Inherently Reactive polyHIPE Material from Dicyclopentadiene.

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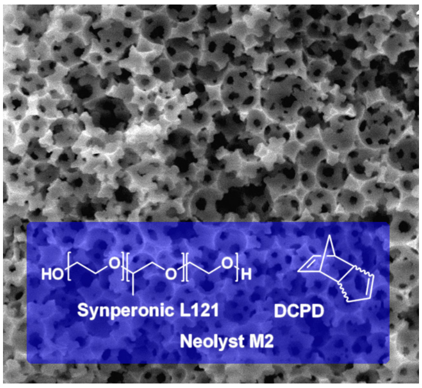
SUPPORTING INFORMATION



Preparation of DCPD PolyHIPE from water-in-oil high internal phase emulsion by ROMP: Dicyclopentadiene (Fluka, 4.4 g, 33 mmol) and Synperonic L121 (Sigma-Aldrich, 0.6 g) were placed in a reactor and the mixture was stirred with an overhead stirrer at 400 rpm. 22 mL of deionised water was added drop wise under constant stirring. Upon further stirring for 1 h a uniform emulsion formed and either **M1** or **M2** (Umicore, 0.015 mol % (in regard to **DCPD**) dissolved in 1 cm^3 of toluene) was added. The formulation was transferred to a mould and cured (20°C, 60°C or 80°C) for either 2h or 24h. The product was purified *via* Soxhlet extraction with dichloromethane/acetone (Sigma-Aldrich) and dried under vacuum.

Figure S1. SEM images of prepared **polyDCPD** materials

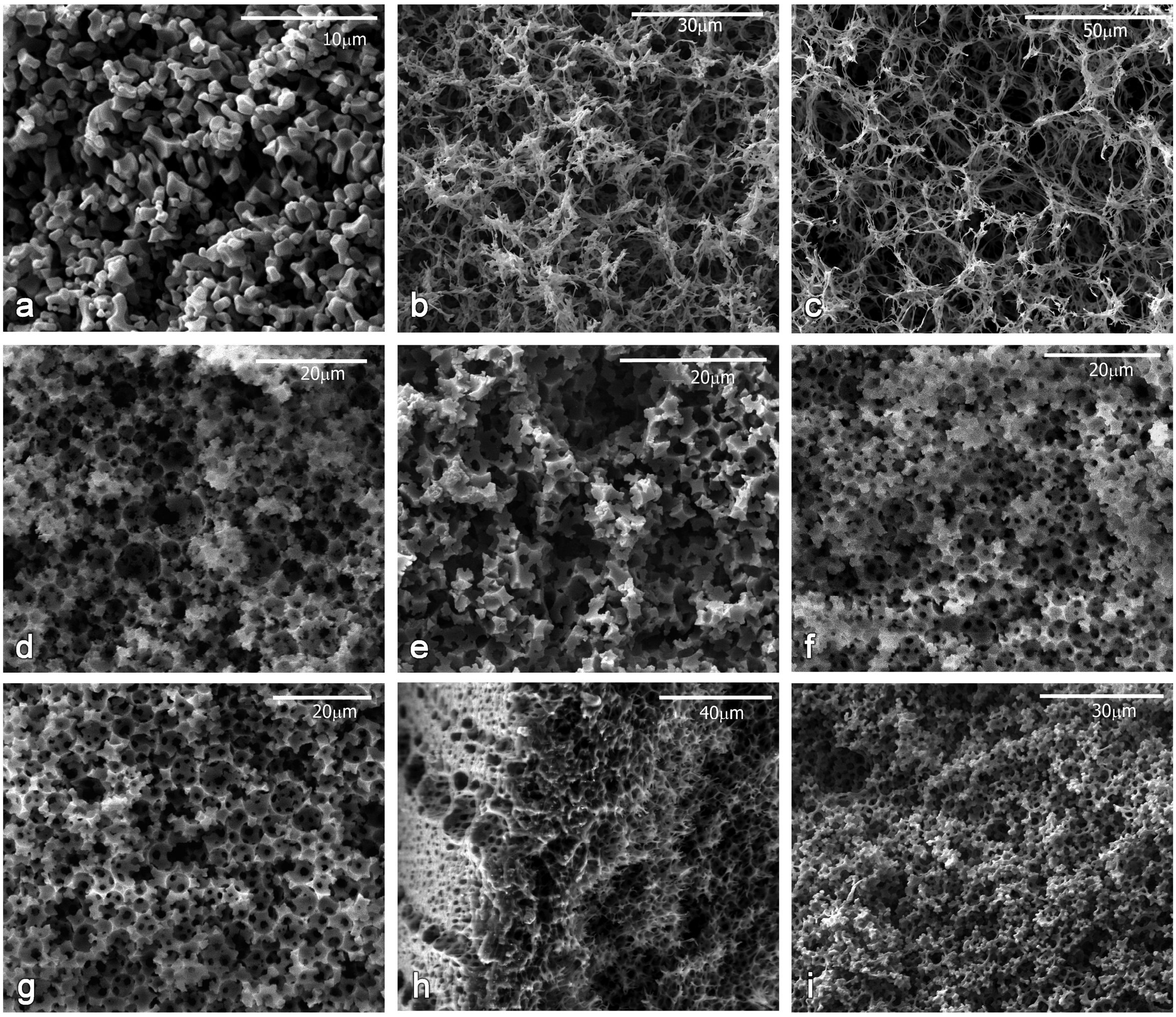


Table S1. Prepared samples & reaction conditions

Sample	Fig. S1 [item #]	w.p./c.p.[a] [vol%]	Initiator	Temperature [°C]	Curing time [h]	Yield [%]
A1	**a**	80/20	**M1**	20	96	56
A2	**b**	80/20	**M1**	60	24	15
A3	**c**	80/20	**M1**	80	24	13
B1	**d**	80/20	**M2**	20	24	88
B2	**e**	80/20	**M2**	60	24	84
B3	**g**	80/20	**M2**	80	24	85
B4	**f**	80/20	**M2**	80	2	84
B5	- [b]	90/10	**M2**	20	24	82

[a] water phase/continuous (organic) phase; [b] for SEM image see Fig. S2

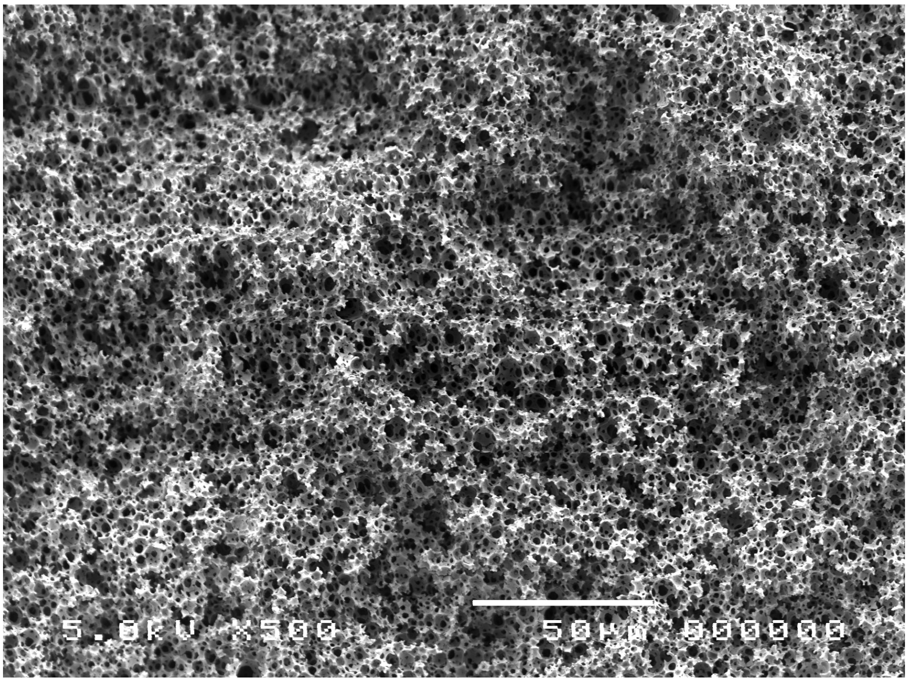
One-pot functionalisation: In the case of sample **B3a**, pentaerythritol tetrakis(3-mercaptopropionate) (**PTMP**, Sigma-Aldrich, 0.470 g, 0.962 mmol) was added together with the initiator azobisisobutyronitrile (**AIBN**, Fluka, 14.1 mg, 3 wt %) directly to the continuous phase of HIPE.

In the case of sample **B3b**, potassium persulphate (**KPS**, Fluka, 24.3 mg, 3 wt %) was added into the internal phase during the HIPE formation and same amount of the **PTMP** was used as in case of **B3a**. After HIPEs were formed, both samples were cured at 70°C for 24 h.

Post-polymerisation functionalisation: In the case of sample **B3d** 0.4g (3.00 mmol) of **B3** was grinded and placed in to the 25 mL flask and dispersed in 30 mL of distilled toluene. 0.08 g (0.162 mmol) of **PTMP** and 2.4 mg of **AIBN** were added. The reaction mixture was stirred for 24h at 80 °C.

For sample **B3e** 0.4g (3.00 mmol) of oxidized **B3** was grinded and 0.37g (7.45 mmol) of hydrazine in 30 mL of dry THF was added. The reaction mixture was stirred for 3h at 60°C.

Figure S2: SEM of sample **B5** (90 % pore volume)



Characterisation of the polyHIPEs: FT-IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR Spectrometer (UATR) and CHN elemental analyses were done on a Perkin-Elmer CHN 2400 analyzer. Scanning electron microscopy (SEM) pictures were taken on a FEI Quanta200 3D (gold sprayed samples). Dry state morphology of the samples was characterized on the base of nitrogen adsorption/desorption data. Measurements were performed using the Tristar 3020 (Micrometrics) porosimeter. Hydrodynamic properties were measured by HPLC pump Knauer K-1001. Mechanical properties were tested by a Zug/Druck-Universalprüfmachine (Typ Z010, Fa. ZWICK).

Elemental Analysis

In the case of sample **B4** calculations from elemental analysis showed 12.56 % of oxygen content right after the preparation and purification (sample stored in argon) and 30.38 % of oxygen content after one month where sample was stored under ambient conditions. Calculations for sample **B3** showed 25.63 % of oxygen right after the preparation and purification (sample stored in argon), 31.03 % of oxygen after one month and 32.54 % of oxygen after 6 months under ambient conditions (Table S3).

One-pot functionalisation procedures were prepared with pentaerythritol tetrakis(3-mercaptopropionate (**PTMP**). In all cases where one-pot procedure was used the oxygen content in the functionalised samples was significantly lower (between 1 and 11%) than in the case of non functionalised samples (between 25% and 32%). In the case of sample **B3c** where only 0.81 g (1.66 mmol) **PTMP** but no radical starter was added to the continuous phase of the emulsion the oxygen content was only 1.27 % (see Table S3).

Table S3. Elemental analysis of functionalised dicyclopentadiene polyHIPE

Sample	**ROMP initiator**	**Elemental analysis**				
	Thyol-ene initiator	**C** **[%]**	**H** **[%]**	**S** **[%]**	**O** **[%]**	**N** **[%]**
B3[a]	**M2**	61.13	6.33	/	32.54	/
B3[b]	**M2**	62.61	6.36	/	31.03	/
B3[c]	**M2**	66.94	7.26	/	25.80	/
B4[d]	**M2**	63.22	6.40	/	30.38	/
B4[e]	**M2**	78.84	8.60	/	12.56	/
B3a[f]	**M2**					/
	AIBN	83.77	9.14	0.34	6.75	
B3b[g]	**M2**					/
	KPS	79.62	8.45	0.62	11.31	
B3c[h]	**M2**					/
	/	88.8	9.67	0.18	1.27	
B3d[i]	**M2**					/
	AIBN	61.80	6.08	2.27	29.85	
B3e[j]	**M2**	59.37	7.53	/	20.18	12.92

[a] **DCPD** polyHIPE polymerised for 24h and stored under ambient conditions (6 month)
[b] **DCPD** polyHIPE polymerised for 24h and stored under ambient conditions (1 month)
[c] **DCPD** polyHIPE polymerised for 24h and stored under argon (1 month)
[d] **DCPD** polyHIPE polymerised for 2h and stored under ambient conditions (1 month)
[e] **DCPD** polyHIPE polymerised for 2h and stored under argon (1 month)
[f] One pot preparation of **polyDCPD** with **PTMP** and **AIBN**
[g] One pot preparation of **polyDCPD** with **PTMP** and **KPS**
[h] One pot preparation of **polyDCPD** with **PTMP** and without radical starter
[i] Post-polymerisation functionalisation of **polyDCPD** (sample **B3**)with **PTMP** and **AIBN**
[j] Functionalisation of oxidized **polyDCPD** (sample **B3**) with hydrazine

Mechanical testing of DCPD polyHIPE

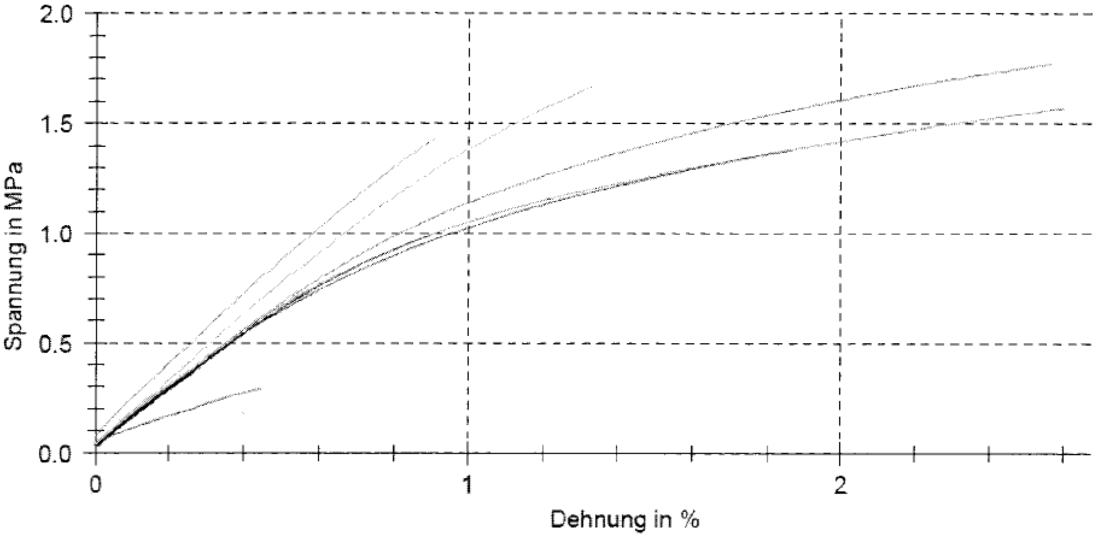
High internal phase emulsion was prepared as described before and HIPE was transferred into dog bone shaped stainless steel template (allowing for a measuring length of 50 mm and a clamping distance of 115 mm) and cured. Samples **B3** and **B4** were tested (modulus determination at a rate of 1 mm/min to an elongation of 0.2% and then 5mm/min until samples broke; resolution was 0.6 µm) with a tensometer, namely a Zug/Druck-Universalprüfmachine (Typ Z010, Fa. ZWICK) equipped with a force measuring range up to 10kN. The elastic modulus was determined from the initial linear slope of the stress/strain plot (Table S4 and Figure S3).

Table S4. Mechanical testing of **DCPD** polyHIPEs

sample	E-Modul [Mpa]	σ_M [MPa]	ε_M [%]
B3	159	1.44	0.9
	145	1.66	1.3
	56 [a]	0.29	0.4
B4	128	0.99	0.9
	126	1.77	2.6
	128	1.57	2.6

[a] Crack of sample results in place where air bubble was trapped during polymerisation

Figure S3: Stress-strain curves



Hydrodynamic properties of dicyclopentadiene polyHIPE material

The columns consisted of a disc of polyDCPD monolith (**B3** or **B4**) with a diameter of 12.0 mm and the thickness of 3.0 mm, placed in the appropriate housing (BIA Separations, Ljubljana, Slovenia), which was connected to the HPLC system. The experiments were performed on monoliths with cavity diameter of approx. 5.5 µm and interconnecting pore diameter of 1.6 µm (**B4**) or with cavity diameter of 5.6 µm and interconnecting pore diameter of 1.6 µm (**B3**). The flow hydrodynamic behaviour of the monoliths was described by the pressure drop of monolithic column at different flow rates (1, 2 and 4 mL/min) using ethanol as the mobile phase. The values of the system pressure without and with the monolith were measured at each flow rate, and the difference between the two values was calculated as the pressure drop across the monolith. Then, hydraulic permeability of the monolith was calculated using the hydrodynamic data from the Darcy's law

$$\frac{\triangle P}{L} = \frac{u \cdot \mu}{B_o}$$

where ΔP stands for back pressure (Pa), L for column length (m), u for superficial velocity (m/s), μ for mobile phase viscosity (Pa s), B_0 for hydraulic permeability (m^2). The value of B_0 can be used as an index for evaluating the quality of monoliths.

Table S5. Permeability (B_0) of **polyDCPD** at different flow rates with ethanol as mobile phase

sample	Flow rate [mL/min]	Permeability [m^2]
B4	1	$4{,}75 \cdot 10^{-15}$
	2	$4{,}75 \cdot 10^{-15}$
	4	$3{,}80 \cdot 10^{-15}$
B3	1	$9{,}50 \cdot 10^{-15}$
	2	$9{,}50 \cdot 10^{-15}$
	4	$4{,}13 \cdot 10^{-16}$

Cavity and interconnects size determination

Cavity sizes were determined by SEM image analysis (Table S6). Over 50 measurments at three SEM micrographs for each sample were taken. Using SEM images analysis, it is necessary to introduce a statistical correction due to the cavities being cut at a random distance from the cavity centre, thus the multiplication of the observed cavity values from SEM images by a statistical factor of $2/3^{1/2}$.

Table S6. Cavity and windows size values

sample	Figure S1	Cavity size [µm]	Windows size [µm]
A1	**a**	/	/
A2	**b**	8.77	1.58
A3	**c**	18.1	5.14
B1	**d**	5.61	1.2
B2	**e**	2.70	1.1
B3	**g**	5.62	1.55
B4	**f**	5.47	1.59
B5	/*	4.95	1.77

* Figure S2

Figure S3: FT-IR spectrum of sample **B3e**