-based DESs and acrylate monomers were screened for their miscibility, and U:ChCl was chosen to conduct this study. Traditionally, nonionic surfactants with low hydrophilic-lipophilic balance (HLB) are used to prepare HIPEs of continuous oil phases. However, nonionic triblock copolymers are becoming more popular in HIPE preparation due to their relatively low HLB and their ability to rapidly align at the interface of the emulsion droplets because of their triblock structure. Recently, poly(HIPEs) have been prepared with nonionic triblock copolymer surfactants, Cithrol[®]¹⁴ and pluronics.⁷ A number of pluronics and Cithrol[®] were tested for their

ability to stabilize HIPEs. Cithrol[®] formed the most stable emulsions, which remained stable for more than a week with the flask inverted (Figure 1). A summary of polyHIPE synthesis is presented on Figure 2.

HIPEs' microstructures were observed by confocal microscopy (Figure 1) where the monomer/crosslinker continuous phase was marked with the fluorescent dye Rh6G. All HIPEs examined, with the exception of MMA10 (Table S1), showed tightly packed droplets with a polyhedral structure unique to HIPEs. After thermal polymerization, resulting poly(HIPEs) were washed with water. The wash containing DES components was freeze-dried and weighed. It has been shown that DES is recovered from 82% to nearly 95%, where ¹H-NMR confirmed samples to be nearly pure with a minor trace of water (Figure S3). Dried monolith conversion was determined gravimetrically and through FTIR. Poly(HIPEs) prepared with 10 wt% of surfactant had a relatively high conversion by mass recovery between 85.9% for pSMA10 and 97.9% for pMMA10. However, a drastic decrease in mass recovery of 62.6% was observed for pLA10. A similar trend was observed for methacrylates having a noticeably higher conversion (Table 1). Reducing the surfactant quantity to 7 wt% increased poly(HIPEs') conversion marginally by 0.8% and 1.2% for pSMA and pMMA respectively. Interestingly, LA7 had a significant increase in mass recovery of 32.6% and its conversion went up from 71.8% to 99.3%. Conversion was drastically increase in the case of long chain monomers but was no different for pMMA.

Figure 1. Images of HIPEs. a) MMA10 (methyl methacrylate) b) LA10 (lauryl acrylate) c) SMA10 (stearyl methacrylate) continuous phases. Confocal micrographs of HIPEs d) MMA7 e) LA7 and f) SMA10 labeled with fluorescent marker rhodamine 6G.



Finished monoliths appeared as low density white solids taking on the dimensions of their preparatory vessel (Figure 3e). A study of their physical properties revealed that monomer type and amount of surfactant used played a critical role in HIPE stability during the polymerization process. Enough surfactant must be added so that a stable emulsion can be achieved. Adding too little results in HIPEs with low stability, but adding too much can be detrimental to structural integrity.¹⁴ PolyHIPE morphologies studied by SEM (Figure 3) demonstrate similar trends earlier observed in FTIR and confocal microscopy. Pore and pore window diameter were calculated in sets of 50 through image analysis; these values were later used to estimate poly(HIPEs') degree of openness using the equation proposed by Pulko and Krajnc (Scheme S1).³ Relative

stability was determined by comparing HIPE droplet diameter to pore diameter of poly(HIPEs) (Table S3).

In most cases, there was no difference between the droplet diameter and pore diameter with the exception of pLA10. A drastic change in chain length of C₁, for MMA, to C₁₈, for SMA, had no effect in stability, but the absence of a methyl group for LA having a C₁₂ long tail was significantly less stable during HIPE polymerization. PolyHIPEs prepared with 10 wt% surfactant, had much larger pore and droplet diameters with the exception of pSMA10 which had smaller diameters than pSMA7. This suggests that pSMA require a greater amount of surfactant to be stabilized. There was no observed trend for pore window diameter and because of these every monolith had a unique degree of openness.

Figure 2. Schematic representation of HIPE formation from U:ChCl DES, Cithrol[®] a)EGDMA b)SMA and its resulting poly(HIPE) after polymerization and subsequent DES removal.

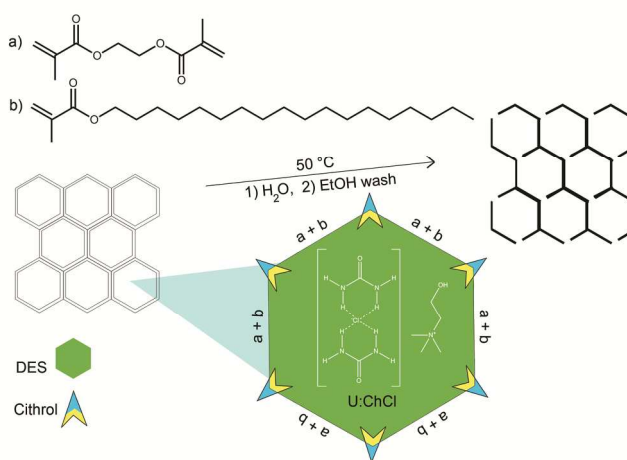


Table 1. Conversion based on gravimetry and FTIR of poly(HIPEs), and percentage of recovered DES after water wash.

Poly(HIPE)	Gravimetry	FTIR	Recover DES (%)
pMMA10	97.9	90.7	-
pMMA7	99.1	90.8	82.4 ^{a)}
pLA10	62.6	71.8	-
pLA7	90.8	99.3	86.1 ^{a)}
pSMA10	85.5	94.8	-
pSMA10v	85.9	81.1	-
pSMA7	86.3	98.9	94.7 ^{a)}

a) Representative extraction samples

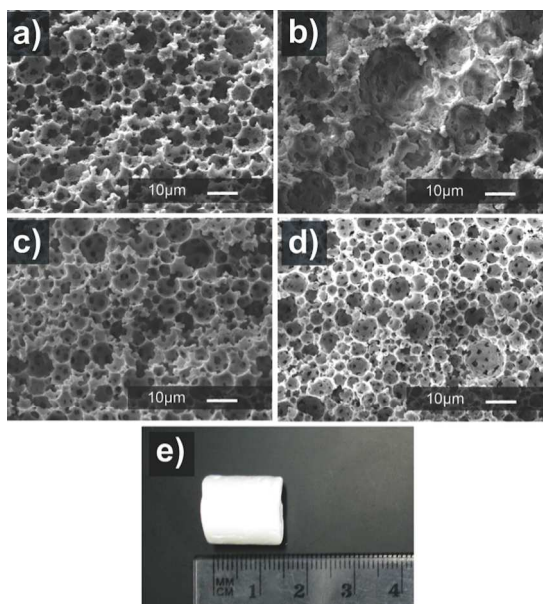
The potential of this technique was further explored through a polymerization of SMA10 under vacuum. pSMA10v had similar morphological qualities to pSMA10 in regards to pore diameter. Nevertheless, pore window diameter differed from pSMA10v to pSMA10 resulting in unique degrees of openness. Conversion and recovery for pSMA10v was also lower than pSMA10.

Based on experimental results, it is possible that the methyl group in methacrylates act as an "anchor" allowing better monomer-surfactant interaction at the monomer-DES interphase and exposing

all methacrylic groups for a more efficient polymerization locking the microstructures in place. This phenomenon would account for the higher conversion and small variance on droplet diameter to pore diameter. In this sense, adding more surfactant can potentially saturate the monomer-DES interphase preventing this effect. Finally, BET analysis showed low surface area of a few m^2g^{-1} for all poly(HIPEs) examined where pSMA10 had the highest surface area. TGA of all Poly(HIPEs) showed thermal decomposition having an onset point beyond 220°C (Table S5), in agreement with (meth)acrylate-based poly(HIPEs) previously reported.^{14, 24, 25}

Aside from alternative polymerization mechanisms, a broader range of polymerization temperatures and the possibility of *in vacuo* polymerizations, nonaqueous preparation of poly(HIPEs) using DESs provides additional advantages. HIPE formation can be achieved with relative ease in one-step at low-cost and without special conditions, preparations, or additives. Poly(HIPE) preparation by means of DESs is a green process because of their demonstrated biocompatibility, biodegradability, and recyclability. We have shown that a recovery of DES of 82% to nearly 95% is possible.

Figure 3. Scanning electron micrographs of poly(HIPEs) after DES removal of a) pMMA7 b) pLA7 c) pSMA10 and d) pSMA10v; e) final monolith after DES extraction.



We propose that DESs may have an effect similar to adding a salt to a HIPE's internal phase²⁶ where the salt helps decrease the cloud point of the surfactant. Therefore, Cithrol[®] has an enhanced interaction at the monomer/crosslinker-DES interface resulting in the rapid stabilization of the DES drops. This interaction is the result of a delicate balance of polarity between the monomers and DES that provides the suitable environment for the surfactant triblock placement. Additionally, HIPEs prepared with DESs also benefit from the relatively high viscosity where the effect of Ostwald ripening is drastically reduced. In a highly viscous system, efficient mixing of the internal phase droplets is lessened preventing the continuous phase's thin walls from collapsing and the HIPEs from breaking.²⁷ The potential to use an array of hydrogen bond donors with different polarities and structures opens up new possibilities for the use of new surfactants and monomers as well as the tuning of

certain physical properties such as pore roughness and to a lesser extent pore diameter.^{28, 29} Further, by taking advantage of the ability of DES to dissolve/disperse nano-objects,^{30, 31} biopolymers and others substances, functionalization of the inner walls and formation of macroporous polymer composites is easy to envisage.

In summary, DESs provide an attractive alternative for the sustainable nonaqueous synthesis of porous materials. Poly(HIPE) preparation by means of DESs is a green process due to the biocompatibility, biodegradability, and recyclability associated with DES. We have also demonstrated that DES's recovery of 82% to nearly 95% is possible. The amount of stabilizer used and the nature of surfactant affect the overall stability of HIPEs during polymerization. We found that methacrylates provided the most desirable systems with high conversions (between 81% and 99%), thermal stability (above 220°C), open porosity, and consistent droplet diameter to pore diameter. DESs enhance HIPE stability through a decrease in the surfactant's cloud point, besides to a relatively high viscosity provided by the proper balance between the component's polarities. By tailoring and designing DES properties (type and ratio of HBD and salt) new monomers and surfactants can be introduced, which in turns will results in different surface properties. Finally, the absence of water allows a wide range polymerization conditions (e.g. temperature and pressure) previously inaccessible due to water evaporation, therefore permitting a future introduction of new polymerization mechanisms that are water sensitive.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental methods, synthetic procedures and full characterization. See DOI: 10.1039/c000000x/

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Table of Content

Deep-eutectic solvents as support in the nonaqueous synthesis of macroporous poly(HIPEs)

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Polymerizations of nonaqueous HIPEs with (meth)acrylic monomers as continuous phase and DES as internal phase produce macroporous interconnected polymer monoliths.

