ARTICLE

Branched Macromonomers from Catalytic Chain Transfer Polymerisation (CCTP) as Precursors for Emulsion-Templated Porous Polymers

Christophe J. Atkins,[a] David K. Seow,[a] Gerard Burns,[a] James S. Town,[a] Rachel A. Hand,[a] Daniel W. Lester,[b] Neil R. Cameron,[c] David M. Haddleton[a]* and Ahmed M. Eissa[a,d]*

Efforts in the synthesis of macroporous polymers have mostly been directed towards the formation of stable high internal phase emulsions (HIPEs) from commercially available monomers, limiting their scope of application. Therefore, the development of simple synthetic approaches to access tailor-made macromonomers that can be used as precursors for the formation of HIPEs, allowing the design of new generations of polyHIPE materials with bespoke chemical and physical properties, is desirable in the search for new applications. In this work, cobalt(II) mediated catalytic chain transfer polymerisation (CCTP) is used to polymerise ethylene glycol dimethacrylate (EGDMA), producing muilti vinyl-terminated branched EGDMA polymers with tuneable branching density and degree of unsaturation. These materials are subsequently implemented as macromonomer crosslinking agents for the formulation of HIPEs. The use of acrylate comonomers as propagation promoters is found to be essential and 2-ethylhexyl acrylate (EHA), isobornyl acrylate (IBOA) and 2-methoxyethyl acrylate (MEA) are investigated as comonomers in the formulations to both facilitate the photochemical curing of the HIPEs and to impart material properties to the products. The CCTP derived branched macromonomers are fully charaterised by GPC, ^{1}H-NMR and MALDI-ToF spectroscopy. Scanning electron microscopy (SEM) is used to explore the morphology of the produced materials. Surface wettability experiments are conducted to evaluate the hydrophilicity of the polyHIPE surface. Compression tests are used to investigate the influence of the branching density of the CCTP macromonomers as well as the nature of comonomers on the mechanical properties of the materials.

Introduction

Macroporous polymers have garnered increasing interest over the last few years.[1–4] Such materials can be used for energy and gas storage,[5,6] heat insulation[7] and cell culture[8,9] applications. Emulsion templating has become one of the most favoured ways of obtaining highly porous materials from high internal phase emulsions (HIPEs).[10] HIPEs are emulsions whereby the internal, droplet phase takes up a volume of at least 74% with regards to the continuous external phase. Usually, HIPEs are produced from water-in-oil emulsions, in which case highly porous structures known as polyHIPEs are obtained by polymerising the external phase. PolyHIPEs can be prepared using various synthetic approaches. Deleuze *et al*.[11] used ring-opening metathesis polymerisation of a norbornene derivative to prepare easy to handle, non-brittle polyHIPEs, while Chen *et al*.[12] synthesised thiol-ene/-yne-based polyHIPEs using a commercially available multifunctional thiol with multi-

functional acrylic, allyl ether- or alkyne-based monomers. It has been previously shown that the mechanical properties of polyHIPE materials correlate with the degree of functionality of monomers used. PolyHIPEs made from dipentaerythritol penta-/hexa-acrylate produced more rigid materials compared to those made from 1,6-hexanediol diacrylate.[12] Other reactions such as Diels-Alder and copper-catalysed azide-alkyne cycloaddition 'Click' reactions have been successfully implemented in the preparation of polyHIPE materials.[13,14] Careful consideration in the selection of monomers helps tune
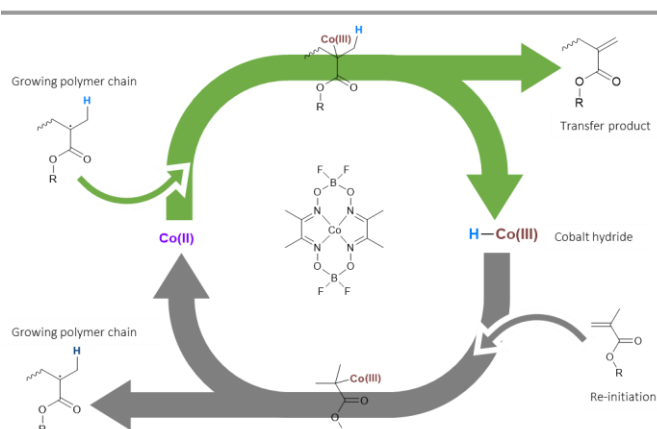
Scheme 1 Polymerisation mechanism for methacrylic monomers utilising a cobaloxime (CoBF) as chain transfer agent.

[a.] Department of Chemistry, University of Warwick, Gibbet Hill, Coventry, CV4 7AL, UK. E-mail: d.m.haddleton@warwick.ac.uk; a.m.eissa@warwick.ac.uk
[b.] Polymer Characterisation Research Technology Platform, University of Warwick, Gibbet Hill, Coventry, CV4 7AL, UK.
[c.] Department of Materials Science and Engineering, Monash University, 22 Alliance Lane, Clayton, Victoria 3800, Australia; School of Engineering, University of Warwick, Coventry, CV4 7AL, UK.
[d.] Department of Polymers, Chemical Industries Research Division, National Research Centre, El Bohouth St. 33, Dokki, Giza 12622, Cairo, Egypt.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x
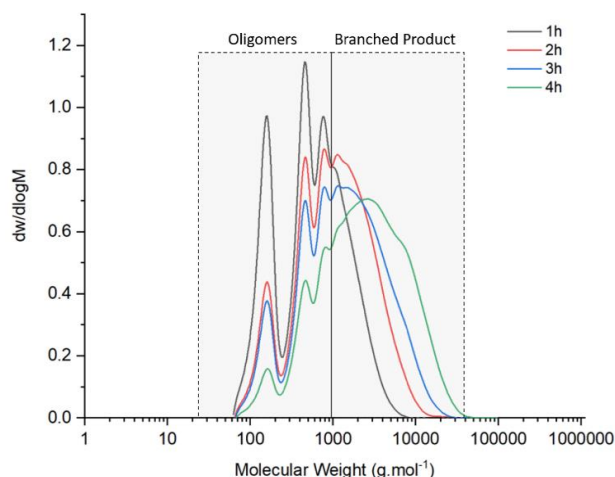
Fig. 1 GPC (CHCl$_3$, 30°C) traces for EGDMA polymerisation monitored hourly from 1 to 4h.

Fig. 3 Evolution of number average molecular weight (M_n) (a) and dispersity (Đ) (b) versus polymerisation time obtained from GPC (CHCl$_3$, 30°C) analysis for the homopolymerisation of EGDMA (**P1**).

the properties of the final polyHIPE material. Therefore, the development of synthetic approaches that allow wider access to designed multifunctional macromonomers and/or crosslinking agents that can be incorporated into the polyHIPE preparation are desirable.

Catalytic chain transfer polymerisation (CCTP) is a facile and interesting controlled polymerisation technique that has been employed for the preparation of low molecular weight functional polymethacrylates.[15–18] This technique relies on the catalytic activity of certain low spin cobalt(II) complexes which have very high chain transfer constants, typically several orders of magnitude higher than conventional thiol chain transfer agents. Much of our current knowledge of CCTP comes from investigations carried out by commercial organisations such as DuPont[19] and ICI/Zeneca,[20,21] complemented in academia by Gridnev,[22,23] Heuts,[24] Davis and Haddleton.[25-26]

The commonly accepted mechanism for a cobaloxime mediated CCTP proceeds *via* a two-step process. A hydrogen atom is first abstracted from a carbon in the α-position to the radical centre of a tertiary polymeric radical. This produces a vinyl terminated
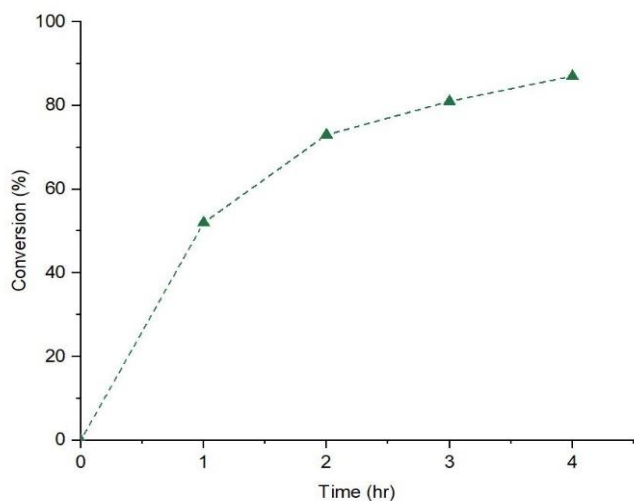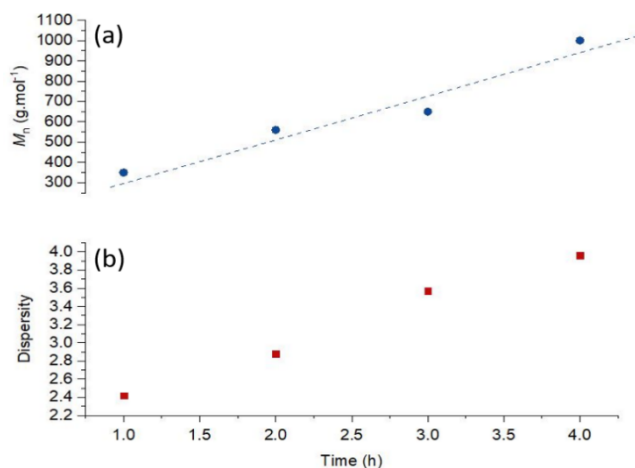
product and a reactive cobalt-hydride Co(III)-H complex able to re-initiate polymerisation through the transfer of the hydrogen to an unreacted monomer, scheme 1. The process is efficient for monomers with an α-methyl substituent, such as methacrylates, weakening the Co-C bond with increased steric hindrance and the thermodynamic stability of the external vinyl group in the product.

McEwan *et al*.[27] for instance utilised CCTP to produce relatively low molecular weight branched polymers containing high levels of terminal vinyl functionalities that showed potential as macromonomers for further chemistries.

The current work was designed to combine CCTP with emulsion templating techniques to produce polyHIPE materials with tuneable properties. CCTP provides control over branching and molecular weight of the CCTP derived branched macromonomer crosslinkers, which would in turn lead to generation of polyHIPE materials where functionality and rigidity can be tightly tailored. To the best of our knowledge, this is the first report of polyHIPE synthesis from CCTP branched macromonomers. In this report, we describe the free radical polymerisation of ethylene glycol dimethacrylate (EGDMA) *via* CCTP to produce vinyl-terminated branched EGDMA-based macromonomers, which are then used as crosslinking agents in the formulation of HIPEs containing various acrylic co-monomers. Photochemical curing of these HIPEs led to well-defined polyHIPE materials. Morphological and mechanical properties of the synthesised materials were studied.

Results and discussion

Branched CCTP macromonomer synthesis

Free-radical polymerisation of multi-vinyl monomers usually yields insoluble crosslinked materials. It can however result in the formation of branched polymers when using chain transfer agents, such as cobaloximes, within a CCTP process. Sherrington and co-workers developed a free radical one-step process to
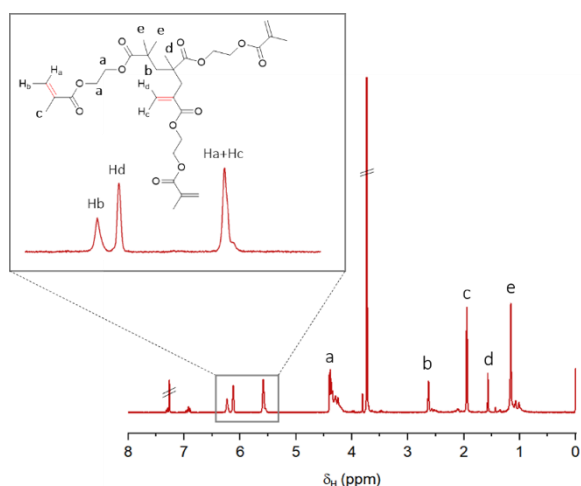

Fig. 2 GC-FID monitored conversion for the homopolymerisation of EGDMA.

Fig. 4 ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of p(EGDMA) branched macromonomers, with detailed zoom in the vinyl functionality area (5.5 – 6.25 ppm).

Table 1 p(EGDMA) branched polymers synthesised for this study.

Polymer	CoBF (mol%)	M_n (g/mol)	M_w (g/mol)	Đ	Conversion (%)	ext_{db}/int_{db}
P1	0.0490	1000	4090	4.0	89.7	1.41
P2	0.0735	650	2150	3.3	92.8	1.21

access branched polymers whereby vinyl monomers are polymerised in the presence of a crosslinking comonomer and balancing levels of a chain transfer agent, often referred to as the ''*Strathclyde methodology*''.[28]

The strategy of balancing the level of a crosslinking comonomer with that of a free-radical chain transfer agent prevents gelation and allows control over the degree of branching to the polymer architecture.[29] However, in this Strathclyde methodology, both large amounts of chain transfer agents are required and adverse organic functionalities (e.g. thiols) are incorporated into the polymer backbone.

Conversely, CCTP offers a convenient and efficient method to control the branching topology of the polymeric product by regulating chain transfer without having to use excessive quantities of chain transfer agent, i.e. ppm levels as opposed to >10 wt%.[30–35] The branched polymers formed from these reactions exhibit low solution viscosity with high surface functionalisation using relatively low levels of chain transfer agents making CCTP an ideal candidate for branched polymer synthesis. Homopolymerisation of EGDMA *via* CCTP has been previously carried out under some specific conditions.[27]

Two different concentrations of CoBF were used for the polymerisation of EGDMA; 0.049 and 0.0735 mol% with respect to EGDMA, table 1. Low molecular weight branched polymers were obtained, along with oligomeric products as seen by GPC, figure 1. As the reaction proceeds, molecular weight and dispersity increase whilst the number of dimers, trimers and oligomeric products decreased accordingly with the increase of branched products. Polymerisation was quenched after four hours while attempts to increase the timeframe of the reaction to 6, 12 and 24 hours, all resulted in gelation. This, along with
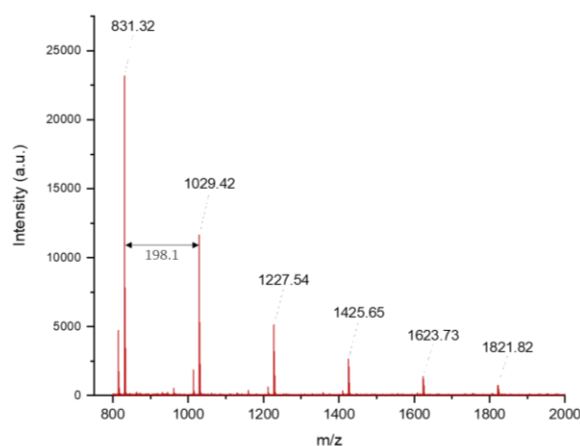

Fig. 5 MALDI-ToF spectrum of branched p(EGDMA) (**P1** macromonomer) synthesised by CCTP.

the drift to higher molecular weight, is indicative of the catalyst being degraded during the reaction. A reaction time of 4 hours was chosen for all subsequent reactions. Conversion of EGDMA to p(EGDMA) was monitored using GC-FID, figure 2.

Rapid monomer consumption was observed within the first hour, which subsequently began to plateau, leading to final conversions of around 90% without observable crosslinking after 4 hours. A linear increase in molecular weight was also observed, reaching values of approximately 4100 g.mol^{-1}, figure 3. As expected, decreasing the concentration of CoBF led to an increase in molecular weight, however, no significant variation in monomer conversion was observed.

^{1}H-NMR spectroscopy confirmed the successful synthesis of the EGDMA branched macromonomers, with external and internal vinyl hydrogen environments characterised by the appearance of peaks observed at 5.6, 6.1 and 6.2 ppm, figure 4. The ratios of external vinyl groups to internal vinylidene were calculated, for p(EGDMA) crosslinker **P1** (see table 1), as approximately 1.40. Similarly, for **P2**, the ratio was calculated to 1.20. Each EGDMA addition to the propagating branched EGDMA provides a further locus from which to branch from as this is a "cascade polymerisation"; hence, the probability of branching increases with molecular weight.

Figure 5 shows a typical matrix assisted laser desorption ionisation–time of flight (MALDI-ToF) spectrum of p(EGDMA). A series of peaks separated by 198.11 Da is observed corresponding to the EGDMA repeat unit. The m/z of the monoisotopic peak, the peak which contains the lowest isotope conformation of all atoms in the species, indicates that each chain contains a number of vinyl terminations equal to the degree of polymerisation plus one. Thus, indicating that the CCTP synthesis has end group fidelity and all crosslinking points have been preserved.

PolyHIPE synthesis

Water-in-oil high internal phase emulsions (HIPEs) were prepared at ambient temperature by the slow addition of deionised water, under constant mechanical stirring, to the continuous organic phase, which contained comonomers,
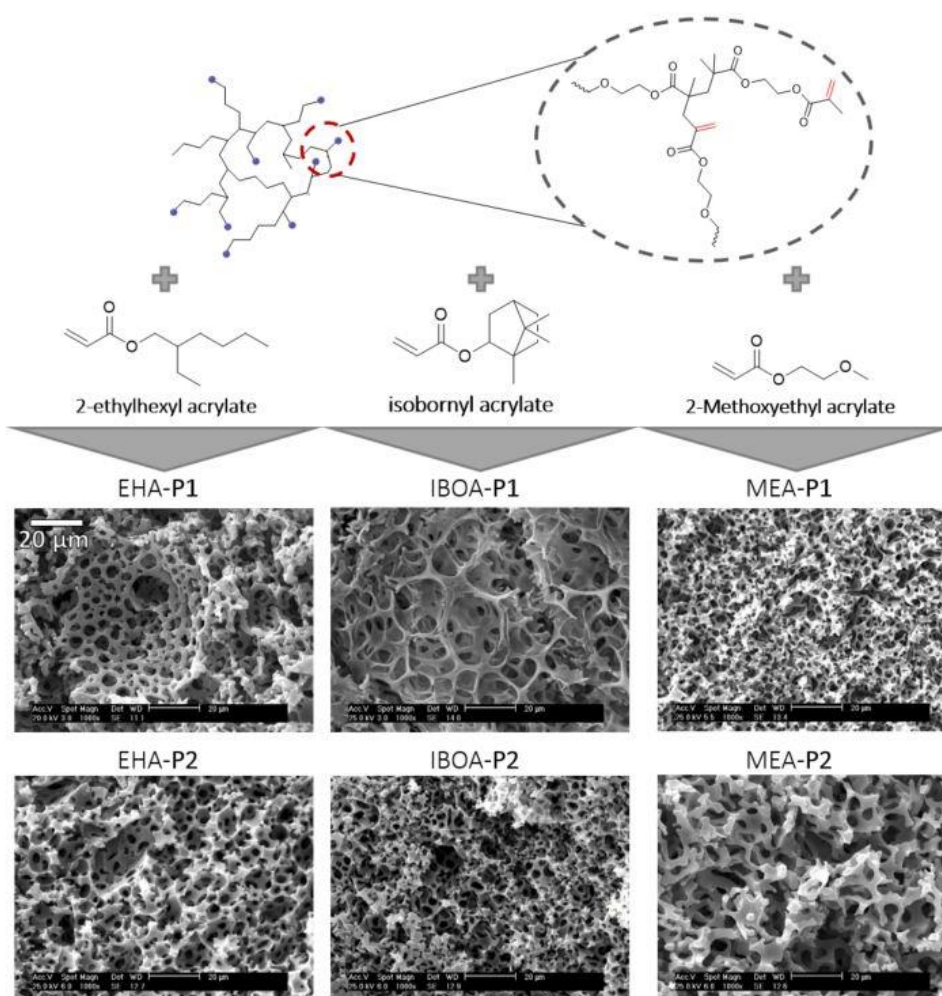
Fig. 6 SEM Images of polyHIPEs synthesised using **P1** or **P2** as cross-linking agents.

surfactant, organic solvent and photo-initiator. A HIPE is achieved when the volume of the internal droplet phase becomes more than >74% of the total emulsion volume.[36] The HIPE internal phase volume fraction (ϕ) used in all preparations was 80% and, following transfer to a mould, the formed HIPEs were cured under UV radiation using a Fusion UV Systems Inc. *Light Hammer® 6* variable power UV curing system with LC6E benchtop conveyor and mercury discharge 'H' bulb that provides broad, high intensity UV light (200 watts/cm).

Branched p(EGDMA) macromonomers (**P1** and **P2**) were used in the preparation of polyHIPEs with the aim of exploiting their vinyl chain ends allowing for the synthesis of highly porous, mechanically stable polymeric networks. Dichloroethane (DCE) has in the past been successfully employed as a porogen in polyHIPE preparation.[37] The optimal porogen to monomer ratio has been previously reported to be between 40-50%, which closely matched the monomer to solvent ratio used in the CCTP of EGDMA. It was therefore reasoned that a one-pot reaction could be employed for the polyHIPE synthesis, which would not only be convenient and cost-effective, but may also lend interesting properties to the material. In order to produce stable HIPEs from EGDMA branched macromonomer, a number

of formulations were tested under various conditions and monomer contents (ESI, table S2). Moreover, due to EGDMA's hydrophilicity making the production of stable HIPEs challenging, UV photochemical curing was chosen over thermal curing as it provided higher reaction rates, thus minimising potential phase separation. In these HIPE formulations, a blend of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and 2-hydroxy-2-methylpropiophenone was used as a photo-initiator and a polymeric surfactant (PEG 30-dipolyhydroxystearate (Hypermer B246); HLB = 4.9) was employed as steric stabiliser, kinetically hindering coalescence and agglomeration.[38,39]

Despite the prolonged exposure to high intensity UV light, initial curing experiment of HIPEs made from branched p(EGDMA) macromonomers **P1** and **P2** proved unsuccessful. It was hypothesised that this was due to the low propagation rate of methacrylate monomers, along with the added steric hindrance surrounding the branched macromonomers' vinyl groups. Acrylate monomers possess propagation rate coefficients that are up to one order of magnitude higher than methacrylate monomers and are therefore able to enhance curing of HIPEs. Consequently, three different acrylate comonomers: 2-ethylhexyl acrylate (EHA), isobornyl acrylate (IBOA) and 2-

methoxyethyl acrylate (MEA) were separately investigated as propagation promoters in the preparation of polyHIPEs.

HIPEs prepared with propagation promoters were found to cure efficiently without any noticeable phase separation. It was however observed that the polyHIPE materials formed displayed different morphologies, figure 6. Morphology of the polyHIPE material plays a key role in determining their appropriate application. EHA-based HIPE prepared at a 25% volume ratio of EHA with respect to the crosslinker solution were found to yield a stable HIPE that cured into a polyHIPE material. However, HIPE formulations with low EHA content were unable to cure. Upon an increase of EHA content, very stable, polymerisable HIPEs were formed (ESI, table S3). This could be potentially attributed to the hydrophobic character of EHA monomer, offering resistance to droplet coalescence in emulsions. Similarly, IBOA-based polyHIPEs were successfully synthesised (IBOA is a hydrophobic monomer, and offers stability to the emulsion through resistance to droplet coalescence).

Due to the rapid curing time provided by photo-polymerisation, an opportunity was presented to attempt the use of unconventional monomers, such as those that may form less stable HIPEs.[18] Therefore, once reliable polyHIPE formulations were established using highly hydrophobic monomers, polyHIPE synthesis using a hydrophilic monomer such as 2-methoxyethyl acrylate (MEA) was explored. MEA is a water-soluble monomer and its resulting polymer is moderately amphiphilic. It has been reported that MEA polymers exhibit excellent blood-compatibility and hence have been explored as a coating material for biomedical devices.[40,41] MEA-based HIPEs were found to be significantly less viscous than their EHA- or IBOA-based counterparts. This is likely to be due to the enhanced partitioning of MEA stemming from its polar nature, thereby increasing the droplet size of the internal phase and reducing the viscosity of the HIPE. Furthermore, it is possibe that there is some diffusion of MEA monomer into the aqueous phase, lowering the concentration of MEA in the continuous oil phase and causing destabilisation of the emulsion. This can, in turn, decrease the rate of polymerisation, therefore impeding the formation of a 3D network.

As it is an important factor in the synthesis of polyHIPEs, we also wished to investigate the effects of variations in the p(EGDMA) crosslinkers' size. To this effect, polyHIPE preparations were carried out with **P2** as crosslinker (ESI, table S4). A correlation between the hydrophobicity of the monomer and the ability to form a polyHIPE was identified.

Table 2. Young's moduli of polyHIPEs prepared.

EGDMA crosslinker/ Acrylate Additive	EHA (KPa)	IBOA (KPa)	MEA (KPa)
P1	3.37 ± 1.47	33.50 ± 6.86	9.17 ± 3.40
P2	9.50 ± 3.27	45.77 ± 12.22	21.40 ± 6.58

The difference in curing ability between the EHA and IBOA compositions is likely due to the difference in propagation rates of the respective monomers.

The bulky IBOA monomer has a lower propagation rate coefficient while EHA propagates significantly faster, typically around 10 and 17 kL.mol^{-1}.s^{-1} at ambient temperature, respectively.[42]

PolyHIPEs characterisation

Morphologies of EHA-, IBOA- and MEA-based polyHIPEs were studied using scanning electron microscopy (SEM), figure 6. SEM showed that all prepared polyHIPE materials possess an interconnected network of pores. PolyHIPEs that exhibit highly interconnected voids have previously been utilised in 3D cell culture and tissue engineering applications as such morphology allows cell infiltration into the material as well as free movement of nutrients and waste products to and from cells.[43–45] It is known that the morphology and pore size distribution of polyHIPEs are governed by both the emulsion droplet diameter at the gel point and the polymerisation rate. The droplet diameter is determined by the emulsion stability and shear during emulsion preparation. Polymerisation rate affects morphology as a slow polymerisation allows emulsion coarsening to occur before gelation, resulting in a larger droplet diameter. The morphologies of polyHIPEs obtained from EHA and IBOA show little variation from each other, most likely due to the fact that these monomers have similar hydrophobicity character and therefore their corresponding emulsions will have approximately the same emulsion stability and droplet diameter. On the other hand, as all comonomers used are acrylates, it is assumed that their polymerisation rates are similar. However, polyHIPEs made from MEA were found to possess a more closed-cell structure compared to those made from EHA and IBOA, presumably due to the hydrophilic character of MEA and hence the lower stability of its emulsions, as discussed above. It seems that comonomer type has a considerable influence on void diameter. PolyHIPEs made from macromonomer crosslinker **P1** and comonomer IBOA exhibited the most well-defined, open cellular morphologies for this set of monomers used in this work. All other polyHIPE materials lacked defined cellular structures, instead resembling macroporous polymer morphologies, consequently, attempts to determine void diameter distributions for these materials were not successful. However, where possible the majority of voids in these materials were found to be in the range of 5 − 20 μm in diameter. A plausible explanation for the loss of cellular morphology is the collapse of the HIPEs before gelation. Nevertheless, no apparent evidence of phase separation of emulsions was observed. An alternative explanation could be due to the influence of the porogen, DCE. Previous work by Cameron *et al.*[46] concluded that the porogen in an emulsion mixture can act as a co-surfactant, lowering the interfacial tension. This induces phase separation of the monomeric continuous phase during polymerisation. This is accompanied by the enlargement of the window to such an extent that the cellular structure is no longer obvious.
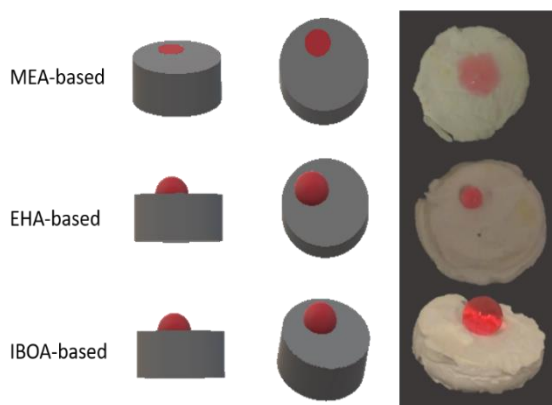
Fig. 7 Surface wettability of polyHIPEs at room temperature, with images taken after 15 seconds.

Good mechanical properties of polyHIPEs are essential in determining their end-applications. Fabrication of polyHIPEs with tuneable mechanical properties proves to be immensely advantageous in the investigation for new applications of these porous materials. For instance, Owen *et al*.[47] showed that stiff pure IBOA-based polyHIPE promoted osteogenic differentiation of mesenchymal cells much better than other types of softer, acrylate-based polyHIPE. Consequently, compression tests were performed on all prepared polyHIPE materials. Stress-strain curves for all materials revealed typical rigid foam behaviour where curves with an initial linear elastic region followed by a plateau were observed. Compressive (Young's) moduli values for all polyHIPE materials are presented in Table 2. Moduli values were calculated from the slope of the linear elastic region at low strain (< 10 %), and each measurement was repeated 3 times for increased accuracy. Results showed that EHA- and MEA-based polyHIPEs are quite flexible and could recover almost completely to their original dimensions after compression. However, IBOA-based polyHIPEs are relatively rigid, showing irreversible deformation as a result of brittle crushing of the foam microstructure. Results also showed that the compressive (Young's) moduli values for polyHIPE materials derived from macromonomer crosslinker **P1** are lower than those for polyHIPE materials derived from **P2**. This can be attributed to the formation of stronger networks when a lower molecular weight macromonomer crosslinker **P2** is used.

Due to extreme surface roughness and high porosity of polyHIPEs, contact angle measurements cannot be related to surface tension and therefore yields unreliable results. Instead, surface wettability has been investigated by depositing a drop of deionised water coloured with red food dye, onto dry polyHIPE surfaces, figure 7. Immediately after application, the coloured water droplet had dispersed on the surface of a MEA-based polyHIPE, with the bulk of the droplet quickly penetrating through the surface, verifying the hydrophilic nature of the polyHIPE. However, the low hydrophilicity of the EHA-based polyHIPE allowed the droplet to maintain its shape for several seconds, before it began to spread across the surface. Conversely, the water droplet did not disperse on the IBOA-based polyHIPE surface and the water droplet held its spherical shape for at least 15 min, remaining on the surface and was not

absorbed into the material through capillary action. These results suggest that hydrophilic / hydrophobic properties of the starting comonomers can be retained in the resulting polyHIPEs, highlighting the tailored surface functionality of these materials.

Conclusions

The preparation of a range of polyHIPE materials by combining catalytic chain transfer polymerisation (CCTP) and emulsion templating using branched macromonomers, and a range of commercially available functional acrylates (EHA, IBOA and MEA), has been described. CCTP was first employed for the facile synthesis of EGDMA-based branched macromonomers to be used as crosslinkers in the HIPE formulations. Control over branching and molecular weight was achieved by using different CoBF concentrations. One-pot preparation of polyHIPEs without any need for purification of CCTP macromonomers was also demonstrated, highlighting the potential of this approach for industrial scale-ups. It was found that it is necessary to use acrylate comonomers to promote propagation and hence formation of crosslinked networks. Comonomers with various hydrophobic characteristics were shown to retain their properties in the resulting polyHIPE, highlighting the tunability of the material for tailored functionality. This was further shown by the surface wettability experiments. SEM confirmed that the produced materials possess high levels of porosity and interconnectivity. The mechanical behaviour under compression of the prepared materials was studied and correlated with the nature of the monomer as well as the molecular weight and degree of branching of the crosslinker, higher molecular weight branched crosslinkers leading to weaker crosslinking and therefore a more fixable material. This synthetic approach can be used as a route to produce the next generation of polyHIPE materials where functionality and rigidity can be tightly tailored for a wide range of applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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