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Covalent incorporation of the surfactant into high internal phase emulsion templated polymeric foams†

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High internal phase emulsions of water in cyclooctene stabilised by sorbitan monooleate (Span 80) were cured by ring-opening metathesis polymerisation to release fully open macroporous polymer foams wherein the surfactant was covalently incorporated into the poly(cyclooctene) strands via chain transfer reactions.

High internal phase emulsion (HIPE) templating has become a powerful method for preparing macroporous polymeric foams.¹ In this approach the continuous phase of the HIPE, consisting of monomers, is cured and the internal phase as well as the surfactant used to stabilize the HIPE is removed after curing to release, in many cases, a fully open macroporous polymer scaffold (often termed polyHIPE). A polyHIPE features pores (also termed cells or voids) and typically windows (also termed interconnecting pores or holes). The pores originate from removal of the internal phase, and pore formation is a direct consequence of HIPE templating. Windows are formed after or during solidification of the monomer phase, and their formation is dependent on the surfactant content in the HIPE-formulation² and on the locus of initiation.³ In water in oil (w/o) emulsions an oil-soluble initiator is preferably producing open porous architectures while water soluble initiators rather create closed porous foams.^{4,5} The latter factor was not recognized for a long time, probably because in the most widely studied polyHIPE formed by radical polymerization of water in styrene/divinylbenzene emulsions stabilized with sorbitan monooleate (Span 80) as a surfactant, and a water soluble initiator (K₂S₂O₈) the openness is hardly dependent on the locus of initiation.⁶ The open porous structure is indispensable for most of the applications of polyHIPE materials such as

tissue engineering, solid phase support for catalysis, and membranes for separation purposes or water purification.⁷ Further, many applications demand surface functionalization of the intrinsically hydrophobic scaffold (as long as w/o HIPEs are considered), which is usually achieved by postpolymerisation transformations^{1,8} or hybrids formation.⁹ Recently, Battaglia *et al.* demonstrated the use of amphiphilic block copolymers as surfactants for w/o HIPEs in which the final surface chemistry is defined by the hydrophilic block segment(s), *i.e.* the surfactant is not removed during purification due to the entanglement of the lipophilic block segments in the polymeric scaffold which prevents leaching of the surfactant.⁴

Herein, we extend this concept and use a HIPE formulation which enables covalent incorporation of the surfactant into the foam's macromolecular scaffold during curing. Key for this endeavour is the use of ring-opening metathesis polymerisation (ROMP)¹⁰ to cure strained cyclic olefinic monomers (as the continuous phase) and a surfactant with double bond(s) in the structure (in particular in its lipophilic part) which is capable to act as a chain transfer agent (CTA). Because ROMP is fast due to ring strain release, it can be anticipated that the oil phase is polymerized in the first instance and in the later stage the surfactant molecules, residing at the oil-water interface, are incorporated into the macromolecules.¹¹ For the sake of demonstration of the proposed concept we did not use the dicyclopentadiene (DCPD) based HIPEs which result in instantly crosslinked, *i.e.* insoluble polymer foams (of intriguing mechanical properties),¹² but cyclooctene (COE) based HIPEs which upon curing result in soluble polymers,¹³ allowing for a better characterization of the underlying chemical processes.

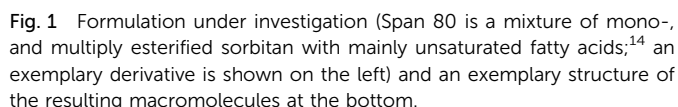
Span 80 (see Fig. 1) was selected as the surfactant since it is able to stabilize w/o HIPEs,⁶ and due to its unsaturated nature of the lipophilic part(s) (at this point it is to state that the common trivial name sorbitan monooleate is misleading since Span 80 is actually a complex mixture of mono- and multiply fatty acid esterified sorbitan; typical fatty acids are oleic (approx. 70%), linoleic and palmitic acid).¹⁴

In this respect, the COE HIPEs were first prepared by mixing COE (20 vol%) as the monomer, deionized water (80 vol%) as

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the internal droplet phase and Span 80 (10, 20 and 30 vol% according to COE) as the surfactant under continuous mechanical stirring. Thus obtained white creamy emulsions were then

cured upon addition of the oil-soluble ROMP initiator **M20**¹⁵ (0.3 wt% according to COE, dissolved in 0.1 mL of toluene) at 20 °C for 20 h, whereupon the samples solidified. The resulting monolithic specimens were removed from the corresponding mould, purified by Soxhlet extraction with acetone (3 d) and finally dried under vacuum. The white and brittle monoliths were first investigated by scanning electron microscopy (SEM), revealing the expected typical open cellular polyHIPE architecture in the case of **pCOE_{sp10}** (*cf.* Fig. 2A), featuring pores (average diameter = $3.7 \pm 1.1 \mu\text{m}$) and interconnected windows (average diameter = $1.1 \pm 0.3 \mu\text{m}$). The micrographs of **pCOE_{sp20}** and **pCOE_{sp30}** (Fig. 2B and C) showed open porous architectures reminiscent of a polyHIPE structure. Even though the structural features in these specimens were more blurred, most likely due to the loss of low molar mass polymeric species during purification, bigger pores and bigger windows than those present in **pCOE_{sp10}** were found (*cf.* Table 1). The skeletal density of all three specimens is similar and their surface area decreases from $6.5 \text{ m}^2 \text{ g}^{-1}$ in the case of **pCOE_{sp10}** to $1.5 \text{ m}^2 \text{ g}^{-1}$ in the case of **pCOE_{sp30}** (Table 1).

In order to evaluate the role of Span 80 and demonstrate the influence of the metathesis/chain transfer polymerization the HIPEs were stabilized also with a non-ionic surfactant that does not contain double bond(s) in the structure. First, we tried to prepare COE HIPEs with Span 60 as the closest equivalent to Span 80 since it contains mainly saturated fatty acids in the structure. Surprisingly, it turned out that Span 60 is not suitable for stabilizing the water in COE HIPE since phase separation occurred already during agitation of the formulation. Further attempts were made

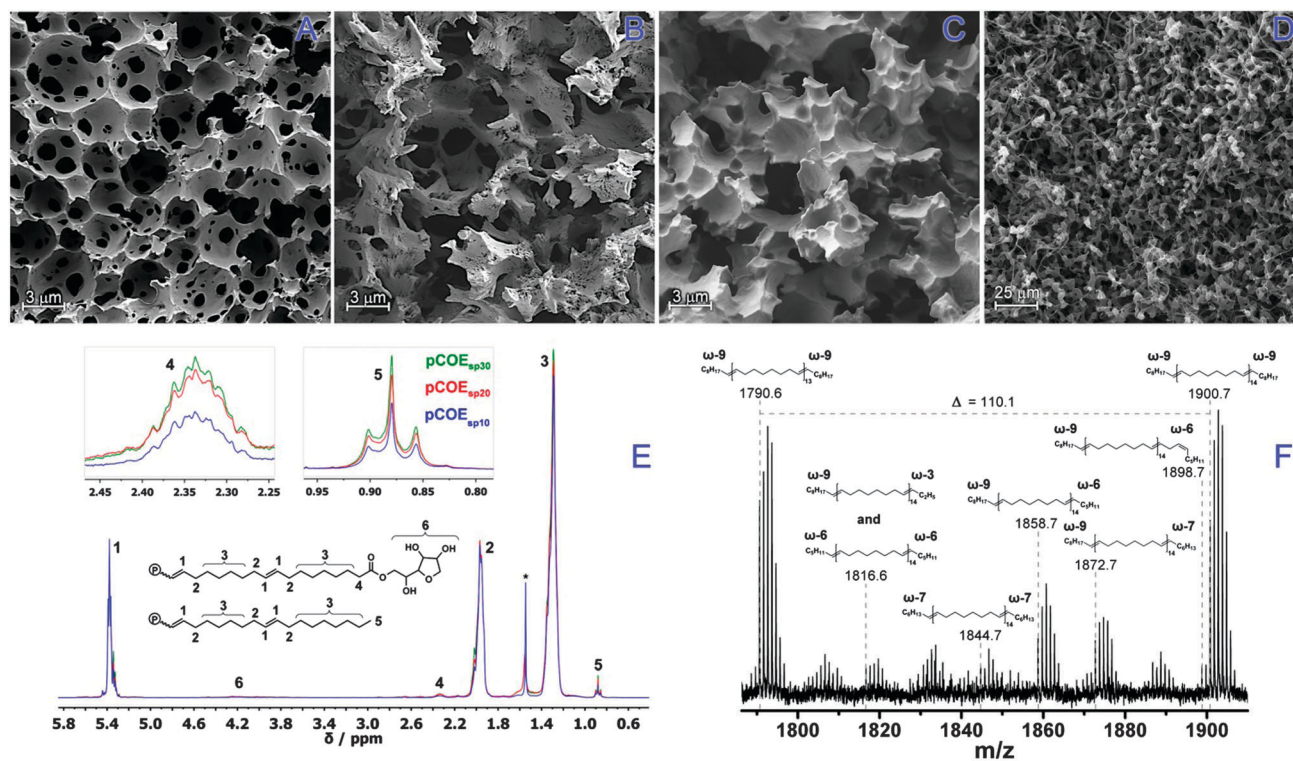


Fig. 2 (above) Scanning electron micrographs of (A) **pCOE_{sp10}**, (B) **pCOE_{sp20}**, (C) **pCOE_{sp30}** and (D) **pCOE_{pl}**; (below) (E) ¹H-NMR spectra of purified **pCOE_{sp10}–pCOE_{sp30}** with peak assignment and two insets showing a magnification of the signals 4 and 5; and (F) detail of the MALDI-TOF mass spectrum of purified **pCOE_{sp30}** ionized with the aid of silver trifluoroacetate showing several distributions of poly(COE) with different end groups.

Table 1 Characterisation data of poly(COE) polyHIPEs

	pCOE _{sp10}	pCOE _{sp20}	pCOE _{sp30}	pCOE _{pl}
Av. window size ^a [μm]	1.1 ± 0.3	1.4 ± 1.8	—	—
Av. pore size ^a [μm]	3.7 ± 1.1	5.5 ± 2.0	4.4 ± 3.1	—
Skeletal density ^b [g cm ⁻³]	0.969	0.977	0.955	n.d.
Surface area ^c [m ² g ⁻¹]	6.5	2.5	1.5	n.d.
Contact angle ^d [°]	70 ± 3	58 ± 3	70 ± 3	91 ± 3
<i>M_w</i> ^e [g mol ⁻¹]	10 500	7600	5100	150 000
PDI ^e (<i>M_w</i> / <i>M_n</i>)	2.4	2.6	2.7	1.4
Polymerization degree ^f (<i>n</i>)	50	37	34	n.d.

^a Estimated from SEM images. ^b Determined by helium pycnometry.

^c Determined by nitrogen adsorption measurements. ^d Determined by contact angle measurements with water. ^e From SEC/MALS measurements. ^f From integration of ¹H-NMR spectra.

with Pluronic L-121 which is known to be a very effective surfactant for the DCPD system.¹² These tries resulted in moderately stable COE HIPEs which were further cured with **M20** as described above. Upon purification, elastic monolithic specimens termed as the pCOE_{pl} were obtained which featured upon SEM analysis, an atypical bicontinuous sausage-like morphology (cf. Fig. 2D).

Having a reference sample at our disposal for which the occurrence of cross-metathesis can be ruled out, we started to analyse the molecular characteristics of the bulk phase of the poly(COE) samples by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), proton nuclear magnetic resonance (¹H-NMR) spectroscopy, size-exclusion chromatography coupled to a multi-angle light-scattering detector (SEC-MALS) and water contact angle measurements. ATR-FTIR analysis of non-purified poly(COE) samples showed the expected absorption band of the C=O stretching vibration representative of Span 80 at 1744 cm⁻¹ (in the case of pCOE_{sp10}–pCOE_{sp30}) and the characteristic absorption of the C–O–C vibration at 1106 cm⁻¹ for Pluronic L-121 (in case of pCOE_{pl}). Purified, i.e. acetone extracted, samples showed the same spectral features in cases of pCOE_{sp10}–pCOE_{sp30}, indicating that the ester moiety was not removed during purification. In contrast, the signal accounting for the presence of Pluronic L-121 was not observed in the FT-IR spectra of extracted pCOE_{pl} samples. ¹H NMR analysis of purified poly(COE) samples pointed into the same direction. While the ¹H NMR spectrum of pCOE_{pl} showed the typical signal pattern of poly(COE) without signs of end-groups (only traces of Pluronic L121 were detected), the spectra of pCOE_{sp10}–pCOE_{sp30} revealed signals assignable to Span 80 substructures (cf. Fig. 2E). Integration of these signals allowed (provided that chain transfer occurred) the estimation of the average polymerization degree (*n*) which is 50 for pCOE_{sp10} (*n* = 50 corresponds to number average molar mass of 5500 g mol⁻¹), while for the pCOE_{sp20} and the pCOE_{sp30} it is 37 and 34, respectively. However, NMR data cannot conclusively prove the occurrence of cross-metathesis. Therefore, SEC-MALS analyses of the raw and purified (before and after extraction) samples were performed. None of the refractive index (RI) traces of the raw and purified samples showed the presence of pure Span 80, except the chromatogram of the unpurified pCOE_{sp30} sample. As a control experiment, 10 wt% of pure Span 80 was added to pCOE_{sp10} and the corresponding SEC-MALS

chromatogram unequivocally showed the presence of free surfactant. The weight average molar mass (*M_w*) of pCOE_{sp10}–pCOE_{sp30} samples decreased with increasing amount of Span 80 from 10 500 to 5100 g mol⁻¹ and the values are distinctly smaller than in the case of pCOE_{pl} sample (150 000 g mol⁻¹). Finally, matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) of pCOE_{sp30} revealed several distributions of poly(COE) with end groups originating from cross metathesis with different unsaturated fatty acid derivatives (see Fig. 2F). The synopsis of all these experiments clearly proofs the incorporation of Span 80 into the polymers.

To gain information on the surface chemistry of such prepared polymer foams their wettability through the contact angle measurements and imbibition in water was investigated (cf. Table 1). A change of contact angle value from approx. 91° for pCOE_{pl} (water contact angle of pCOE films is 87.7°)¹⁶ to values around 60–70° for pCOE_{sp} samples supports the presence of polar groups at the polymer/air interface. Moreover, placing the samples in deionized water resulted in sinking the pCOE_{sp20} sample under the water surface, while the pCOE_{pl} sample was swimming on the surface, thus confirming the hydrophilic character of the pores' surface in case of the pCOE_{sp} samples (cf. Fig. S14, ESI†). However, characterization data prompt that the chain transfer not only occurred at the surface but also within the bulk of the polymer-scaffold. This is easily conceivable since Span 80 is soluble in COE and, particular in cases where high surfactant loading is used, the share of surfactant which is not necessary for stabilizing the w/o interface will be located in the monomer phase and will act as chain transfer agent during ROMP.

We have demonstrated the use of Span 80 as a surfactant for HIPE templating of ROMP-able monomers resulting in the formation of fully open macroporous polymeric foams wherein the surfactant is covalently bound to the polymer matrix. The covalent functionalization of the poly(COE) strands with Span 80 results in increased polarity of the foam's surface. Applications of this fundamental concept to other ROMP-able formulations are currently ongoing in our laboratories.

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