Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Branched Macromonomers from Catalytic Chain Transfer Polymerisation as Precursors for Emulsion Templated Porous Polymers

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Experimental

Chemicals

EGDMA, DCE, diphenyl(2,4,6-trimethylbenzoyl) phosphene oxide/2-hydroxy-2-methyl-propiophenone and anisole were obtained from Sigma Aldrich and used without further purification. Hypermer B246 and V-601 were obtained from Croda international and Wako Chemicals respectively, and both were used without further purification. CoBF was synthesised according to literature.[1]

Instruments

DMA analysis was carried out on a Perkin Elmer DMA 800 SYS Quarts Window equipped with titanium clamps using Pyris Instrument Managing Software, Version 11.

SEM imaging was carried out on a Zeiss SUPRA 55-VP FEGSEM operating at 25 kV. Fractured polyHIPE pieces were sputter-coated with gold using a QUORUM sputter coating system. Images were taken with an OXFORD X-ray analysis system and GATAN CL system. Average void size distribution was calculated using Image J Version 1.50i. A statistical correction factor was applied to the measured values.

All GC-FID analysis was performed on a Shimadzu GC2014 equipped with a Shimadzu A0C20i autosampler, the injection temperature was 250 °C. The GC was fitted with a Restek Rxi-1ms (15 m length, 0.25 mm ID and 0.25 µm film thickness). The carrier gas was hydrogen, supplied by an external hydrogen generator. The injection volume was 1 µl with a 39 split ratio. The detector was a flame ionisation detector (FID) with a flame temperature of 320 °C, and a sampling rate of 40 ms. The heating profile was 60 °C for 1 minutes and then heated to 320°C at 40 °C min^{-1} where it remained for a further 2.5 minutes. Data processing was carried out using Shimadzu GC solutions software.

GPC analysis was carried out on an Agilent Infinity II MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and multiple wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 µm guard column. The $CHCl_3$ eluent was used without additive. Samples were run at 1 mL.min^{-1} at 30°C. Poly(methyl methacrylate) standards (Agilent EasyVials) were used for calibration between 900 000–550 g.mol^{-1} and were fitted with a 3rd order polynomial. Analyte samples were filtered through a GVHP membrane with 0.22 µm pore size before injection. Experimental molar mass ($M_{n,SEC}$) and dispersity ($Đ$) values of synthesised polymers were determined by conventional calibration using Agilent GPC/SEC software.

NMR was carried out on Bruker HD-400 MHz spectrometer. Samples were dissolved in deuterated $CDCl_3$ obtained from Sigma Aldrich.

The mechanical behaviour of polyHIPE materials under compression was evaluated using a Shimadzu EZ-LX compact table-top universal tester equipped with a 500 N load cell fitted with compression plates tested at ambient temperature. The polyHIPE samples were cubes of 0.5 mm in dimension. Compression was continued until a final strain of around 50% was reached. Experiments were repeated in triplicates using three different samples of each material to obtain average Young's modulus values.

EGDMA Homopolymerisation

A 100 mL round bottom flask (RBF) with CoBF and a stirrer bar was degassed for 1 h via nitrogen bubbler. A separate 100 mL RBF with EGDMA (20 mL), DCE (25 mL), anisole (1 mL) and V-601 (200 mg) was immersed in an ice bath and degassed for 20 min *via* nitrogen bubbler. The liquids was transferred to the solids under positive nitrogen pressure. The solution was degassed for a further 5 min under continuous stirring. The RBF was immersed in an oil bath at 70 °C for 4 hours under nitrogen. Samples were taken hourly (approx. 0.1 ml) via degassed syringe in order to obtain GPC, GC-FID and ^1H NMR measurements. The reaction terminated by removal from heat and introduction of oxygen.

^{1}H NMR (400 MHz, TMS at 25 °C): δ 6.20- 6.35 (internal $CH_a\underline{H}_b$=C), 6.05-6.15 (terminal $CH_a\underline{H}_b$=C), 5.50-5.60 (terminal $C\underline{H}_aH_b$=C + internal CH_aH_b=C), 4.15-4.45 ($OC\underline{H}_2C\underline{H}_2O$), 2.45-2.60 (backbone CH_2), 2.15-2.20 (backbone CH_2), 1.85-2.05 (terminal CH_3), 1.00-1.50 (backbone CH_3),

Table S1 – Amount of CoBF used in EGDMA homopolymerisations.

Code	CoBF (mg)	CoBF (mol%)
P1	20	0.049
P2	30	0.0735

GPC:
P1: M_n = 1030 $g.mol^{-1}$, M_w = 4090 $g.mol^{-1}$, *Đ* = 4.0;
P2: M_n = 660 g mol^{-1}, M_w = 2150 g mol^{-1}, *Đ* = 3.3

PolyHIPE preparation

In a 100 mL two-necked RBF covered in foil, an oil phase consisting of PEGDMA solution (2.4 mL), acrylate (EHA, IBOA or 2-methoxyethyl acrylate) and Hypermer B246 (0.2 g unless stated) was sonicated until homogenous. The photoinitiator (0.8 mL unless stated), a blend of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and 2-hydroxy-2-methylpropiophenone, was added to the mixture with continuous stirring at ambient temperature using a D-shaped PTFE paddle attached to an overhead stirrer at 350 rpm. An aqueous phase of deionised water was added drop-wise to the oil phase over 20 min, with continuous stirring, to form a HIPE with an internal (aqueous) phase volume fraction of 80%. Once all the aqueous phase was added, the HIPE was transferred into cylindrical PTFE moulds (diameter 15 mm, depth; 2 mm, 3.5 mm and 5 mm) that was secured between two glass plates. The HIPE was passed under a UV irradiator (Fusion UV Systems Inc. Light Hammer® 6 variable power UV curing system with LC6E benchtop conveyor and mercury discharge 'H' bulb) 25 times on each side, at a belt speed of 5.0 m min^{-1}. The cured polyHIPE material was washed by immersion in acetone and dried at ambient temperature for 24 h.

Table S2 Initial HIPE formulations with **P1**.

Entry	**P1 (mL)**	**Distilled Water (mL)**	**Photo Initiator (mL)**	**Surfactant (g)**	**H_2O Rate of addition (mL/min)**	**HIPE**	**PolyHIPE**
1	2.5	22.5	0.4	0.4	4.5	Not Stable	N/A
2	2.5	22.5	0.4	0.4	1.125	Stable	No
3	2.5	22.5	0.8	0.4	1.125	Stable	No
4	2.5	22.5	0.8	0.4	1.125	Stable	No

Table S3 PolyHIPE formulations using **P1** and acrylate propagation promoters.

Entry	**Propagation promoter**	**P1 (mL)**	**propagation promoter (mL)**	**Distilled Water (mL)**	**Surfactant (g)**	**HIPE Stability**	**PolyHIPE**
1	EHA	0.5	**0.5**	9	0.1	Not stable	No
2	EHA	0.5	**0.5**	9	0.2	Not stable	No
3	EHA	0.6	**0.15**	6.75	0.1	Stable	No
4	EHA	2.4	**0.2**	23.5	0.2	Stable	No
5	EHA	2.4	**0.4**	25	0.2	Stable	Yes
6	EHA	2.4	**0.6**	27	0.2	Stable	Yes
7	EHA	2.4	**0.8**	29	0.2	Stable	Yes
8	IBOA	2.4	**0.6**	27	0.2	Stable	Yes
9	IBOA	2.4	**0.8**	29	0.2	Stable	Yes
10	MEA	2.4	**0.6**	27	0.2	Stable	Yes
11	MEA	2.4	**0.8**	29	0.2	Stable	Yes
12	MEA	2.4	**1**	30	0.2	Stable	Yes
13	MEA	2.4	**1.4**	33	0.2	Stable	Yes
14	MEA	2.4	**1.8**	37	0.2	Stable	Yes
15	MEA	2.4	**2.2**	41	0.2	Semi-stable	No

Table S4 PolyHIPE formulations using **P2** and acrylate propagation promoters.

Entry	**Propagation promoter**	**P2(mL)**	**propagation promoter (mL)**	**Distilled Water (mL)**	**Surfactant (g)**	**HIPE Stability**	**PolyHIPE**
1	EHA	2.4	**0.8**	29	0.2	Stable	Yes
2	IBOA	2.4	**0.8**	29	0.2	Stable	Yes
3	MEA	2.4	**0.8**	29	0.2	Stable	Yes

References

1. A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1984, **106**, 5197–5202.