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Hydrophilic porous polymers based on high internal phase emulsions solely stabilized by poly(urethane urea) nanoparticles

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ABSTRACT

Stable oil-in-water (o/w) Pickering high internal phase emulsions (HIPEs) having an internal phase of up to 95 vol% were prepared with a low-energy emulsification method. A poly(urethane urea) (PUU) aqueous nanodispersion was used as aqueous phase. The PUU nanoparticles of the aqueous nanodispersion acted as a mechanical barrier, and prevented droplet coalescence in the Pickering HIPEs. In addition, open porous hydrophilic polymer foams were obtained by polymerization of the Pickering HIPEs, and the morphology of the foams were tailored by changing the oil:water ratio, PUU nanoparticle and NaCl concentrations. The method used herein provides a simple way to prepare morphology controlled hydrophilic polymer foams using o/w Pickering HIPEs as template.

1. Introduction

High internal phase emulsions (HIPEs) are important for a wide range of applications in food, cosmetic, pharmaceutical, and petroleum industries [1,2] If the continuous phase contains one or more monomeric species that are polymerizable, HIPEs can be used as templates [3,4] for the synthesis of highly porous polymer foams (polyHIPEs) with potential applications as scaffolds in tissue engineering [5,6] sensor materials [7] and as support for heterogeneous catalysis [8–11] and separation media [12]. HIPEs are often defined as very concentrated emulsions where the internal phase occupies more than 74 vol% of the emulsions [3,4,13]. HIPEs are commonly stabilized against coalescence by large fractions (5–50 vol%) of non-ionic surfactant, although some HIPEs stabilized by < 1.0 wt.% sole cationic surfactant have been prepared [14,15].

Particle-stabilized emulsions, also known as Pickering emulsions, [16] seem a good choice to prepare polyHIPEs without surfactants. The addition of particles not only potentially stabilizes emulsion templates but may also produce a number of benefits in the resulting polyHIPEs which are not achievable when using conventional low-molecular-weight surfactants, for example, functionalizing the void walls of the polyHIPEs, and enhancing the surface roughness for a variety of applications in the future [17,18].

Although considerable progress has been made on preparation of Pickering emulsions, most of previous reports on Pickering emulsions deal with emulsions for which the volume fractions of internal phases are less than 70 vol% [16]. Kralchevsky et al. [19] developed a thermodynamic model, and predicted that Pickering emulsions will phase-invert above an internal phase volume fraction of 50 vol%. Actually, phase inversion is usually observed at an internal phase volume fraction of 70 vol% after kinetic factors are considered. Binks et al. [20,21] have experimentally demonstrated that Pickering emulsions phase-invert between volume fractions of 65 and 70 vol%. Recently, Colver et al. [18] prepared poly(styrene/divinylbenzene) (P(St/DVB)) based polyHIPEs from water-in-oil(w/o) emulsion templates that are stabilized by crosslinked polymer particles. However, these emulsion templates were prepared by forced sedimentation and centrifugation of Pickering emulsions with original internal phase < 50 vol%. Bismarck and coworkers [17,22,23] reported on the preparation of styrene/divinylbenzene (St/DVB) formation based w/o emulsions stabilized by inorganic particles such as carbon nanotubes, titania nanoparticles, and functionalized silica nanoparticles with up to 60, 85, and 92 vol% internal phase, respectively. Silverstein et al. [24] reported the synthesis of crosslinked polyacrylate polyHIPEs based on Pickering HIPEs stabilized using silane-modified silica nanoparticles. The effects of the nanoparticle content, the silane content, the silane's chemical structure, the intensity of mixing, and the locus of initiation on the porous structure were discussed. Zhang et al.

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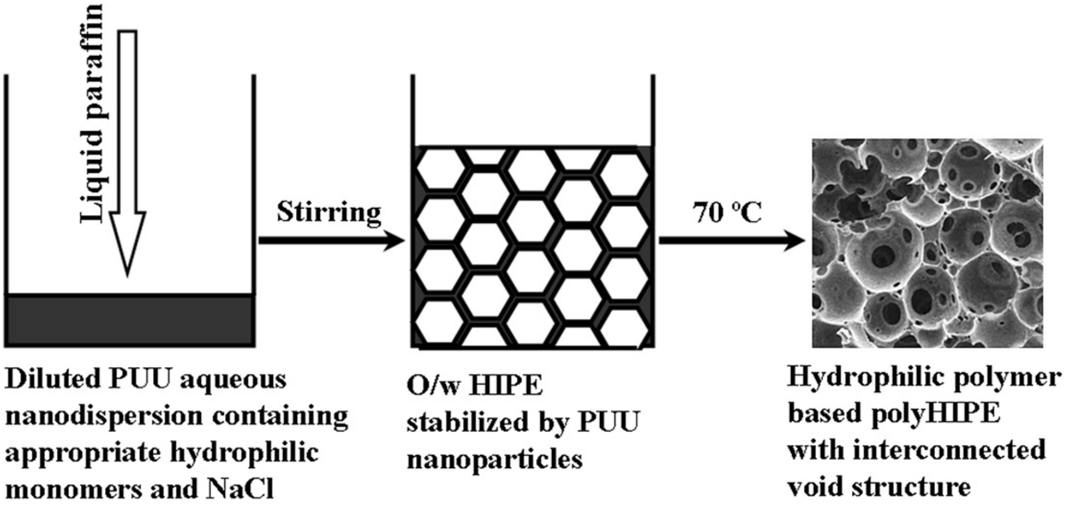

Scheme 1. Preparation of o/w HIPE and its resulting polyHIPE using PUU aquoeus dispersion as aqueous phase.

[25] prepared a series of poly(methyl methacrylate) (PMMA) based polyHIPEs using w/o HIPE templates. The copolymer particles [26] that could partially dissolve in the organic phase were used as stabilizer. However, few work concerning oil-in-water(o/w) Pickering HIPEs and Pickering HIPEs templated hydrophilic polymer based polyHIPEs were reported. Hydrophilic polymer based polyHIPEs have widely attracted attention due to their potential applications such as scaffolds for tissue engineering and control release [27–31]. Arditty et al. [32] described silicone oil-in-water Pickering emulsions with up to 90 wt.% internal phase using hydrophilic silica particles. Ngai and coworkers [33] reported o/w Pickering HIPEs with internal phase volume fraction up to 90 vol% using poly(N-isopropylamide)-*co*-(methacrylic acide) (PNIPAM-*co*-MAA) as sole stabilizer. They prepared porous polymers by drying the Pickering HIPEs in air. Whereas, these o/w Pickering HIPEs were prepared by homogenizing at 13,500 rpm, which limits the fabrication of polyHIPEs on large scale. Furthermore, to prepare the hydrophilic polymer based polyHIPEs, the particles synthesized by polymerization of the corresponding hydrophilic monomers were required. The synthesis of particles that can be used to stabilize HIPEs requires additional strict control over the reaction chemistry, which may be challenging. Hence, the fabrication of porous materials using polymerization of hydrophilic monomers in the HIPEs templates that are prepared with low-energy emulsification and easily extended to a wide variety of chemical compositions is highly desired.

Table 1
Synthesis of o/w Pickering emulsion-templated polymers using PUU particles as sole stabilizer.

Sample[a]	C_{PUU}[b] [wt.%]	C_{NaCl}[c] [mol l^{-1}]	$F_{internal}$[d] [vol%]	D[e] [μm]	d[f] [μm]	Yield [wt.%]
a	8	0.2	86	74.2	13.2	96.4
b	12	0.2	86	41.4	7.4	97.2
c	16	0.2	86	22.4	4.7	96.6
d	12	0.1	86	62.6	12.4	96.8
e	12	0.3	86	50.8	12.6	96.4
f	12	0.2	80	10.6	1.5	97.5
g	12	0.2	92	82.6	14.2	96.2

[a] The aqueous phase containing AM and MBAM of 5 and 0.5 mol l^{-1} respectively.
[b] PUU content, relative to the aqueous phase.
[c] NaCl concentration, relative to the aqueous phase.
[d] Internal volume fraction of the HIPEs.
[e] Average void diameter, calculated from SEM images.
[f] Average interconnecting pore diameter determined by Hg porosimetry.

In this work, stable o/w Pickering HIPEs with internal phase fractions of up to 95 vol% were prepared using poly(urethane urea) (PUU) nanoparticles as sole stabilizer. The emulsification was carried out under gentle stirring between 400 and 800 rpm. Furthermore, the Pickering HIPEs as emulsion templates were used to synthesize hydrophilic polymer based polyHIPEs with acrylamide (AM) and *N,N*-methylene bisacrylamide (MBAM) as monomers. The PUU nanoparticles were from PUU aqueous nanodispersions [34]. The PUU nanoparticles used herein not only potentially stabilize the emulsion templates but may also introduce other benefits to the resulting polyHIPEs including, for example, biocompatibility, [35] improved mechanical property [36] which would be of interest for 3D cell culture and tissue engineering scaffold applications [37].

2. Experimental

2.1. Materials

Difunctional poly(neopentylene adipate) polyol (P756; hydroxyl number = 56 mg of KOH/g) was produced by Qingdao Yutian Chemical Co. and was dried in vacuo at 110 °C for 2 h. Dimethylpropionic acid (DMPA) was provided by Perstop Co. and was dried in vacuo at 60 °C for 24 h. Isophorone diisocyanate (IPDI) was supplied by Hüls Co. AM (97%, Aldrich), MBAM (98%, Aldrich) and sodium chloride (NaCl, Merck) were used as received. Ammonium persulphate (APS, 98%, Shanghai Lingfeng Chemical Reagent Ltd. Co.) was purified via recrystallization. Other materials were standard laboratory reagents and were used as received, except that *N*-methylpyrrolidone (NMP) and ethylenediamine were treated with 4-Å molecular sieves for over 1 week before use. Water was freshly deionized.

2.2. Preparation and characterization of PUU aqueous nanodispersion

The synthesis and characterization of the PUU aqueous nanodispersion was described earlier [34]. A stoichiometric amount of P756, DMPA (dissolved in NMP), and IPDI ([NCO]/[OH] = 1.8, molar ratio) were charged into a 250 ml, four-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a condenser, and a thermometer, and the mixture was reacted at 85 °C for 4 h until the theoretical NCO value was reached. The obtained NCO-terminated

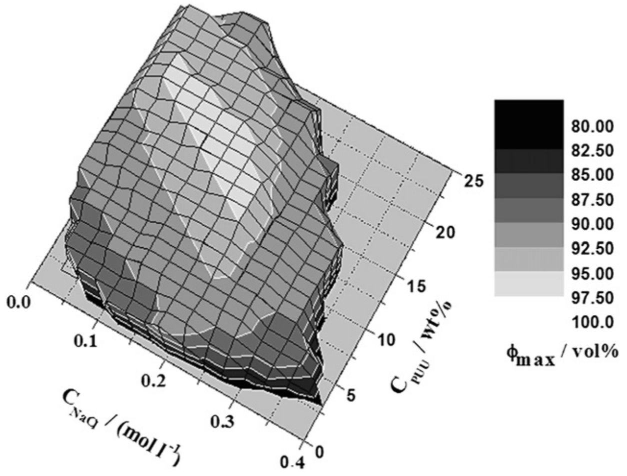

Fig. 1. Upper limit of the internal phase volume fraction (φ_{max}) as function of PUU nanoparticles concentration (C_{PUU}) and NaCl concentration (C_{NaCl}) relative to the aqueous phase of the o/w Pickering HIPEs.

prepolymer was neutralized by addition of tertiary amine at 45 °C for 30 min and then dispersed into deionized water under vigorous stirring at 40 °C. PUU aqueous nanodispersion was prepared after chain extension by the dropwise addition of ethylene amine. The concentrations of DMPA and hard segments in the aqueous nanodispersion were 4 and 37.5 wt.% (based on the total mass of PUU), respectively. This PUU aqueous nanodispersion had a solid concentration of about 33 wt.%.

The particle size and distribution of the PUU nanoparticles in the aqueous dispersion were measured with a Beckman Coulter LS230 particle size analyzer. The average particle size and its polydispersity of the PUU nanoparticles were 52 nm and 0.11 respectively, as determined from dynamic light scattering (DLS, see Figure S1 in Electronic Supplementary Material).

2.3. Preparation and characterization of HIPE and polyHIPE

The preparation of polyHIPE could be summarized as Scheme 1. The PUU aqueous nanodispersion above was diluted by added deionized water to target a given PUU concentration. And appropriate amount of NaCl was added to the diluted PUU aqueous nanodispersion to target a given NaCl concentration. For example, in order to get 3 ml aqueous phase containing PUU of 12 wt.% and NaCl of 0.2 mol l^{-1}, 2.55 g freshly deionized water was added to 1.45 g original PUU aqueous dispersion, Then 3 ml of the diluted PUU aqueous dispersions was transferred into a 100 ml beaker, and 0.0351 g (0.6 mmol) NaCl was added to the beaker. Thus, 3.0 ml aqueous phase containing PUU of 12 wt.% and NaCl of 0.2 mol l^{-1} was obtained. The diluted PUU aqueous nanodispersion containing NaCl, as aqueous phase, was added to a 100 ml beaker and stirred with a magnetic stirrer at 400 rpm. Then appropriate amount of liquid paraffin as oil phase was added dropwise to the aqueous phase to target the given internal phase volume fraction while stirring at 400 rpm. The mixture was stirred further at 800 rpm for 5 min after the addition of oil phase was completed, then the HIPE was obtained. The total volume of each HIPE was 30 ml. For example, Pickering HIPEs with internal phase volume fraction of 90 vol% was prepared as following. Twenty seven ml liquid paraffin as oil phase was dropwise added to 3 ml aqueous phase while stirring at 400 rpm. The aqueous phase contained 0.2 mol l^{-1} NaCl and 12.0 wt.% PUU nanoparticles. After the addition of oil phase was completed, the emulsion was stirred at 800 rpm for 5 min, then Jelly-like o/w emulsion was formed. The emulsion could be stable for more than one week at room temperature (See Figure S2 in Electronic Supplementary Material).

To prepare hydrophilic polymer based polyHIPEs, AM, MBAM and APS of 5, 0.5 and 0.018 mol l^{-1}, respectively, were added to the aqueous phases before the oil phases were added (see Table 1 for summary). After the HIPEs were prepared, they were transferred into molds and polymerized at 50 °C in oven for 24 h. The resulting polyHIPEs were immersed in cyclohexane for 24 h and then in acetone for 24 h. The immersion was repeated for 3 times. Finally, the polyHIPEs was dried under vacuum at 50 °C.

The optical microscopy images of HIPEs were taken on a Nikon Optical Rheology Microscope (LV100POL, Nikon). The morphology of polyHIPEs was detected by a JSM-6360LV SEM. The average void diameters and its distribution of the polyHIPEs were performed using the image analysis software Image J (NIH image, the details were shown in Electronic Supplementary Material). Average interconnecting pore diameters were recorded by mercury (Hg) intrusion porosimeter using a Micromeritics Autopore IV 9500 porosimeter. Samples were subjected to a pressure cycle starting at approximately 0.1 psia, increasing to 33,000 psia in predefined steps to give interconnect diameter [15]. The polymerization yields of polyHIPEs were determined by gravimetric method (The details were shown in Electronic Supplementary Material).

3. Results and discussion

Changes in the oil:water ratio, particle and electrolyte concentration are major role in destabilization of Pickering HIPEs [17,18,22–25] In this work, the influence of particle and NaCl

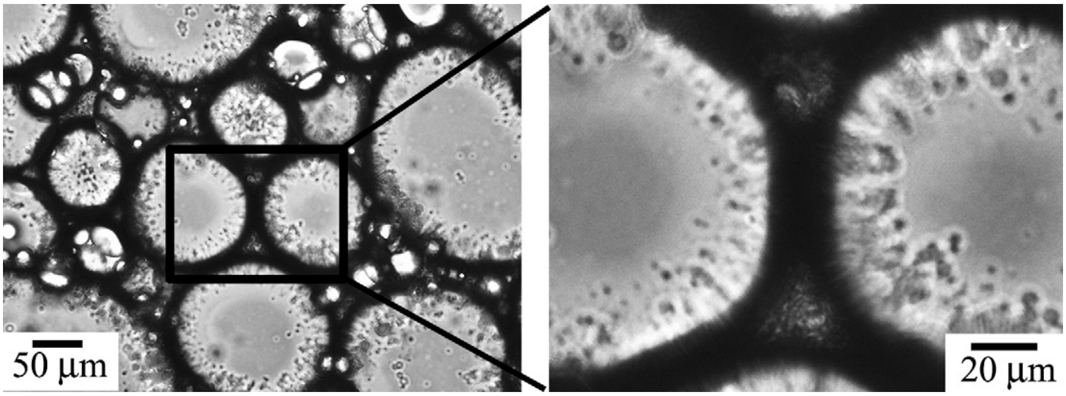

Fig. 2. Optical microscope images of o/w HIPE stabilized by PUU nanoparticles of 12.0 wt.%. The internal volume fraction of the HIPE was 90 vol%.

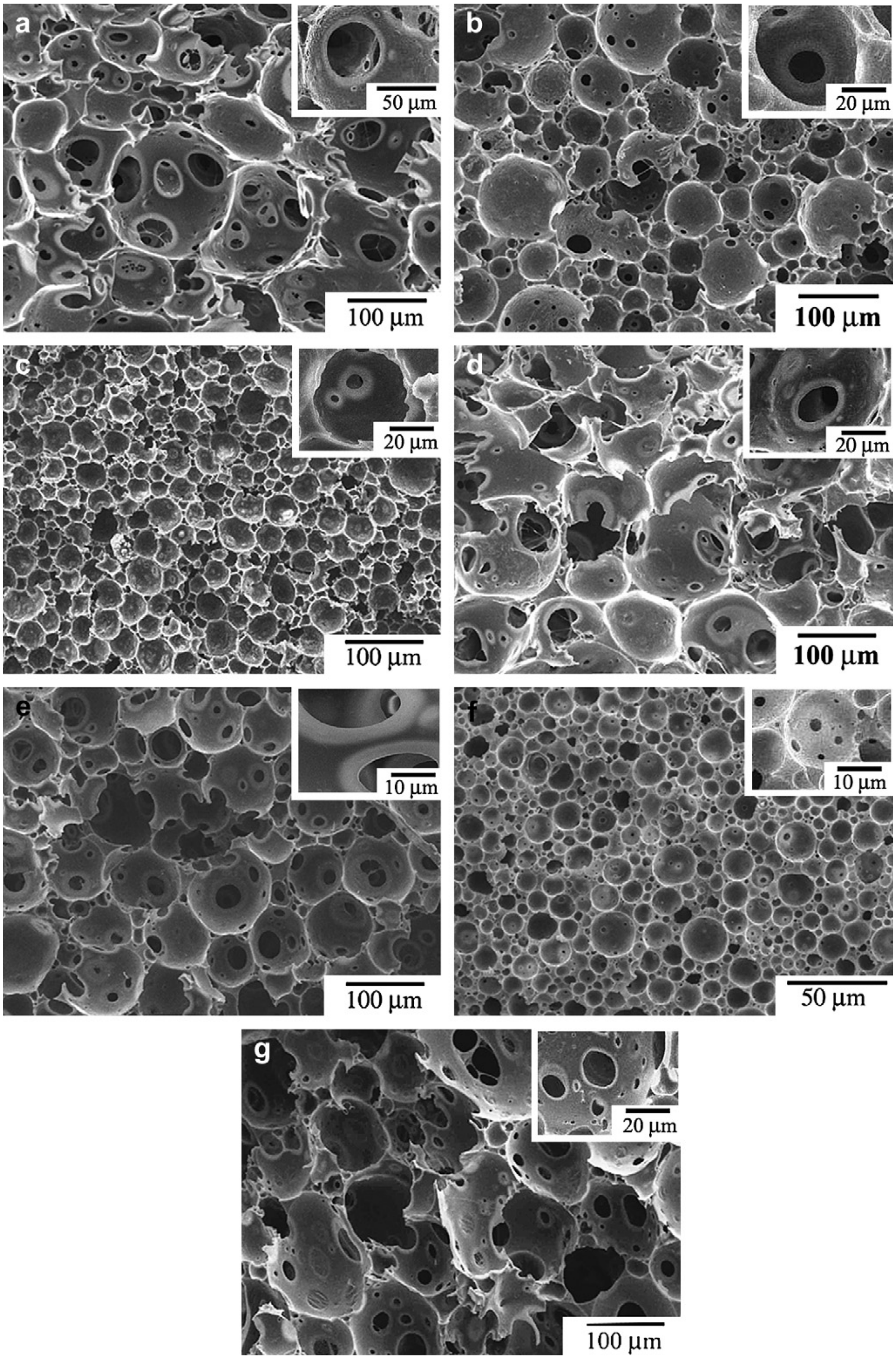

Fig. 3. SEM images of hydrophilic polymer based polyHIPEs derived from o/w Pickering HIPEs a–g. The details of feed components of HIPEs a–g are shown in Table 1.

concentration on the emulsion stability were investigated, as well as the upper limit of internal phase volume fraction within the emulsions. Stable o/w Pickering HIPEs using liquid paraffin as organic phase were obtained in a wide rang of NaCl concentration (C_{NaCl}, from 0.025 to 0.4 mol l^{-1}, relative to the aqueous phase) and PUU nanoparticles concentration (C_{PUU}, from 1 to 25 wt.%, relative to the aqueous phase) (Fig. 1). Binks et al. [38] reported that stable emulsions can only be formed if the particles are weakly flocculated to some extent, achieved by addition of salt. When the C_{NaCl} was less than 0.025 mol l^{-1}, HIPEs was not formed due to the high hydrophilicity of PUU particles. Whereas, when the C_{NaCl} was more than 0.4 mol l^{-1}, the HIPE could not be prepared because of the complete flocculation of the particles before preparation of the emulsions (See Figure S3 in Electronic Supplementary Material). Futhermore, decreasing C_{PUU} to 0.5 wt.% resulted in phase destabilization of the HIPE (See Figure S4 in Electronic Supplementary

Material), which was most likely arisen from the lack of sufficient numbers of particles that are required to act as a mechanical barrier to droplet coalescence. While, when high C_{PUU} (such as 26 wt.%) was used, only the emulsions with upper limit of the internal phase volume fraction $\leq$ 70 vol% could be formed. Further addition of liquid paraffin to the emulsion resulted in a highly viscous emulsion surrounded by liquid paraffin (See Figure S5 in Electronic Supplementary Material).

With delicate selecting C_{PUU} (between 8 and 16 wt.%) and C_{NaCl} (between 0.075 and 0.225 mol l^{-1}), the Pickering HIPEs could be prepared with upper limit of the internal phase volume between 95 and 97 vol% (Fig. 1), this value is much higher than the reported Pickering HIPEs [17,18,22–24,26–31]. Such a high upper limit of the internal phase volume may be attributed to the combination of two effects. Firstly, PUU particles adsorbed at the oil–water interface and remain there forming a dense film around the dispersed droplets against coalescence. Secondly, there are 3D network of particle-filled films surround the aqueous phase droplets (Fig. 2), which led to a significant increase of the continuous phase viscosity.

When the PUU aqueous nanodispersions containing AM and MBAM respectively of 5 and 0.5 mol l^{-1} were used as continuous phases, it was found that the corresponding emulsions were still stable to coalescence. Unlike the close structure of the reported polyHIPEs that based on Pickering HIPEs, [17,18,22,23] the polymerization of the continuous phase of emulsions herein resulted in polyHIPEs with clear open porous network structure (Fig. 3, Table 1). The clear open porous network structure makes the materials interesting for a wide range of applications [3,4]. The polymerization yields were high (in the range of 96–97 wt.%, Table 1), and were nearly not affected by the emulsion preparation conditions.

It was found that with increase of PUU content in the aqueous phase from 8 to 12 and 16 wt.%, the average void diameter of the resulting polyHIPEs decreased respectively from 74.2 to 41.4 and 22.4 μm, and the average interconnecting pore diameter decreased respectively from 13.2 to 7.4 and 4.7 μm (Table 1). With increase of PUU content in the aqueous phase, more particles can be used to stabilize the emulsions, which enhanced the stabilization of the emulsions, and thus decreased the average void diameter of the resulting polyHIPEs, and narrowed the void diameter distribution (Fig. 4).

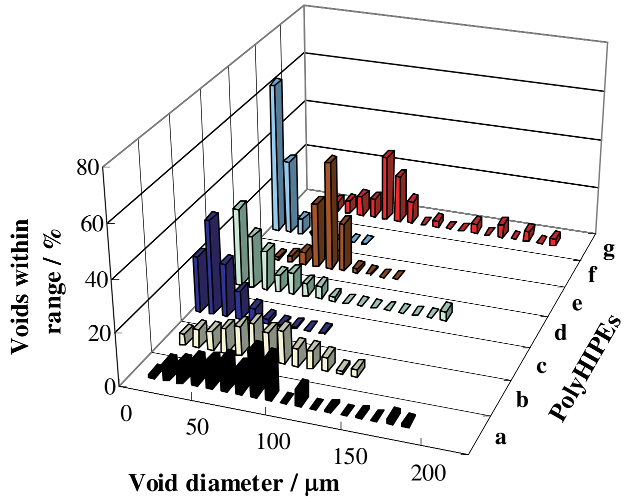

Fig. 4. Void diameter distributions of polyHIPEs a–g.

The influence of NaCl concentration in the aqueous phase on the morphology of the resulting polyHIPEs was investigated. Increasing NaCl concentration from 0.1 to 0.2 mol l^{-1} decreased the average void diameter of the polyHIPEs from 62.6 to 41.4 μm. However, further increasing NaCl concentration from 0.2 to 0.3 mol l^{-1} caused an increase of the average void diameter (from 41.4 to 50.8 μm, Table 1). This can be attributed to the aggregation of the PUU particles caused by the presence of NaCl. The phenomena also confirmed that flocculation of particles to some extent caused by addition of salt is beneficial for formation of stable emulsions. However, further addition of salt caused completely flocculation of the PUU nanoparticles, which resulted in less stable emulsions [16]. Although the average void diameter was affected by changing NaCl concentration, the average interconnecting pore diameter nearly unchanged with varied NaCl concentrations (Table 1).

Changing internal phase fraction from 80 to 86 and 92 vol% was also investigated. It was found that increasing internal phase fraction of the Pickering emulsions increased the average void diameters of the resulting porous polymers (Table 1), and broadened the void diameter distribution (Fig. 4). When the internal phase was increased, it could be envisaged that because of the larger surface over which the PUU particles had to spread and taking into account that the amount of PUU particles (kept constant relative to the continuous phase) decreased, the Pickering HIPE stability decreased [2,16]. Decreasing HIPE stability resulted in a larger average droplet size, and thus caused a larger average void diameter and broader void diameter distribution. At the same time the skeletal framework (continuous phase in HIPEs) of the polyHIPEs became progressively thinner, which caused a concomitant thinning of the film of continuous phase around the droplets. As a result, increasing internal phase volume fraction caused an increase in average interconnecting pore diameter (Table 1).

4. Conclusion

Stable o/w Pickering HIPEs having an internal phase of up to 95 vol% were prepared using PUU aqueous nanodispersion as aqueous phase and with a low-energy emulsification method (just simple strring). The PUU particles are effectively adsorbed onto the oil–water interface to hinder droplet coalescence. In addition, open porous hydrophilic polymer based polyHIPEs were obtained, which means that it is now possible to prepare hydrophilic polymer foams using o/w Pickering HIPEs as templates. Moreover, the morphology of the hydrophilic polymer foams can be tailored easy by changing the oil:water ratio, particle and NaCl concentration.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.06.008

References

[1] Bamfield HA, Copper J. In: Becher P, editor. Encyclopedia of emulsion tech., vol. 3. New York: Marcel Dekker; 1988. p. 281–306.
[2] Cameron NR, Sherrington DC. Adv Polym Sci 1996;126:163–214.
[3] Cameron NR. Polymer 2005;46:1439–49.
[4] Zhang H, Cooper AI. Soft Matter 2005;1:107–13.
[5] Akay G, Birchand MA, Bokhari MA. Biomaterials 2004;25:3991–4000.

[6] Bokhari M, Carnachan RJ, Przyborski SA, Cameron NR. J Mater Chem 2007;17:4088–94.
[7] Zhao C, Danish E, Cameron NR, Kataky R. J Mater Chem 2007;17:2446–53.
[8] Féral-Martin C, Birot M, Deleuze H, Desforges A, Backov R. React Funct Polym 2007;67:1072–82.
[9] Mercier A, Deleuze H, Maillard B, Mondain-Monval O. Adv Synth Catal 2002;344:33–6.
[10] Zhang S, Chen J, Perchyonok VT. Lett Org Chem 2008;5:304–7.
[11] Ottens M, Leene G, Beenackers A, Cameron NR, Sherrington DC. Ind Eng Chem Res 2000;39:259–66.
[12] Krajnc P, Leber N, Štefanec D, Kontrec S, Podgornik A. J Chromatogr A 2005;1065:69–73.
[13] Lissant KJ, editor. Emulsions and emulsion technology part 1. New York: Marcel Dekker Inc; 1974.
[14] Zhang S, Chen J. Polymer 2007;48:3021–5.
[15] Zhang S, Chen J, Perchyonok VT. Polymer 2009;50:1723–31.
[16] Binks BP. Curr Opin Colloid Interface Sci 2002;7:21–41.
[17] Menner A, Ikem V, Salgueiro M, Shaffer MSP, Bismarck A. Chem Commun; 2007:4274–6.
[18] Colver PJ, Bon SAF. Chem Mater 2007;19:1537–9.
[19] Kralchevsky PA, Ivanov IB, Ananthapadmanabhan KP, Lips A. Langmuir 2005;21:50–63.
[20] Binks BP, Lumsdon SO. Langmuir 2000;16:2539–47.
[21] Binks BP, Lumsdon SO. Langmuir 2000;16:8622–31.
[22] Menner A, Verdejo R, Shaffer M, Bismarck A. Langmuir 2007;23:2398–403.
[23] Ikem VO, Menner A, Bismarck A. Angew Chem Int Ed 2008;47:8277–9.
[24] Gurevitch I, Silverstein MS. J Polym Sci Part A Polym Chem 2010;48: 1516–25.
[25] Zhang S, Chen J. Chem Commun; 2009:2217–9.
[26] Zhang S, Chen J, Taha M. J Appl Polym Sci 2009;114:1598–605.
[27] Zhang H, Cooper AI. Chem Mater 2002;14:4017–20.
[28] Krajnc P, Štefanec D, Pulko I. Macromol Rapid Commun 2005;26:1289–93.
[29] Kovačiči S, Štefanec D, Krajnc P. Macromolecules 2007;40:8056–60.
[30] Fernández-Trillo F, van Hest JCM, Thies JC, Michon T, Weberskirch R, Cameron NR. Adv Mater 2009;21:55–9.
[31] Barbetta A, Dentini M, De Vecchis MS, Filippini P, Formisano G, Caiazza S. Adv Funct Mater 2005;15:118–24.
[32] Arditty S, Whitby CP, Binks BP, Schmitt V, Leal-Calderon F. Eur Phys J E 2003;11:273–81.
[33] Li Z, Ming T, Wang J, Ngai T. Angew Chem Int Ed 2009;48:8490–3.
[34] Su T, Wang GY, Xu XD, Hu CP. J Polym Sci Part A Polym Chem 2006;44:3365–73.
[35] Lin DT, Young TH, Fang Y. Biomaterials 2001;22:1521–9.
[36] Lépine O, Birot M, Deleuze H. Polymer 2005;46:9653–63.
[37] David D, Silverstein MS. J Polym Sci Part A Polym Chem 2009;47:5806–14.
[38] Binks BP, Lumsdon SO. Phys Chem Chem Phys 1999;1:3007–16.