

Supporting Information

Towards highly efficient continuous-flow catalytic carbon dioxide cycloadditions with additively manufactured reactors

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1. Experimental Section

1.1. Materials

All reagents and solvents used were commercially available: Glycidyl methacrylate (97%, Aldrich), poly(ethylene glycol) dimethacrylate (97%, Aldrich), ethylene glycol dimethacrylate (98%, Aldrich), 1,4-Butanediol diacrylate (90%, Aldrich), phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide (97%, Aldrich), 1-methylimidazole (98%, Aldrich), 1-butylimidazole (98%, Aldrich), 1-octylimidazole (98%, Aldrich), 1-decyl-2-methylimidazole (97%, Aldrich), hydrochloric acid (37%, Scharlab), ink (ELEGOO translucent LCD UV-Curing), styrene oxide (97%, Aldrich), glycidol (96%, Aldrich), epichlorohydrin (98%, Aldrich). All the solvents were used as received from Scharlab.

1.2. General characterization protocols

Fourier Transform Infrared (FT-IR) spectra were acquired with a Pike single-reflection ATR diamond/ZnSe accessory in a JASCO FT/IR-4700 instrument. The Raman spectra were acquired with a *Raman Confocal Microscope apyron (WITec)* with three optical fibers connected to the laser sources to excite the samples (532nm) with long pass filters and two optimized spectrometers, the first for the visible range with an EMCCD ultra-high efficiency detector and the second one optimized for the NIR region with a high efficiency CCD detector and equipped with different Zeiss optical lenses (x10, x20 LD, x50 LD, x100 (LD: long focal length)). Wettability of discs was determined by using a static contact angle goniometer in open air (Phoenix150, Surface Electro Optics). The conversion of CO₂ cycloaddition reactions was calculated by ¹H NMR spectra, carried out using a Bruker Avance III HD 300 or 400 spectrometer (300 or 400 MHz for ¹H).

1.3. Synthetic protocols

Synthesis of the epoxy support without crosslinker (S0)

Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide (1% w regarding to glycidyl methacrylate (GMA)) was added to GMA(90% w) and then the commercial translucent photopolymer resin (10% w) was added to this mixture. The polymerization was carried out by depositing 1.0 mL of the resulting solution into a circular glass mold and exposing the mixture to a 370 nm lamp.

After 2 min. a solid disc was obtained that was extracted from the mold and washed with IPA (3 x 5 mL) and cured at 60 °C for 24 h.

Synthesis of the epoxy support with methacrylate crosslinker (S1)

Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide (1% w regarding to GMA) was added to a mixture of GMA (45-90% w), with the correspondent crosslinker, ethylene glycol dimethacrylate (EGDMA) (5-45% w) for epoxy 2, and poly(ethylene glycol) dimethacrylate (PEGDMA) (5-45% w) for epoxy-3. Then the commercial translucent photopolymer resin (10% w) was added to this mixture, see the complete composition in Table S2 and S3. The polymerization was carried out by depositing 1.0 mL of the resulting solution into a circular glass mold and exposing the mixture to a 370 nm lamp. After 2 min. a solid disc was obtained that was extracted from the mold and washed with IPA (3 x 5 mL) and cured at 60 °C for 24 h.

Synthesis of the epoxy support with acrylate crosslinker (S2)

Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide (1% w regarding to GMA) was added to a mixture of GMA (50% w) and 1,4-Butanediol diacrylate (1,4-BUDA) (50% w). The polymerization was carried out by depositing 1.0 mL of the resulting solution into a circular glass mold and exposing the mixture to a 370 nm lamp. After 2 min. a solid disc was obtained that was extracted from the mold and washed with IPA (3 x 5 mL) and cured at 60 °C for 24 h.

Functionalization of epoxy-based support

Synthesis of SILs: A 5.0 mL of solution of chloride salt in ethanol of corresponding alkyl-imidazole (6.5 mol L^{-1}), prepared from 1:1 molar equivalent of hydrochloric acid and NH-imidazole-based compounds, was added to the disc. The reaction mixture was maintained with orbital shaking (125 rpm) for 24 h at 40 °C. Finally, the disc was washed with IPA (3 x 5 mL) and dried at 60 °C for 24 h.

Modification of polymeric beads of commercially available resin (Purolite Lifetech™ ECR8209M) (P-SIL): Purolite beads were functionalized with butyl-imidazole using similar procedure described for SIL materials. After the functionalization, the resins were washed with methanol and dried under vacuum at 70 °C till constant weight to remove water and any traces solvent.

Preparation of 3DP objects

S0 composition: The printer tank was filled with 50.0 mL a monomeric solution containing 90% by weight of GMA and 10% by weight of the commercial translucent photopolymer ink. This solution contains 1% by weight of the photoinitiator (Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide) regarding to GMA. The 3D structure was obtained according to the digital design downloaded in the printer (cube and letters). Once the 3D structure was printed, the object was extracted from the build platform, washed with IPA (3 x 25 mL), dried at 60 °C for 24 h, and cured under UV light 40 °C for 30 min.

S1 composition: The printer tank was filled with 50.0 mL a monomeric solution containing 50% by weight of GMA, 40% by weight of EGDMA and 10% by weight of the commercial translucent photopolymer ink. This solution contains 1% by weight of the photoinitiator (Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide) regarding to GMA. The 3D structure was obtained according the digital design downloaded in the printer (cube, letters or column D1 and D2). Once the 3D structure was printed, the object was extracted from the platform, washed with IPA (3 x 25 mL), dried at 60 °C for 24 h, and cured under UV light 40 °C for 30 min.

S2 composition: The printer tank was filled with 50.0 mL a monomeric solution containing 50% by weight of GMA, 50% by weight of 1,4-BUDA, and 1w% of the photoinitiator (Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide) regarding to GMA. The 3D structure was obtained according the digital design downloaded in the printer (column D1 and D2). Once the 3D structure was printed, the object was extracted from the platform, washed with IPA (3 x 25 mL), dried at 60 °C for 24 h, and cured under UV light 40 °C for 30 min.

Printing Parameters of 3DP objects:

Cube: layer height: 0.05 mm, 60 s exposure time, 120 s bottom exposure time, 3 h 59 min total printing time. **PILs Letters:** layer height: 0.05 mm, 120 s exposure time, 120 s bottom exposure time, 13 h 35 min total printing time.

Columns: SIL1-D1 and SIL1-D2: Layer height: 0.05 mm, 120 s exposure time, 120 s bottom exposure time, total printing time: 44 h 7 min. **SIL2-D1:** layer height: 0.05 mm; 30 s exposure time, 60s bottom exposure time, total printing time: 17 h 23 min.

Functionalization of 3D printed object (Synthesis of SIL1-D1, SIL1-D2 and SIL2-D1): A solution of the chloride salt of butyl imidazole (6.5 mol L⁻¹) in ethanol was added to the 3D printed object. The reaction mixture was left in contact with the polymer at room

temperature and under orbital shaking (125rpm) for 24 h. Finally, the 3D object was washed with IPA (3 x 25 mL) and dried at 60 °C under vacuum for 24 h.

General procedure for the reaction of styrene oxide and CO₂

Batch experiments: For the reactions under pressure, a Verghof R-300 high pressure reactor connected to a pressurized CO₂ source and a back-pressure regulator from Jasco was used. The heater was first brought to the desired temperature (100 °C). The reactor was then loaded with styrene oxide (1 mL) and the catalyst (1.0 g aprox.). The reactor was connected to the CO₂ pump and the back-pressure regulator and immersed in the bath. CO₂ was liquefied and pumped into the reactor up to the desired pressure, under stirring. After 12 h, the high-pressure reactor was cooled down and depressurized. Afterwards, the reactor was opened, and the contents collected using 1 mL of deuterated chloroform to dissolve the reaction mixture. The catalyst was separated by decantation. Experimental procedures were replicated for all experiments. The average deviation of styrene carbonate formation was less than 5%.

Continuous flow experiments: Styrene oxide was pumped using a Jasco HPLC pump at a rate of 5 $\mu\text{L min}^{-1}$. CO₂ was pumped with a refrigerated CO₂ Jasco pump at a flow rate of 50 $\mu\text{L min}^{-1}$. Once CO₂ and epoxide entered in contact in a mixer, they passed through a preheater and the catalytic reactor(s) maintained in an oven to achieve the required experimental temperature. A Jasco back pressure regulator was connected at the outlet of the reactor to establish the desired pressure. All required connections were made with stainless-steel 1/16-inch coil. The reaction stream of crude product was collected in a cold trap at the outlet of the back-pressure regulator. Samples were taken and analyzed by ¹H-NMR spectroscopy to determine the conversion and selectivity of the reaction.

2. Results table and figures

2.1. Material composition tables

Table S1. Initial composition of poly-epoxy resins (S0) and polymerization time[a]

Entr y	Epoxy Support (S0)	GMA [%]	Photopolymer resin ^[b] [%]	BAPO ^[c] [%]	BAPO ^[d] [%]	Loading ^[e] [mmol g ⁻¹]	Pol. time ^[f] [min.]
1	A	90	10	1.0	0.9	6.3	2.0
2	B	90	10	0.5	0.4	6.3	5.5
3	C	90	10	5.0	4.5	6.3	3.0

[a] In % w/w. [b] Commercial photopolymer resin Elegoo translucent. [c] Photoinitiator BAPO, w% regarding to glycidyl methacrylate (GMA). [d] % w regarding to the total mix. [e] Theoretical epoxide unit loading. [f] Polymerization time using a UV lamp of 36 W, gel curing, wavelength of highest peak: 370nm. The polymerization time is defined, as the time required the monomeric solution to evolve from a liquid to a solid state. To determine the polymerization time the polymerization mixture was exposed to the light using 30 seconds cycles until verifying that it became completely solid. Once the disc was solid, it was removed from the mold, washed with IPA (3 x 5 mL) and cured for 24 hours at 60 °C.

Table S2. Composition of poly-epoxy supports using different acrylate-based cross-linkers.^[a]

Entry	Support (S)	GMA [%]	Cross-linker	Cross-linker [%]	Loading ^[b] [mmol g ⁻¹]	Pol. time ^[c] [min.]	Swelling ^[d] [%]	Swelling time [min.]
1	1.a	90	EDGMA	0	6.3	2	251	60
2	1.b	90	EDGMA	10	6.3	4	140	30
3	1.c	85	EDGMA	5	5.9	2	154	30
4	1.d	80	EDGMA	10	5.6	2	101	30
5	1.e	70	EDGMA	20	4.9	2	12	150
6	1.f	60	EDGMA	30	4.2	2	34	1140
7	1.g ^[e]	50	EDGMA	40	3.5	2	10	1140
8	1.h ^[e]	45	EDGMA	45	3.1	2	8	1140
9	1.i	90	PEGDMA	0	6.3	2	251	60
10	1.j	90	PEGDMA	10	6.3	4	218	30
11	1.k	85	PEGDMA	5	5.9	4	168	30
12	1.l	80	PEGDMA	10	5.6	4	63	30
13	1.m	70	PEGDMA	20	4.9	3	134	30
14	1.n	60	PEGDMA	30	4.2	2	61	120
15	1.o	50	PEGDMA	40	3.5	2	49	180
16	1.p	45	PEGDMA	45	3.1	2	20	180
17	2 ^[e]	50	1,4-BUDA ^[f]	50	3.5	1	3	180

[a] Values in % w/w. Polymerization performed with 10w% of commercial photopolymer resin Elegoo and Photoinitiator BAPO, 1% regarding to glycidyl methacrylate. [b] Theoretical epoxide unit loading. [c] Polymerization time using a UV lamp of 36 W, gel curing, wavelength of highest peak: 370nm. The polymerization time is defined, as the time required the monomeric solution to evolve from a liquid to a solid state. To determine the polymerization time the polymerization mixture was exposed to the light using 30 seconds cycles until verifying that it became completely solid. Once the disc was solid, it was removed from the mold, washed with IPA (3 x 5mL) and cured for 24 hours at 60 °C. [d] Swelling in CH₂Cl₂. [e] The epoxy **S1.g**, **S1.h** and **S3** do not break, all the other EPOXY break. [f] Polymerization performed without commercial photopolymer resin Elegoo Clear resinTM and Photoinitiator BAPO, 1%

$$\text{Swelling} = \left(\frac{\text{Wet mass} - \text{Dry mass}}{\text{Dry mass}} \right) \cdot 10^2$$

regarding to glycidyl methacrylate.

Table S3. Swelling of poly-epoxy disc (S1g) in different solvents. ^[a]

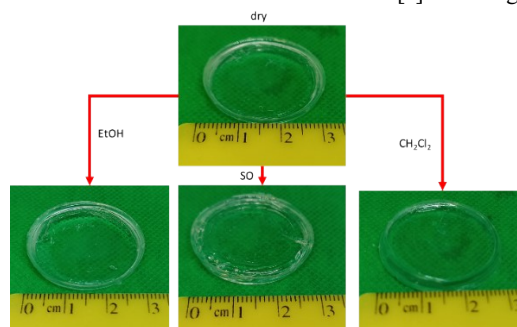
Entry	Solvent	Dry Mass [g]	Wet mass [g]	Swelling ^[b] [%]
1	Styrene oxide	1.0400	1.1325	8.9
2	EtOH	1.1718	1.2040	1.5
3	Hexane	1.0365	1.0377	0.1
4	miliQ® H ₂ O	1.0574	1.0620	0.4
5	CH ₂ Cl ₂	1.1256	1.2381	9.9

[a] Swelling time: 1 h. [b]. $Swelling = \left(\frac{Wet\ mass - Dry\ mass}{Dry\ mass} \right) \cdot 10^2$. [c] The weight loss is due to partial solubility.

Table S4. Swelling of disc SIL-1c in different solvents. ^[a]

Entry	Solvent	Dry Mass [g]	Wet mass [g]	Swelling ^[b] [%]
1	Dichloromethane	1.0674	1.0774	1
2	Styrene oxide	1.0082	1.1080	10
3	EtOH	0.9648	0.9804	2

[a] Swelling time: 1 h. [b]. $Swelling = \left(\frac{Wet\ mass - Dry\ mass}{Dry\ mass} \right) \cdot 10^2$. [c] The weight loss is due to partial solubility.

**Table S5.** Swelling of 3D printing SIL2-D2 device in different solvents. ^[a]

Entry	Solvent	Dry Mass [g]	Wet mass [g]	Swelling ^[b] [%]
1	Styrene oxide	0.5997	0.6560	9
2	Dichloromethane	0.4848	0.5122	6
3	EtOH	0.4982	0.5239	5
4	Toluene	0.6393	0.6838	7

[a] Swelling time: 1 h. [b]. $Swelling = \left(\frac{Wet\ mass - Dry\ mass}{Dry\ mass} \right) \cdot 10^2$. [c] The weight loss is due to partial solubility.

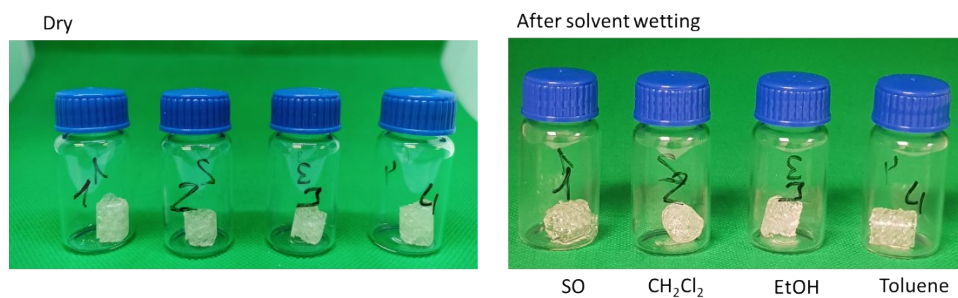


Table S6. Composition of catalyst (SILs) after functionalization of epoxy-based supports.

Entry	Name	Crosslinker	IL Loading ^[a] [mmol g ⁻¹]	R	R'
1	S1	EDGMA ^[a]	0	-	-
2	SIL1.a	EDGMA ^[a]	0.076	CH ₃	H
3	SIL1.b	EDGMA ^[a]	0.075	CH ₃	CH ₃
4	SIL1.c	EDGMA ^[a]	0.088	CH ₃ (CH ₂) ₃	H
5	SIL1.d	EDGMA ^[a]	0.087	CH ₃ (CH ₂) ₃	CH ₃
6	SIL1.e	EDGMA ^[a]	0.091	CH ₃ (CH ₂) ₇	H
7	SIL1.f	EDGMA ^[a]	0.071	CH ₃ (CH ₂) ₉	CH ₃
8	SIL2	1,4-BUDA ^[b]	0.071	CH ₃ (CH ₂) ₃	H

[a] Imidazolium unit loading calculated by elemental analysis.

2.2. 3D printed geometries of optimized supports

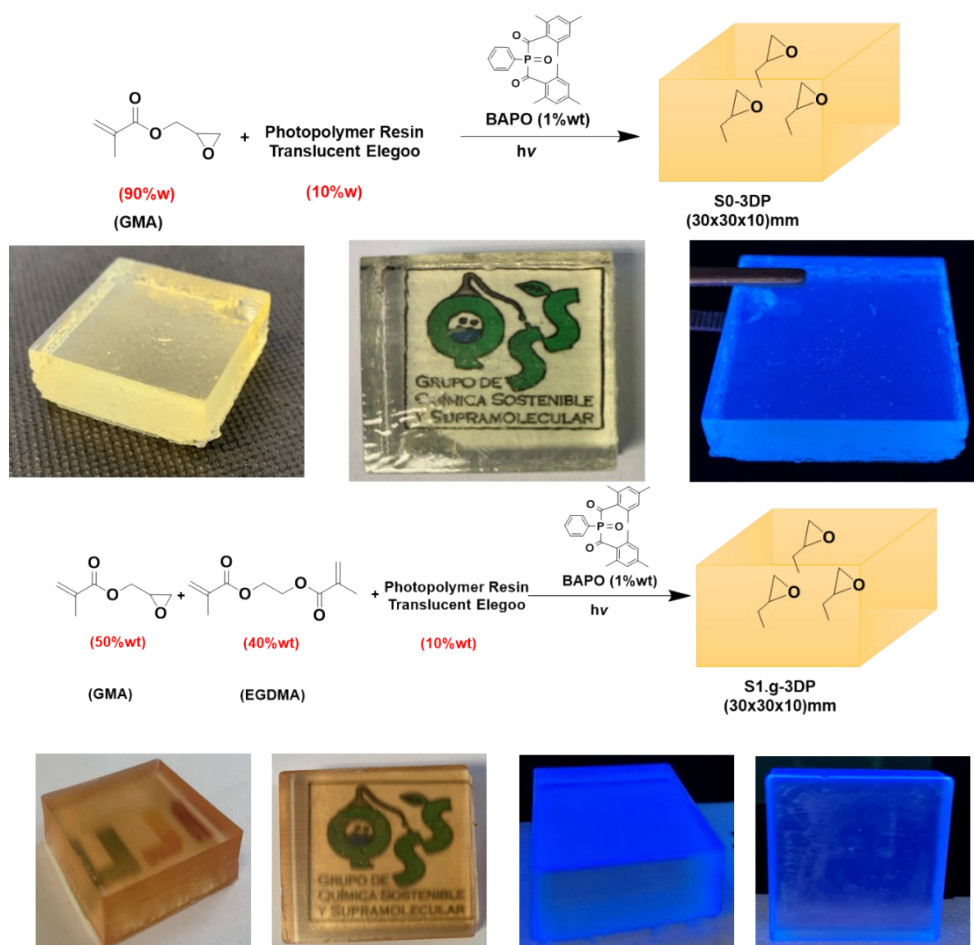


Figure S1. Reaction scheme and pictures of the epoxy resins obtained as 3D square objects by 3D printing. Top: S0 Exposure time: 60 s. Bottom: S1.g Exposure time: 120 s. Total printing time: 3 h 59 min. 33 s.

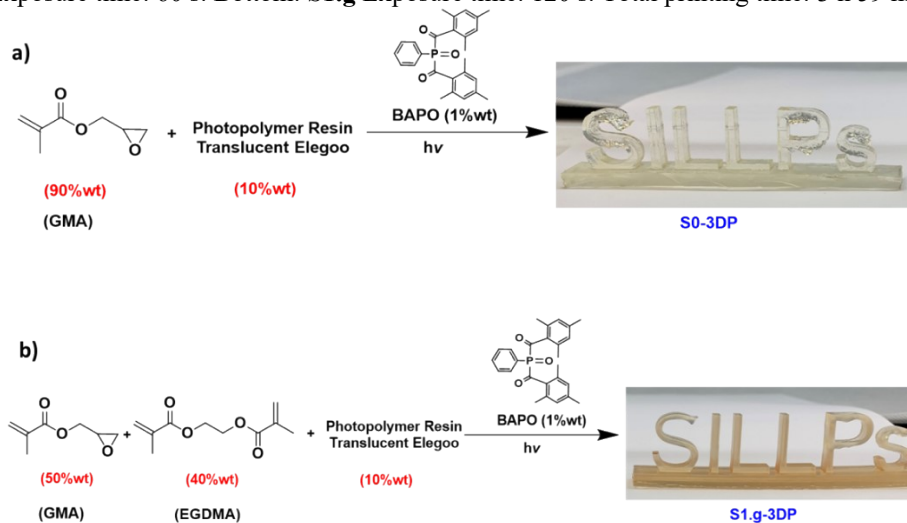


Figure S2. Images of the word “SILLPs” obtained by 3DP using the optimised inks. Exposure time: 120 s. Total printing time: 13 h 35 min. a) S0 and b) S1.g.

2.3. Material characterization (Support and SIL)

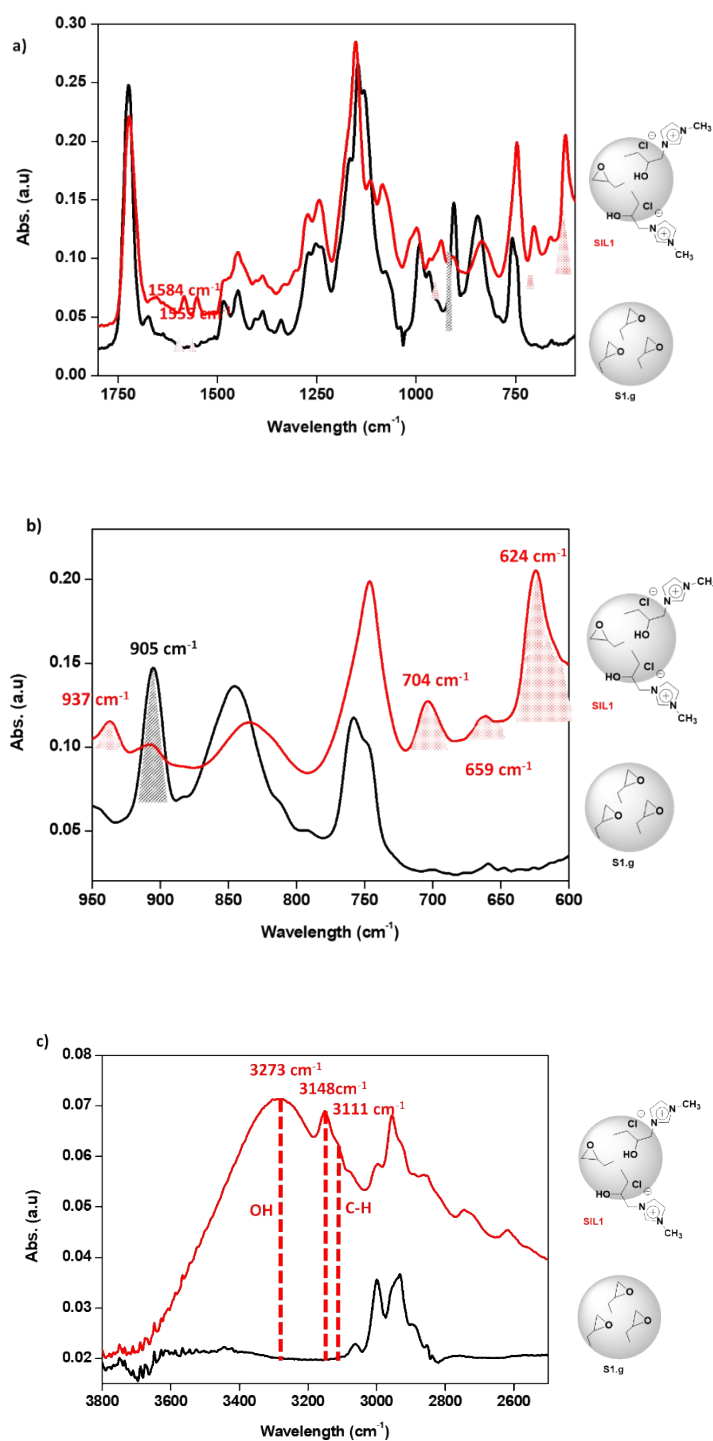


Figure S3. FT-IR-ATR of the polymeric support S1.g before and after (SIL1.a) functionalization with methylimidazole. a) 1800-600 cm⁻¹ region; b) 950-600 cm⁻¹ region; c) 3800-2500 cm⁻¹ region. Black: before functionalization (S1.g). Red: after functionalization SIL1.a.

TGA Analysis

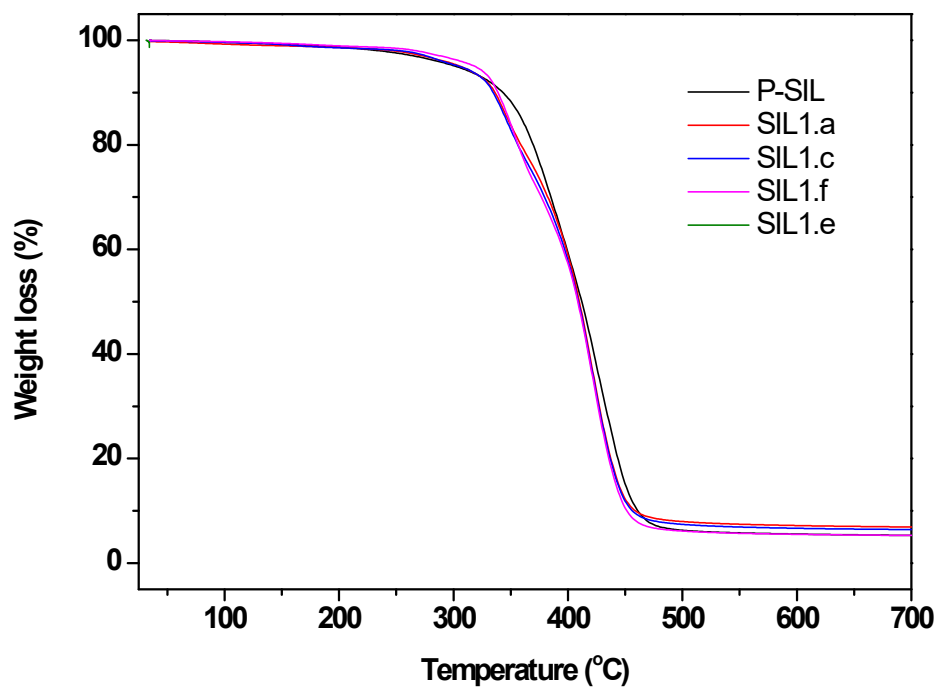


Figure S4. TGA Analysis of the different supported alkyl-imidazolium polymers obtained from the resin **S1.g**.

Water contact angle (WCA) measurements

From the WCA (Figure S4) it is possible to observe that the resin **S1.g** showed a WCA of 42.9° , which changed upon the modification with the corresponding alkyl imidazole. In the case of methyl imidazole (**SIL1.b**), the WCA value was reduced in comparison with the unmodified epoxy polymer (from 42.9° to 30.8°) due to the introduction of more hydrophilic groups (OH and methylimidazolium chloride). However, the modification with more hydrophobic alkyl chain as substituent (C_4 , C_6 , C_{10}) led to an increase of the WCA (47.0° , 56.9° and 58.2°) for the other **SIL1**.^[1] This indicates that upon modification of the surface, the aliphatic chains are oriented towards the polymer/air interface. The WCA values are in good agreement with the wettability found for Au surfaces coated with monolayers of thiol-functionalized ILs. These results not only confirmed the modification of the surface, but also that the nature of the N-alkyl-imidazole involved can be used to modulate the hydrophilicity/hydrophobicity of the surface.

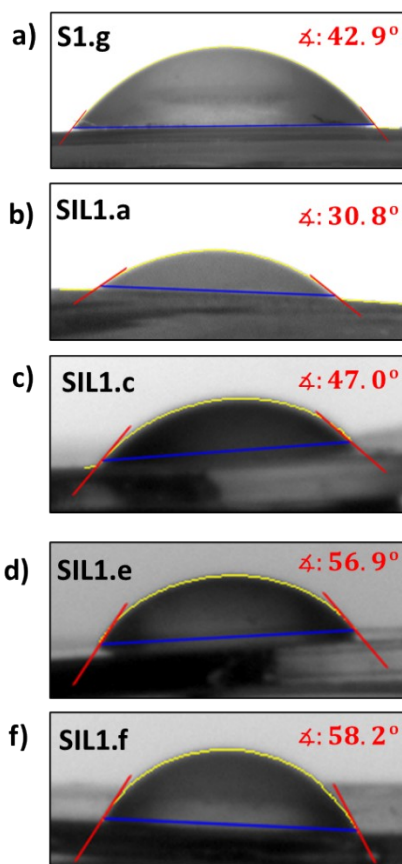


Figure S5. The pictures show the water contact angle (WCA) of the modified discs.

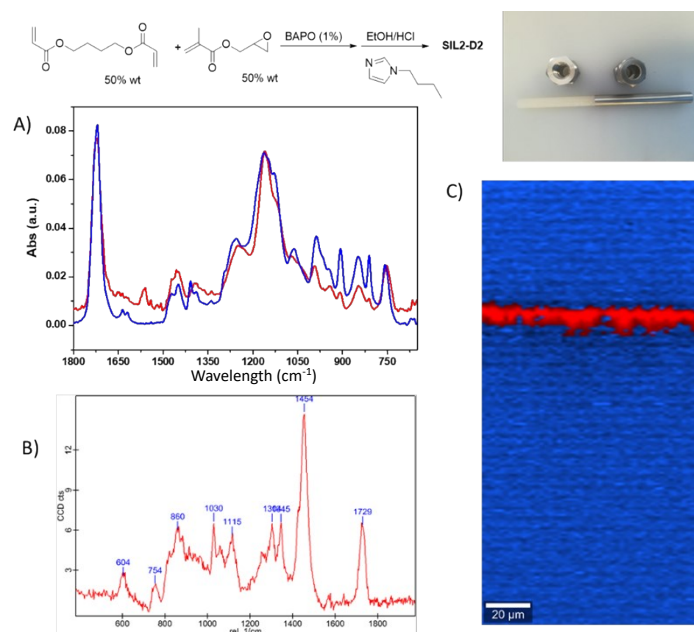


Figure S6. Characterisation of **SIL2-D1** reactor. A) FT-IR-ATR of the reactor **SIL2-D1** before (in blue) and after (in red) imidazolium functionalization. B) Raman confocal microscopy study Raman spectra corresponding to the surface (red) regions associated with the imidazolium substituted polymeric material C) Mapping for the initial 120 μm depth of the reactor showing the trace (red) associated with modification material with imidazolium units, blue region up corresponds with air and the blue region down to the unmodified epoxy region.

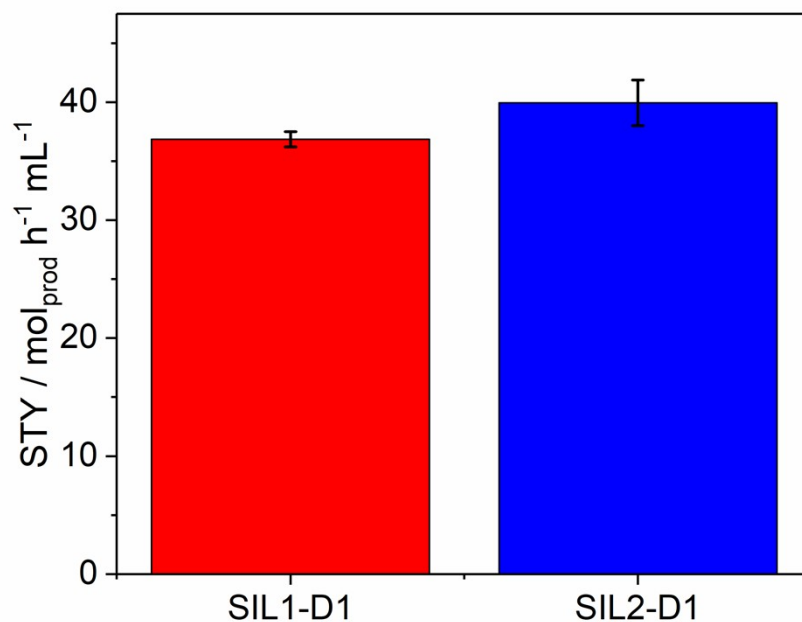


Figure S7. Comparison of the space time yield of reactors SIL1-D1 and SIL2-D1. Reaction between neat styrene oxide and CO₂ at 120 °C, flow rate of 5 μL min⁻¹ styrene oxide and 50 μL min⁻¹ of CO₂.

References

- [1] Y. Shen, Y. Zhang, Q. Zhang, L. Niu, T. You, A. Ivaska, *Chemical Communications* **2005**, 4193-4195.