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Ionic Liquid-Filled Polyamide Microcapsules Obtained by Interfacial Polymerization

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Microencapsulated ionic liquids (ILs) have a wide range of exciting properties. They can be synthesized by a variety of methods, of which interfacial polymerization represents a very simple, fast, and reliable production process, but the number of available shell materials that can be obtained by this method is limited. However, recent advances in the field of interfacial polymerization have described the formation of a polyamide membrane at the IL/organic phase interface, which is extended in this work to the first microencapsulation of ILs with a polyamide shell, providing an additional and versatile shell material. The IL-filled microcapsules are obtained using a surfactant-free synthesis process and inexpensive, low-toxicity monomers and solvents and feature an exceptionally high core-to-shell weight ratio enabling a broad range of possible applications.

1. Introduction

Ionic liquids (ILs) are compounds with a melting point below 100 °C entirely composed of ions.[1] They possess a set of intriguing merits such as extremely low vapor pressure, high stability, powerful solvency, and a highly designable molecular structure[2] which make them viable candidates for a broad range of applications.[1,3] To further extend their field of application, they can be encapsulated by a shell consisting of a polymer or an inorganic material.[4] For example, the confined structure can overcome the often limiting high viscosity of ILs, allowing high mass transfer rates across the large surface area.[4–6] This also enables the heterogenization of a catalyst[7] and easier phase separation[8] since the IL can be filtered off or handled as a powder.[9] This has led to promising potential applications for IL-filled microcapsules, including carbon storage,[10] microreactors,[11] and functional materials applications.[12,13]

IL-filled microcapsules can be synthesized using a variety of preparation techniques, resulting in different core- and shell materials. A detailed overview of materials and techniques is given by Yan et al.[4] Of these, interfacial polymerization represents a very simple and reliable process that can be easily scaled up.[14,15] It is therefore a highly versatile reaction which is described in more detail in the following.

1.1. Interfacial Polymerization

Interfacial polymerization at the water/alkane interface was first described in detail by Wittbecker and Morgan in 1959.[16] In this process, two highly reactive monomers (typically an organic amine and an acid chloride) react at the interface between two immiscible liquids: a polar phase, such as water, and a nonpolar (oily) phase, like a hydrocarbon, to form a polyamide film. This reaction was subsequently utilized by Chang and Koishi et al. in the 1960s for the synthesis of hydrocarbon-filled microcapsules.[17,18] Hereby, the hydrocarbon containing one of the monomers is emulsified in water whereupon the second monomer is added to the aqueous phase, and the droplets are enveloped by a polyamide membrane as the monomers react at the water/hydrocarbon interface (see **Figure 1**, left).[14,19] During this synthesis process, the capsule diameter and the shell thickness can be easily regulated[20,21] in addition to the membrane properties such as permeability and mechanical stability, which can be controlled by the monomers used.[20]

The microencapsulation of ionic liquids by an interfacial reaction was first described by Weiss et al. who encapsulated 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) with a silica shell formed by interfacial hydrolysis.[7,22] Later, Ma et al. prepared ([BMIM][PF_6])-filled polyurethane microcapsules using isocyanate and diamine monomers.[23] The preparation of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf_2]) and 1-hexyl-3-methylimidazolium counterpart ([HMIM][NTf_2])-filled microcapsules with polythiourethane shells by an interfacial polymerization process are also known in the literature.[9]

Recently, Liu et al. reported an interfacial polymerization process at the interface of an alkane and an ionic liquid with an organic acid chloride and amine producing a polyamide membrane.[24] This interfacial polymerization at the IL/oil interface bears some inherent advantages in comparison to the reaction at the oil/water interface. First of all, the reaction can be carried out water-free, so a hydrolyzation of the acid chloride at the interface cannot occur, avoiding

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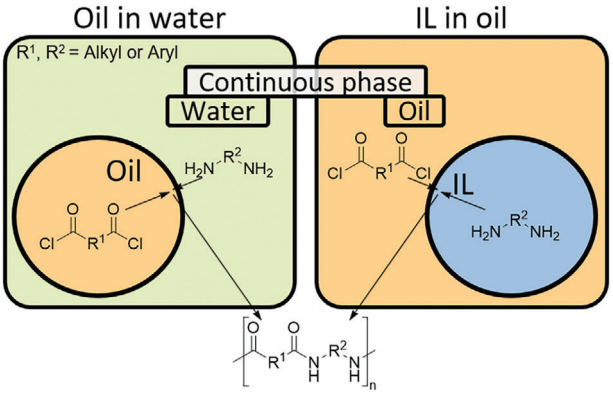


Figure 1. Comparison of the general reaction mechanism of interfacial polymerization with an organic amine and acid chloride for an oil-in-water (left) and IL-in-oil (right) system forming a polyamide membrane around the droplets.

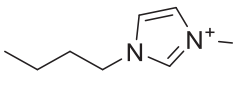
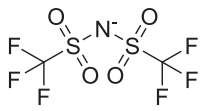
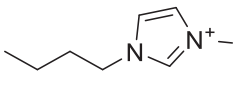
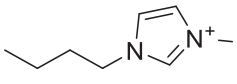
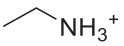
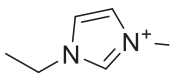
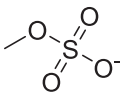
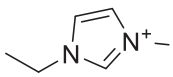
defects in the resulting polymer.[24,25] Furthermore, the IL acts as a universal solvent, allowing a broad range of amines to be utilized while also forming sharp interfaces with various alkanes.[24]

In contrast to these above-mentioned, already-known shell materials for IL-filled microcapsules prepared by interfacial polymerization, a polyamide membrane would have the advantage of using cheap, easy to handle, and far less toxic monomers (an organic amine and acid chloride) compared to volatile and highly toxic isocyanates. In addition to that, polyamide shells expand the potential application range of the capsules, in particular through the high customizability of the monomers used, especially the amine.[24]

In this work, we extend the method described by Liu et al. to synthesize IL-filled microcapsules by interfacial polymerization with a polyamide shell, which, to the authors' knowledge, has not been described before. Figure 1 (right) depicts the interfacial polymerization at the interface of an IL droplet in an oily continuous phase (CP), as it is targeted in this work. For this, the organic amine is dissolved in the IL-phase which is then emulsified in the continuous oily phase. Hereafter, the acid chloride monomer is added to the CP and rapidly reacts with the amine at the interface, forming a membrane around the droplet. This results in an inversed presence of the monomers in the two phases compared to the synthesis of hydrocarbon-filled microcapsules in an aqueous phase, where the acid chloride is dissolved in the core material and the amine is added to the CP (Figure 1, left).[14,26]

Therefore, both systems have in common, that the CP monomer diffuses faster through the membrane than its counterpart, so in both cases, the membrane grows internally at the core-membrane interface.[14,24] As the reaction proceeds, the polymerization rate decreases over time, as the reaction is restrained by the diffusion speed of the monomers through the growing membrane and eventually proceeds until one of the monomers is consumed.[14,27] Consequently, it is useful to add the CP-monomer in excess to speed up the reaction.[26] The hydrogen chloride generated during the reaction most likely remains in the more polar IL phase, where it could potentially react with the IL, restricting the choice of ILs. However, it is expected, that the amine will trap and neutralize the HCl.

Table 1. Chemical structures of the ionic liquids used in this work.

Ionic liquid	Cation	Anion
[BMIM][NTf_2]		
[BMIM][PF_6]		
[BMIM][OAc]		
EAN		
[EMIM] [$MeSO_4$]		
[EMIM] [SCN]		

2. Results and Discussion

2.1. Emulsification Experiments

For the synthesis of microcapsules by interfacial polymerization, a stable IL/CP emulsion is necessary to be produced. To evaluate, which IL/CP mixtures form a stable emulsion, a screening of the emulsion properties of different ILs in a variety of CPs has been conducted after **EP1** (see Supporting Information). For this, the IL was shaken by hand and then after 30 s, visually

Table 2. Results of the emulsification experiments of ILs in different continuous phases after **EP1** (✓: Stable emulsion; ×: Phase separation ○: Soluble mixture).

Continuous phase	[BMIM][NTf_2]	[BMIM][PF_6]	[BMIM][OAc]	EAN
Acetone	○	○	○	○
n-Decane	×	×	×	×
Dichloromethane	○	✓	○	×
Diethyl ether	×	×	×	×
Ethyl acetate	○	○	×	×
2-Isopropoxyethanol	○	○	○	○
Isopropyl alcohol	○	×	○	○
Oleic acid	✓	×	○	✓
Paraffin oil	×	×	×	×
Silicone oil	✓	✓	✓	×
Sunflower oil	✓	✓	✓	✓

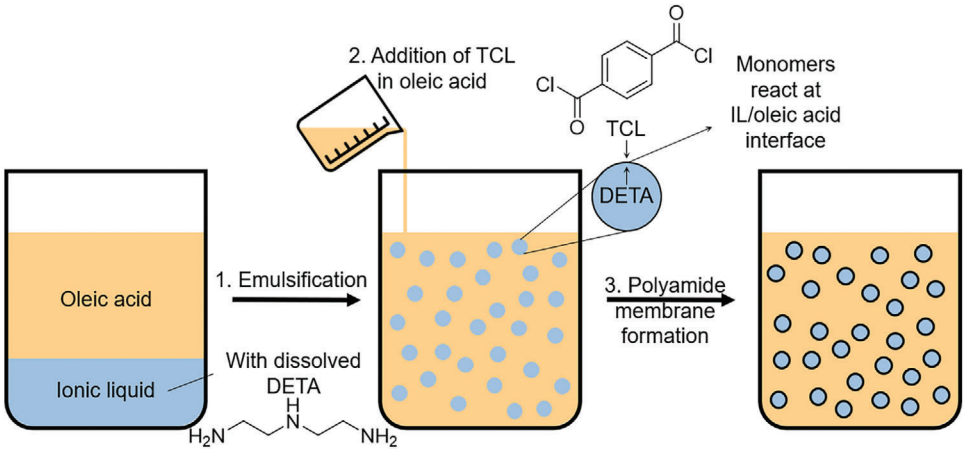


Figure 2. Preparation process of IL-filled polyamide microcapsules by interfacial polymerization with DETA and TCL in oleic acid as used in this work.[29,30]

categorized as a stable emulsion, nonemulsifiable (phase separation), or soluble mixture The ILs were chosen, as some of them are already known as core materials for IL-filled microcapsules ([BMIM][NTf_2] and [BMIM][PF_6]). Others were selected since they would be very interesting for potential application as fuels in space propellants, including investigations of our group concerning mixtures of fuel-filled microcapsules and highly concentrated hydrogen peroxide resulting in a monopropellant with the performance of a typical bipropellant system.[28–30] These are 1-butyl-3-methylimidazolium acetate ([BMIM][OAc], ethyl ammonium nitrate (EAN), 1-ethyl-3-methylimidazolium methylsulfate and thiocyanate ([EMIM][$MeSO_4$] and [EMIM][SCN]). The chemical structures of the used ionic liquids are shown in **Table 1**. The results of the emulsification experiments are presented in **Table 2**. [EMIM][$MeSO_4$] and [EMIM][SCN] were also tested for their emulsifying properties after **EP1**, but they appeared to react with the monomers required for the subsequent encapsulation reaction (**EP2**) at once ([EMIM][$MeSO_4$] with DETA and [EMIM][SCN] with TCL). To investigate this behavior, infrared (IR) spectra of the monomers, the ILs, and the reaction mixture were taken (see Supporting Information for the spectra and more details), and it does indeed appear that a reaction is taking place between the DETA and [$MeSO_4$]- as well as the TCL and [SCN]-ions. Therefore, ILs with [$MeSO_4$]- or [SCN]-anions can be considered unsuitable for the interfacial polymerization reaction with these monomers.

2.2. Synthesis of IL-Filled Microcapsules by Interfacial Polymerization

Following the experiments on the emulsification behavior, the IL/CP mixtures which form a stable emulsion after **EP1** were submitted toward the synthesis of IL-filled microcapsules according to **EP2** (compare to **Figure 2**, see Supporting Information for more information). The IL with the dissolved diethylenetriamine (DETA) was emulsified in the CP by mechanical agitation, whereupon terephthaloyl chloride (TCL), dissolved in the continuous phase was added to react at the IL/CP in-

Table 3. Results of the encapsulation experiments of the stable IL/CP emulsions (from EP1) conducted after EP2 (✓: Successful synthesis of IL-filled microcapsules; ×: No microcapsules obtained; -: Not a stable emulsion).

Continuous phase	[BMIM][NTf_2]	[BMIM][PF_6]	[BMIM][OAc]	EAN
Dichloromethane	–	×	–	–
Oleic acid	✓	–	–	×
Silicone oil	×	×	×	–
Sunflower oil	✓	✓	×	×

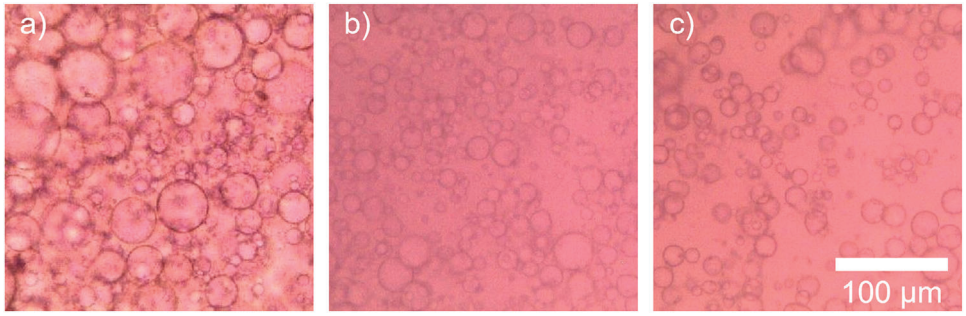


Figure 3. Optical microscopy image of polyamide microcapsules obtained by interfacial polymerization (**EP2**) with [BMIM][NTf_2] core in oleic acid (a) and sunflower oil (b) as well as [BMIM][PF_6]-filled microcapsules in sunflower oil (c).

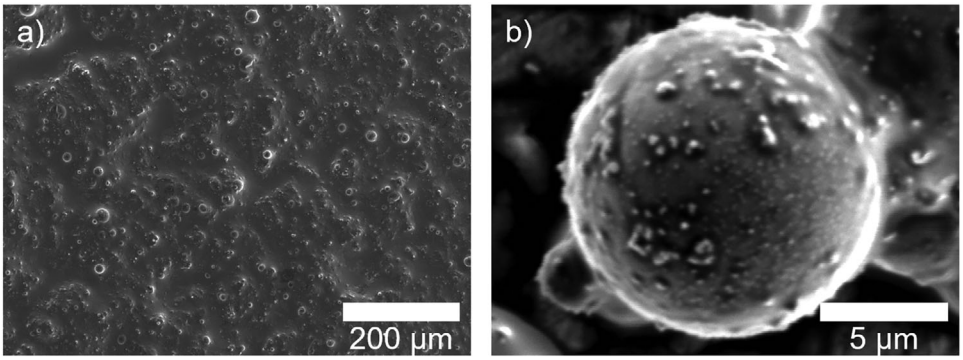


Figure 4. SEM images of [BMIM][NTf_2]-filled polyamide microcapsules prepared in oleic acid after washing with *n*-heptane.

terface to form IL-filled microcapsules. DETA and TCL were chosen as monomers because they are inexpensive and, due to the highly cross-linked structure of the resulting polyamide, produce a polyamide membrane with very low permeability.[20] The amounts of monomer used result in a ratio of 2.08% shell mass to core mass, assuming complete conversion, which equates to 30.0 mg of capsule material per 1 mL of core material.

In **Table 3**, the results of these synthesis efforts are shown. The only IL/CP emulsions that yielded microcapsules were [BMIM][NTf_2] in oleic acid and [BMIM][NTf_2] as well as [BMIM][PF_6] in sunflower oil. In this work, we will focus from

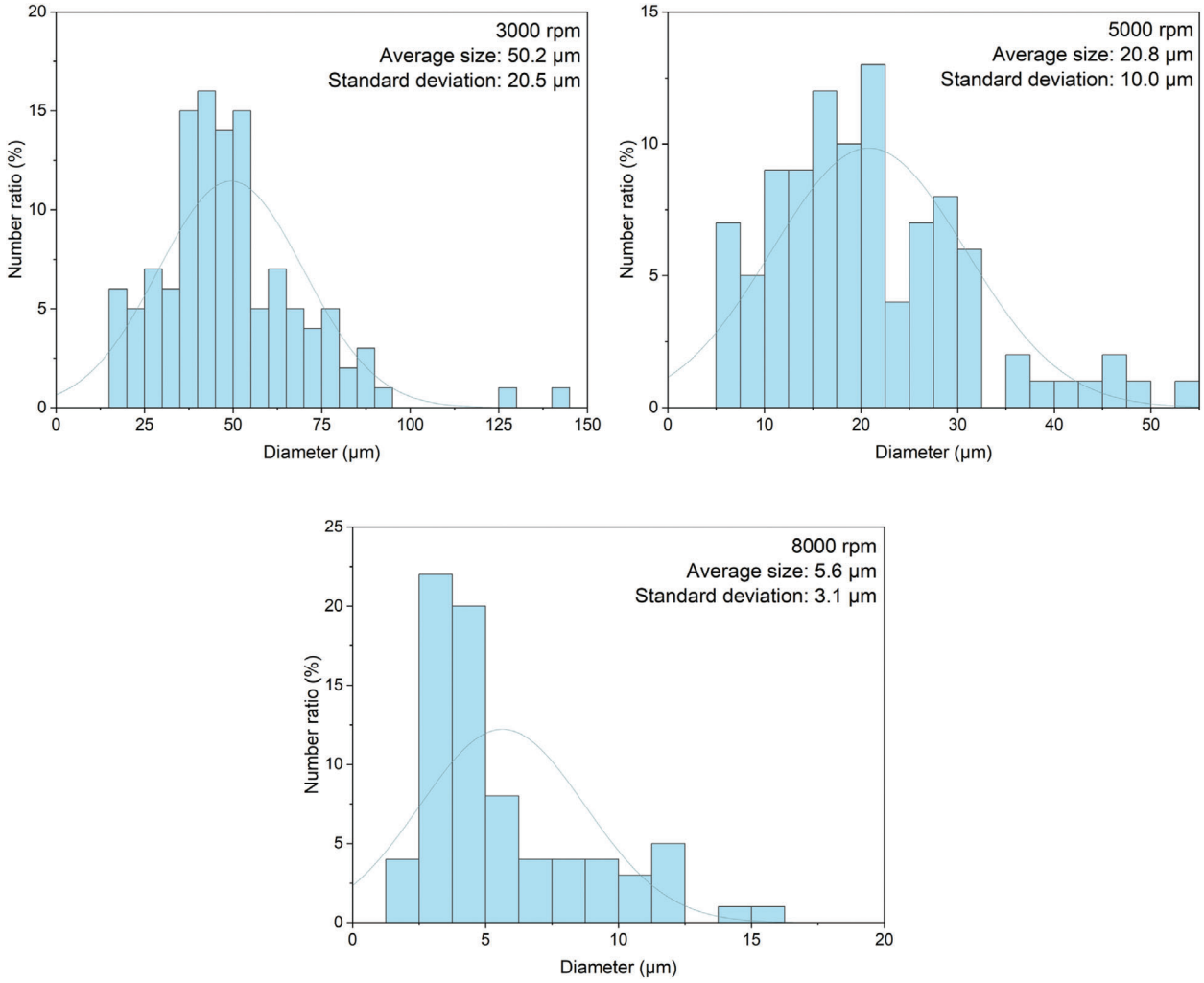


Figure 5. Size distribution diagrams of the [BMIM][NTf_2]-filled microcapsules prepared in oleic acid at 3000, 5000, and 8000 rpm.

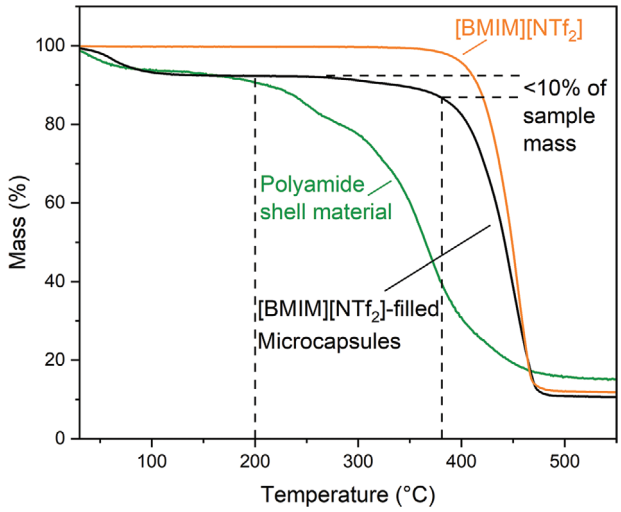


Figure 6. TGA measurements of pure core material, polyamide shell, and IL-filled polyamide microcapsules.

this point on, on the use of oleic acid as CP due to its higher homogeneity. Since the IL/CP emulsions produced in the synthesis process are stable themselves, they do not require a surfactant for the emulsification procedure while using an innocuous oily phase, simplifying the production as well as the purification of these IL-filled microcapsules with polyamide shell further in comparison to other IL-filled microcapsules, which are remarkable advantages.[9,23]

2.3. Characterization of [BMIM][NTf_2]-Filled Polyamide Microcapsules

Figure 3, shows the resulting microcapsules from the successful synthesis procedures (compare to Table 3), the [BMIM][NTf_2] in oleic acid (a) and [BMIM][NTf_2] well as [BMIM][PF_6] in sunflower oil (b and c).

After the washing of the microcapsules to remove the continuous phase, also SEM images of these microcapsules were taken, showing a spherical shape with a rough morphology (**Figure 4**).

The size of the microcapsules can be controlled by adjusting the agitation rate during the mechanical stirring.[29,31] In addition to the standard preparation of [BMIM][NTf_2]-filled microcapsules in oleic acid at 5000 rpm, other stirring rates—3000, 8000, and 12000 rpm—were investigated. As expected, increased agitation rates led to a reduction in average capsule size, with the diameter decreasing from 50.2 µm (at 3000 rpm) to 5.6 µm (at 8000 rpm) as the stirring speed increased. At 12 000 rpm the reaction was unsuccessful and no microcapsules could be obtained. The average microcapsule sizes were determined by the measurement of 100 microcapsules under the optical microscope. The size distribution histograms of the microcapsules prepared at 3000, 5000, and 8000 rpm are shown in **Figure 5**. To be able to control the size of the reaction can be very useful for some applications because it controls the core volume to surface area which may be an important parameter for possible applications.

To study the thermal properties and the internal structure of the microcapsules, TGA measurements were carried out (**Figure 6**). Hereby, the thermal behavior of the [BMIM][NTf_2]-filled microcapsules is compared to the core and the dried shell material (obtained after **EP3**). Figure S1 (Supporting Information) shows the infrared spectrum of the dried shell material, which has characteristic absorption bands typical of polyamides. It can be observed that the polyamide shell material decomposes at lower temperatures than the core material, allowing the core-to-shell ratio to be determined. The mass loss of the microcapsule sample begins at a temperature of 200 °C, due to the decomposition of the polyamide shell, and continues until 380 °C, when the [BMIM][NTf_2] starts to decompose. At this temperature, 5.4% of the total mass of the microcapsule sample has been lost. In comparison, pure polyamide loses 64% of its mass at this temperature, suggesting that the microcapsule sample consists of ≈8.4% shell material. This results in a core-to-shell ratio of well over 90%. Compared to other IL-filled microcapsules synthesized by interfacial polymerization, this is a very high ratio, in literature it varies ≈70% IL-mass of the microcapsule mass.[7,9,23] A high core mass makes this method even more versatile and especially beneficial for propulsion applications, where a high fuel content is essential.[30]

3. Conclusion

In summary, the first microencapsulation of ionic liquids with a polyamide shell obtained by interfacial polymerization with an exceptionally high core-to-shell weight ratio has been described using a versatile and simple synthesis procedure, which allows for easy control of the microcapsule size. Furthermore, the synthesis process is free of water, resulting in a defect-free membrane, and features the use of inexpensive, low-toxicity monomers and solvents without any additional surfactants.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

interfacial polymerization, ionic liquids, microencapsulation, polymerization

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