

# Stiffening of poly(dicyclopentadiene) based polyHIPEs by using a norbornene-ester based crosslinker

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## Introduction

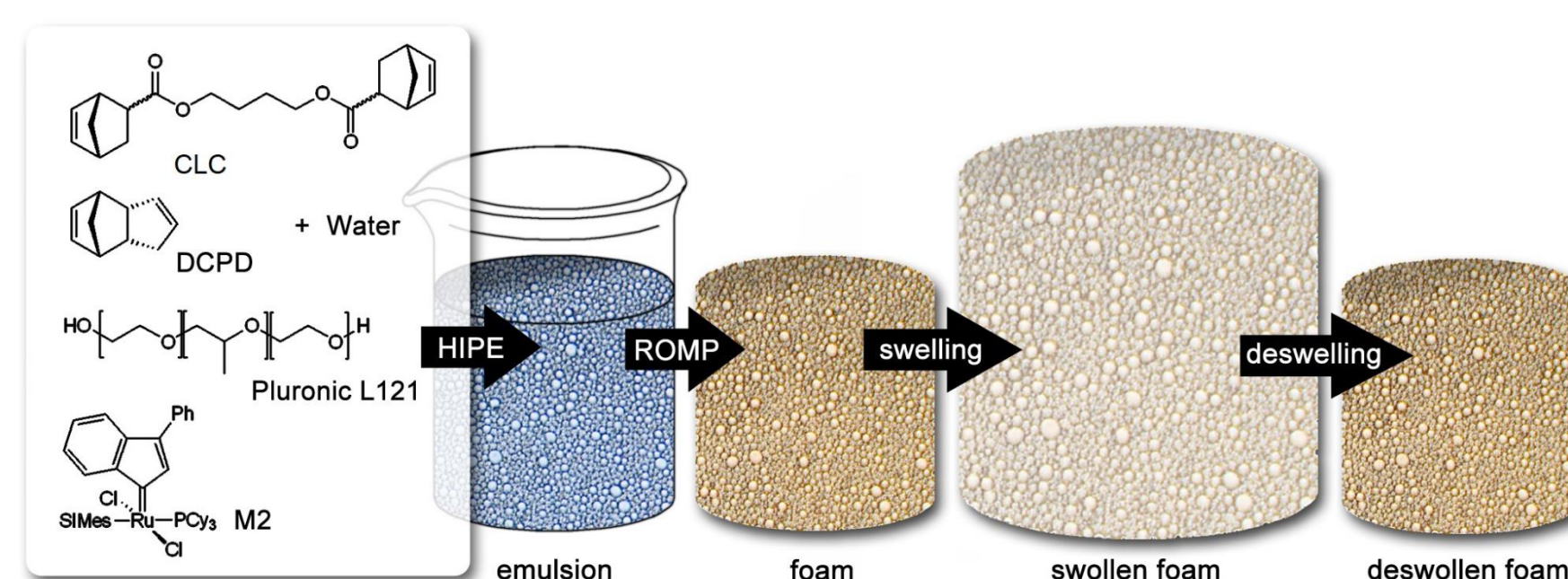
High internal phase emulsion templating of dicyclopentadiene (DCPD) and subsequent curing via Ring-opening Metathesis Polymerization (ROMP) is a straight forward way to prepare throughout open macroporous polymer foams characterized by outstanding mechanical properties<sup>1</sup> and a high degree of unsaturation facilitating further functionalization.<sup>2</sup> The polymer foams show high uptake of nonpolar solvents (up to about 1500 w%). However, upon deswelling the original porous structure is corrupted or even lost, narrowing the possible selection of solvents for post-polymerization functionalization.<sup>3</sup>

Herein we wish to report foams of nominal porosity of 80% made from a formulation containing DCPD and a second difunctional monomer bearing two polymerizable norbornene moieties which overcome the said limitation. It will be shown that swelling and subsequent deswelling of monolithic foam specimens in solvents like toluene results in the same macroscopic as well as microscopic structure of the monoliths as the untreated samples, facilitating post-polymerization functionalization.

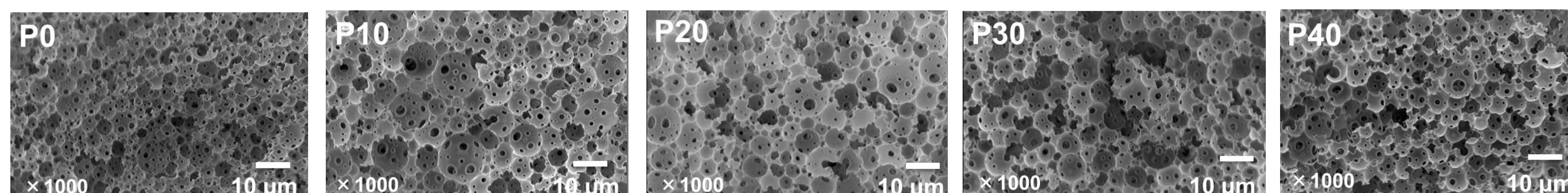
## Preparation

Foams of 80% nominal porosity were prepared by DCPD and a varying content of a second crosslinking comonomer (CLC) (10-40 wt% in respect to DCPD). The DCPD homopolymers was also prepared. A total amount of 10 g of monomers and 0.7 g of Pluronic L-121 surfactant (7 wt% in respect to the total amount of monomers) were added into a 250 mL three necked round bottom flask.<sup>2</sup> Additionally, 100 mL toluene were added in order to maintain the DCPD in liquid state. Subsequently, the mixture was stirred with a mechanical stirrer at 400 rpm while 40 mL distilled water were added dropwise. Afterwards, stirring was continued for 1 h. Then, the initiator M2 with molar ratio 1:15000 was dissolved in 200  $\mu$ L toluene and added under severe agitation. The pinky viscous mixture was poured into molds and cured at 80 °C for 2h. The resulted white monoliths were put into acetone for 15 min and subsequently dried under ambient conditions.

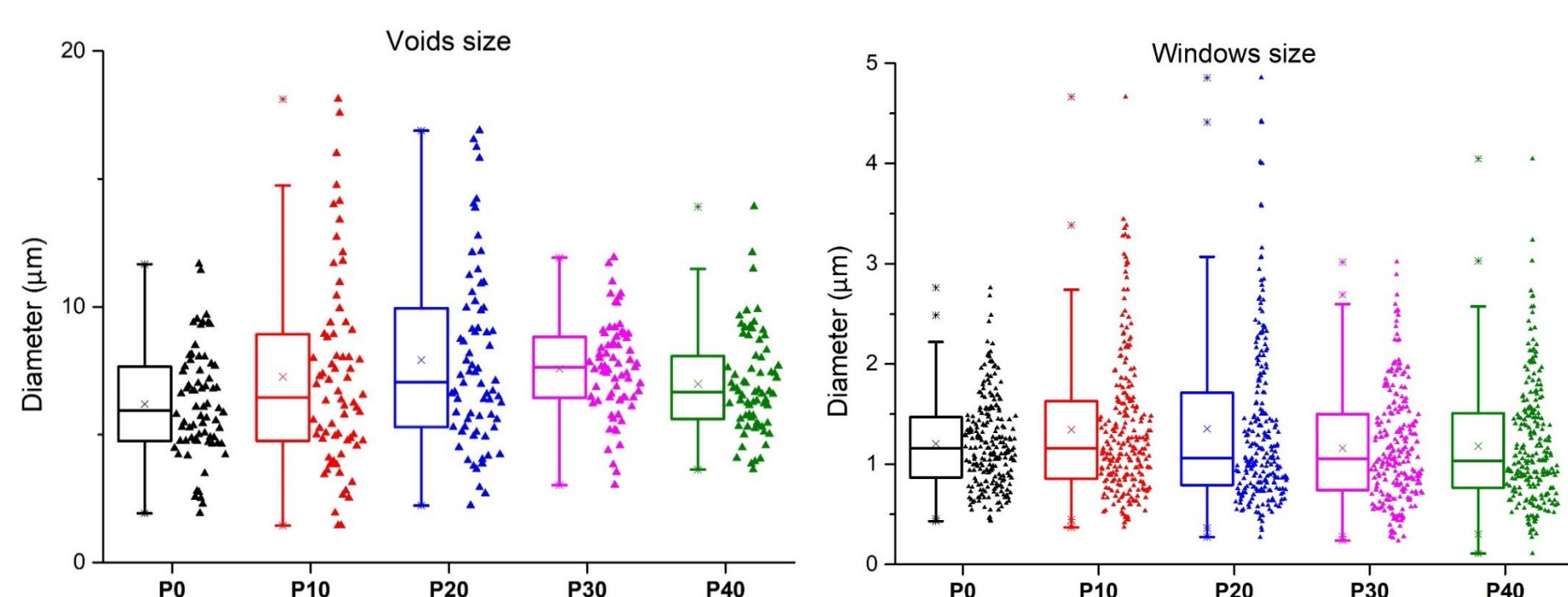
	DCPD, g (mmol)	CLC, g (mmol)	Catalyst, mg (mmol)
P0	10 (75.6)	-	4.8 (0.0050)
P10	9 (68.1)	1 (3.0)	4.5 (0.0047)
P20	8 (60.5)	2 (6.1)	4.2 (0.0044)
P30	7 (52.9)	3 (9.1)	3.9 (0.0041)
P40	6 (45.4)	4 (12.1)	3.6 (0.0038)



## Characterization of the foams

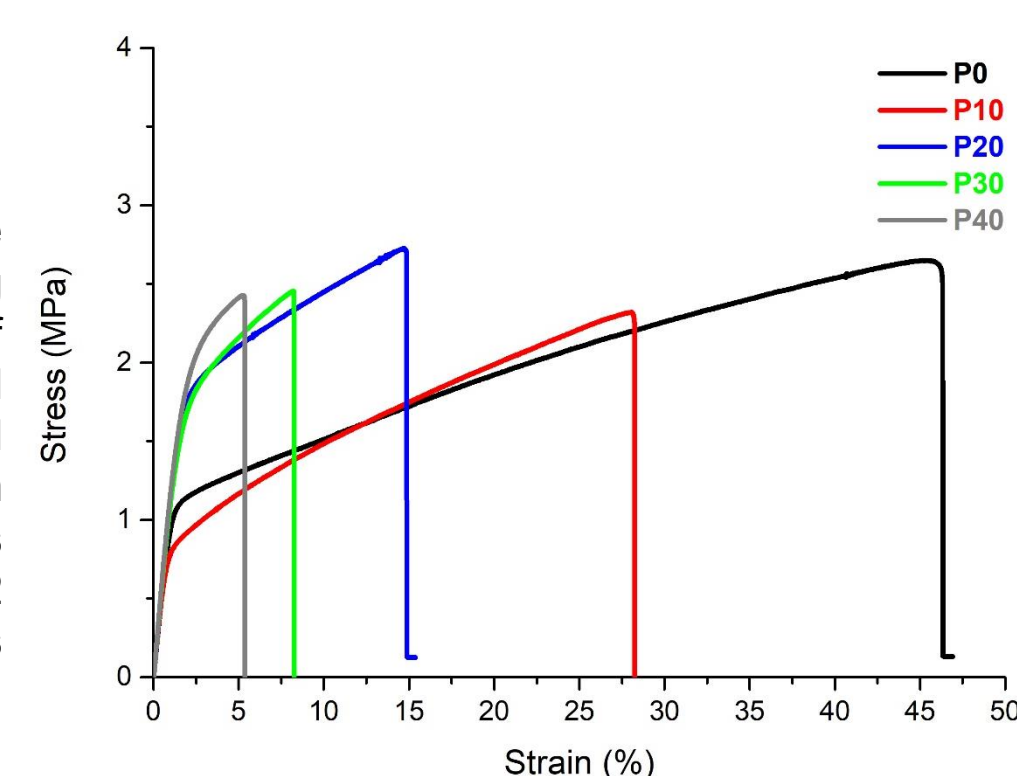


Scanning electron micrographs of the foams: P0 neat DCPD, P10 10w% 1, P20 20w% 1, P30 30w% 1, P40 40% 1; (average) void diameters: 6-8  $\mu$ m, (average) window diameters: 1.0-1.3  $\mu$ m.

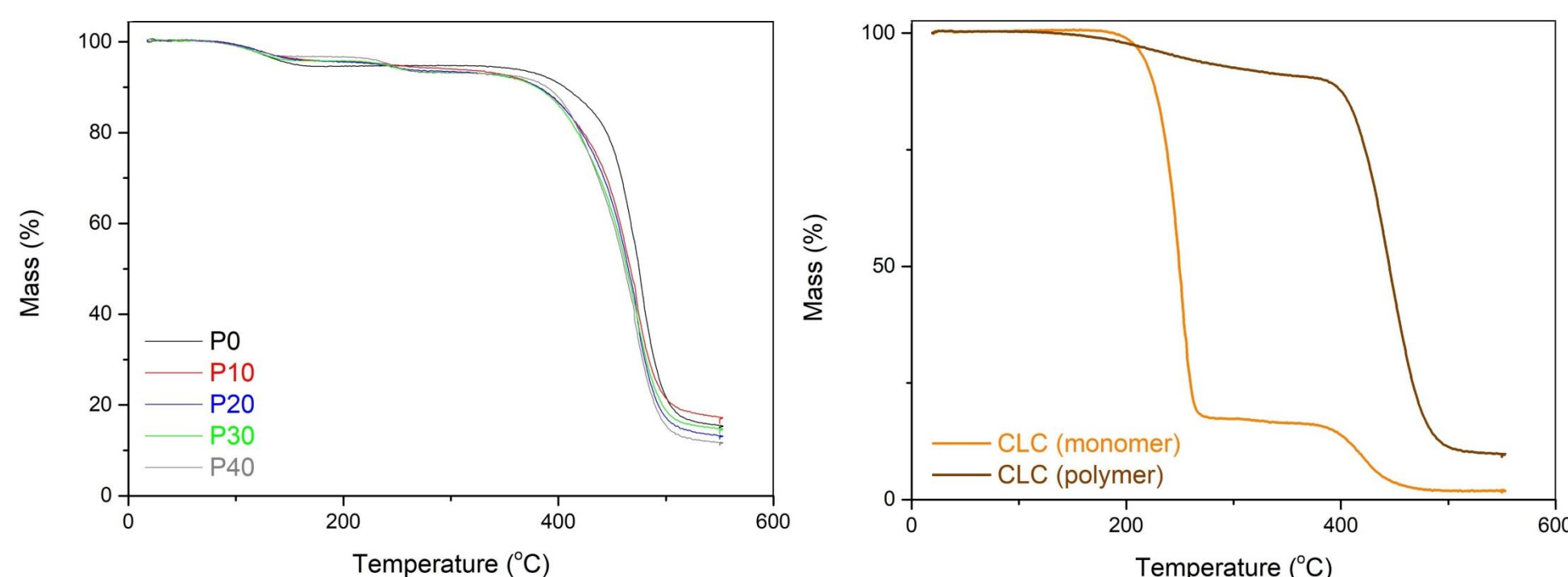


Box-whisker/bee swarm plot of void and window size distribution (median: horizontal line in the box; quartiles: upper and lower limit of the box, the boxes represent a restricted area where half of the overall values are included; average:  $\square$ ; whiskers: 1.5-IQR. Bee swarm plot showing a one-dimension dispersion of densely packed and non-overlapping data points)

Mechanical properties were assessed by stress strain testing at room temperature at a rate of 10 mm/min. HIPE was casted into Teflon molds (shouldered tensile test specimens, of 5 mm width at breaking point, thickness of 3 mm, 43 mm gage length, 62 mm distance between shoulders and 100 mm overall length).



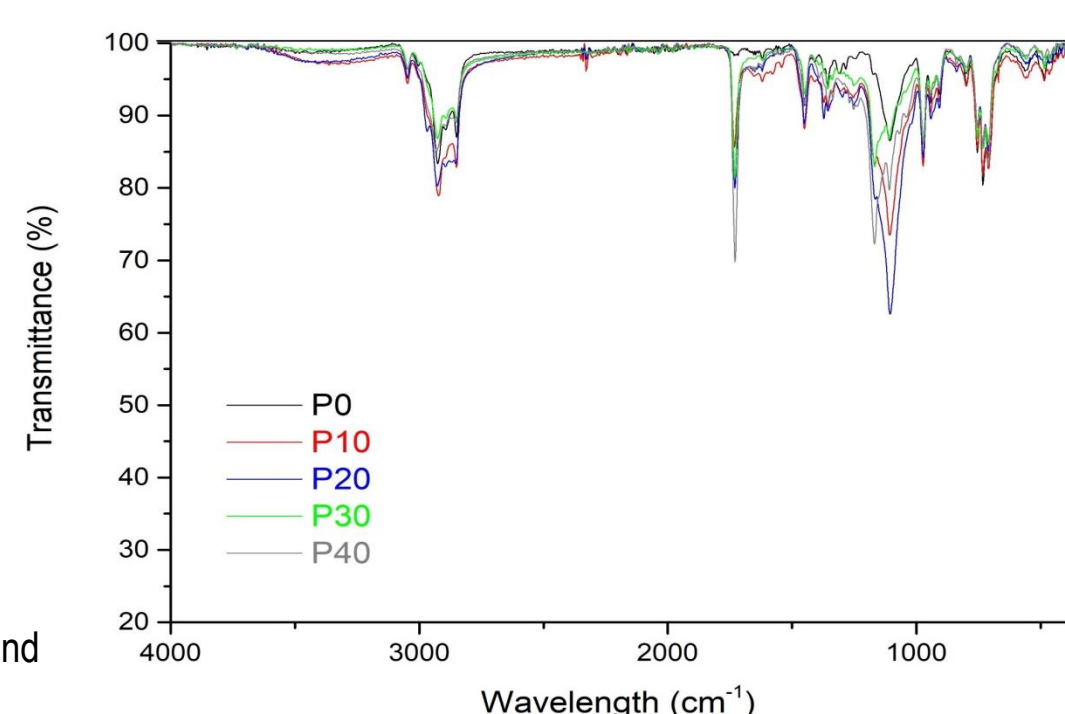
## CLC crosslinking degree



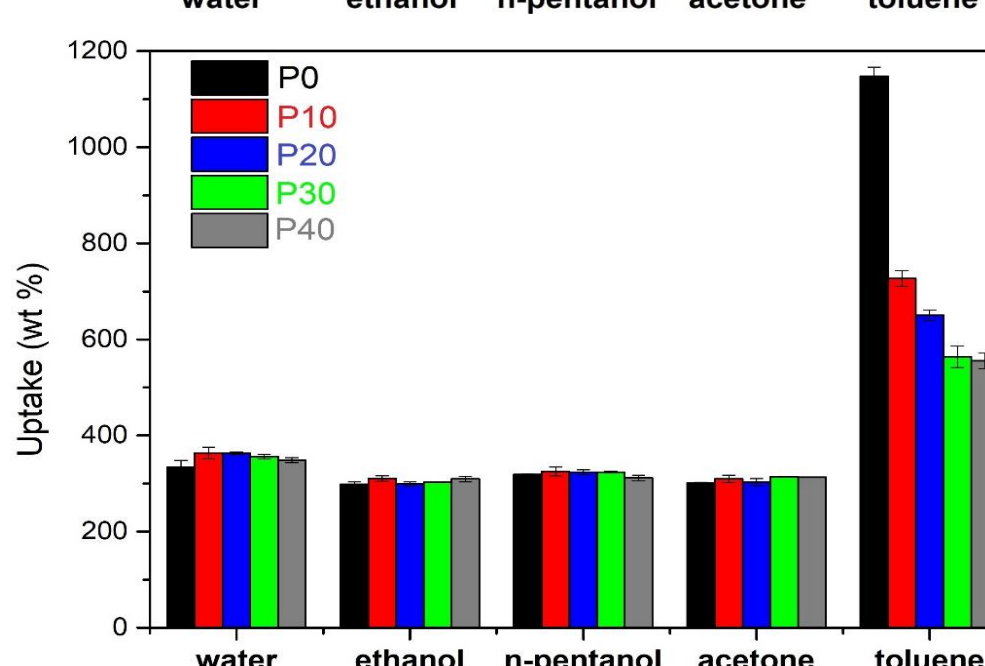
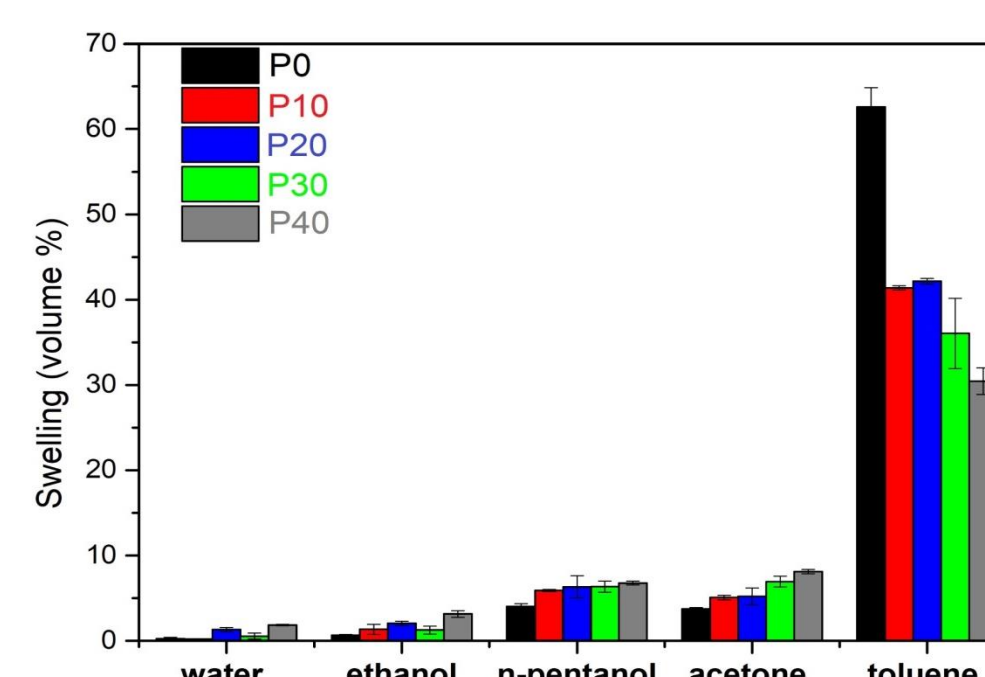
Thermogravimetric analysis (TGA) was performed on DCPD and DCPD/CLC polyHIPEs with heating rate 10 °C/min until the final temperature of 500 °C. The mass loss at 240 °C corresponds to retro-Diels-Alder reaction that occurs on free norbornene moieties of CLC monomer.

	Crosslinked fraction (%)	CLC crosslinking degree (%)
P10	72.4	7.2
P20	71.4	14.3
P30	72.0	21.6
P40	68.7	27.5

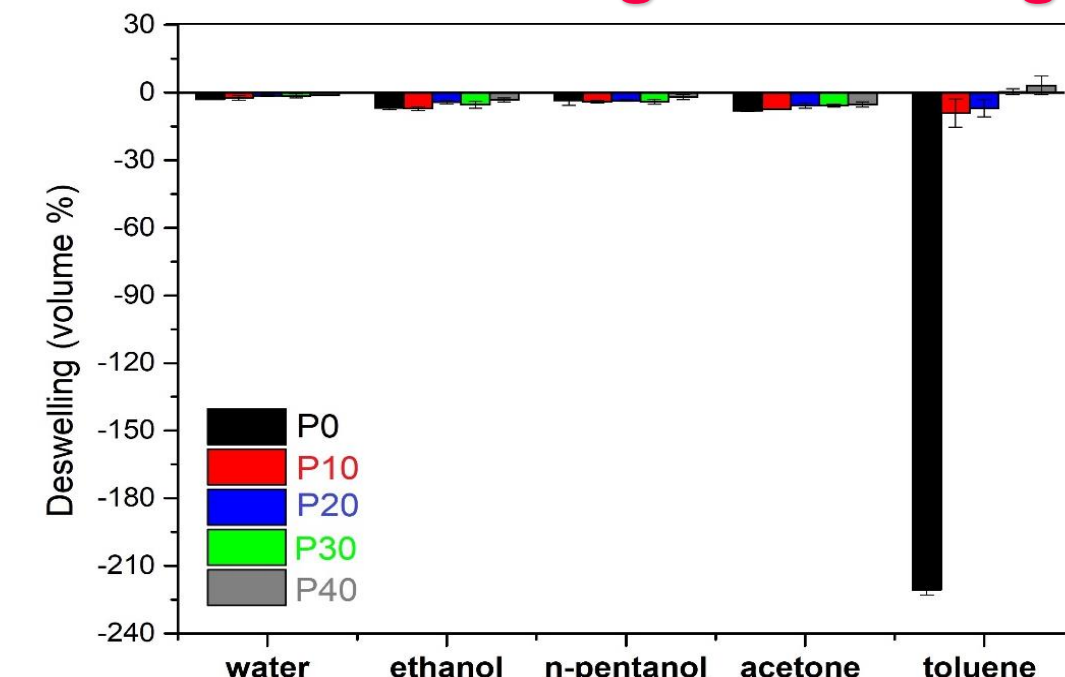
IR spectra of unoxidized DCPD and DCPD/CLC foams.



	mechanical properties/porosity				
DCPD/CLC	P0	P10	P20	P30	P40
Young's modulus (MPa)	103 $\pm$ 3	106 $\pm$ 5	114 $\pm$ 5	115 $\pm$ 2	117 $\pm$ 3
ultimate tensile strength (MPa)	2.65 $\pm$ 0.12	2.18 $\pm$ 0.21	2.72 $\pm$ 0.24	2.51 $\pm$ 0.18	2.61 $\pm$ 0.13
max strain (%)	42.0 $\pm$ 3.5	23.8 $\pm$ 4.6	17.1 $\pm$ 1.3	9.2 $\pm$ 2.0	8.0 $\pm$ 1.5
Modulus of toughness (MJ/m <sup>3</sup> )	0.84 $\pm$ 0.07	0.39 $\pm$ 0.10	0.36 $\pm$ 0.03	0.19 $\pm$ 0.06	0.16 $\pm$ 0.04
0.2 % offset yield point (MPa)	1.00 $\pm$ 0.16	0.80 $\pm$ 0.08	1.44 $\pm$ 0.20	1.64 $\pm$ 0.15	1.67 $\pm$ 0.04
0.2 % offset yield point (%)	0.012 $\pm$ 0.002	0.009 $\pm$ 0.001	0.015 $\pm$ 0.002	0.017 $\pm$ 0.001	0.017 $\pm$ 0.001
Porosity (%)	71.3 $\pm$ 2.8	77.0 $\pm$ 1.2	79.4 $\pm$ 0.5	78.3 $\pm$ 0.9	76.8 $\pm$ 2.0



## Swelling/deswelling



Swelling/deswelling procedure was done at room temperature in five solvents. HIPEs were casted into disk molds (thickness of 2 mm and diameter of 30 mm).



Photographs of specimens during and after swelling procedure in toluene.

## Conclusion

HIPEs consisting of DCPD and a second difunctional monomer bearing two polymerizable norbornene moieties in various compositions were cured via ROMP yielding foams of 80% nominal porosity. The approx. 30% of free norbornene moieties and the ability of the monoliths to maintain their macrostructure after swelling/deswelling in solvents like toluene facilitate post-functionalization reactions. Tensile tests on samples revealed that the addition of CLC results in stiffer but less tough foams.

## References

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- Knall, A.-C.; Kovačič, S.; Hollauf, M.; Reishofer, D. P.; Saf, R.; Slugovc, C.; *Chem. Commun.* **2013**, *49*, 7325-7327.
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