Electronic Supplementary Material (ESI) for Polymer Chemistry.

An Environmentally Benign Post-Polymerization Functionalization Strategy Towards Unprecedented Poly(vinylamine) PolyHIPEs

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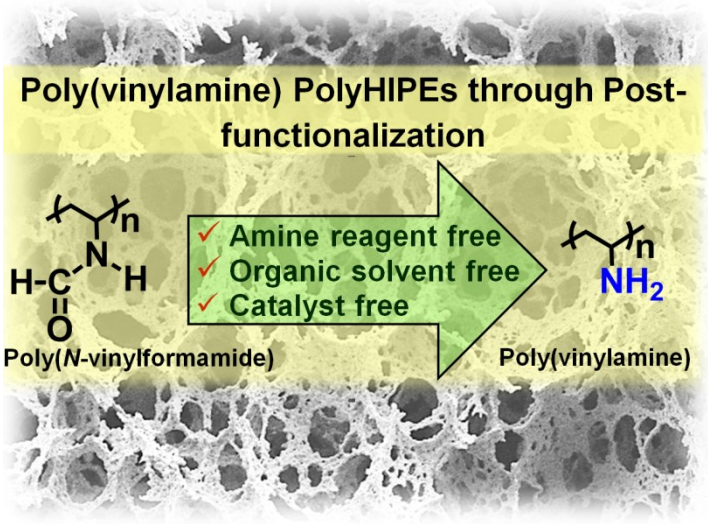
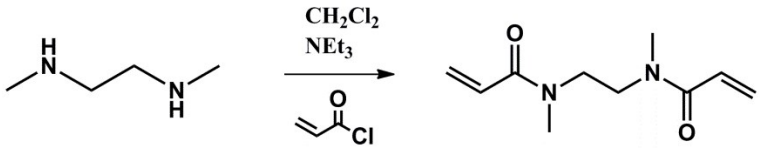
Supplementary Information



Synthesis of *N,N´*-(ethane-1,2-diyl)bis(*N*-methylacrylamide)

N,N´-dimethylethylenediamine (300 mg, 3.4 mmol) was dissolved under argon in 30 mL CH_2Cl_2 and treated with 1.5 mL NEt_3. A solution of acid chloride (7.0 mmol) in 20 mL CH_2Cl_2 was slowly added and the resulting solution was stirred at r.t. for 18 h. The solvent was then evaporated and the product was isolated by column chromatography (silica gel, DCM : acetone 1.75 : 1; 65% yield).



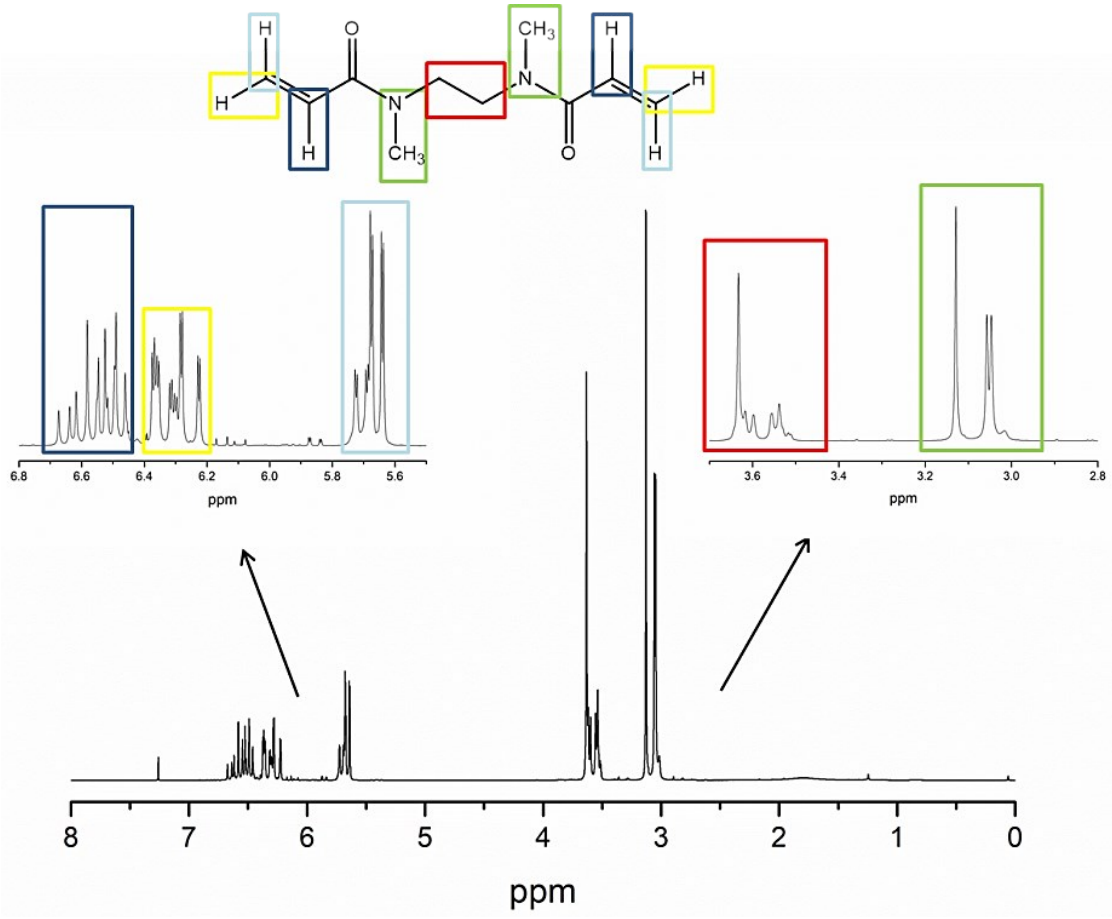


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$) of eBIS crosslinker: δ (ppm) 3.05, 3.06, 3.13 (3s, 6H, *N*CH_3); 3.54 – 3.63 (3s, 4H, *N*CH_2); 5.63 – 5.72 (m, 2H, CH=CH_2); 6.22 – 6.37 (m, 2H, CH=CH_2); 6.46 – 6.67 (m, 2H, CH=CH_2).

	PNVF-eBIS$_{10}$	PNVF-eBIS$_{20}$	PNVF-BIS$_{10}$	PNVF-mBIS$_{10}$
Aqueous External Phase (wt.%)				
H_2O	20.96	20.64	21.02	20.98
NVF	3.25	3.19	3.25	3.25
eBIS	1.00	2.21	/	/
BIS	/	/	0.79	/
mBIS	/	/	/	0.92
F108	1.28	1.48	1.27	1.28
APS	0.42	0.54	0.40	0.42
temed	0.13	0.13	0.13	0.13
Total	27.04	28.19	26.86	26.98
Organic Internal Phase (wt.%)				
Toluene	72.96	71.81	73.14	73.02
Total	72.96	71.81	73.14	73.02

Table S1. Recipes for NVF-based O/W HIPEs

Elemental analyses

Table S2. Elemental analysis data

Content, wt.%	PNVF-eBIS$_{10}$	PNVF-eBIS$_{20}$	PVAM-eBIS$_{10}$	PVAM-eBIS$_{20}$
C	45.1	46.5	41.3	44.4
H	7.4	7.7	7.2	7.8
N	16.1	17.1	16.8	17.2
S	0.8	1.1	1.4	0.8
O	30.6	27.6	33.3	29.8

The nitrogen content in *mmol* of nitrogen per gram of polyHIPE was determined from the elemental analysis data as follows (Table S3). The following example is for the PNVF-eBIS$_{10}$ polyHIPE.

$$N_{(\text{found})} = \frac{0.1605 \cdot \frac{g\ (N)}{g\ (polyHIPE)}}{14.01\ g/mmol} = 11.45\ \frac{mmol\ (N)}{g\ (polyHIPE)}$$

Further, we calculated the percent of nitrogen atoms belonging to the formamide groups using the following equation:

$$\%\ \text{of nitrogen atoms from formamide} = 0.9 \cdot (\frac{1}{\overline{1}}) + 0.1 \cdot (\frac{0}{\overline{2}}) = 0.90 \qquad (2)$$

where 0.9 and 0.1 correspond to the mole fraction of NVF and eBIS monomers, respectively. Numerators and denominators used in fractions in brackets denote that in the case of NVF one nitrogen atom out of one and in the case of eBIS zero nitrogen atoms out of two belong to the formamide group and participate in the hydrolysis.

Then, the amount of formamide groups per gram of polyHIPE, which equals the amount of the nitrogen from the formamide group, was determined as indicated below for the PNVF-eBIS$_{10}$ and PVAM-eBIS$_{10}$ polyHIPE.

$$NVF = 11.45\ \frac{mmol\ (N)}{g\ (polyHIPE)} \cdot 0.90 = 10.30\ \frac{mmol\ (NVF)}{g\ (polyHIPE)}$$

$$VAM = 12.00\ \frac{mmol\ (N)}{g\ (polyHIPE)} \cdot 0.90 = 10.80\ \frac{mmol\ (VAM)}{g\ (polyHIPE)}$$

Table S3. The calculated nitrogen and functional group contents for PNVF-eBIS and PVAM-eBIS PolyHIPEs.

Sample	Nitrogen Content		NVF or VAM Content
	[wt.%][a]	[mmol/g] [b]	[mmol/g]
PNVF-eBIS$_{10}$	16.05	11.45	10.30
PNVF-eBIS$_{20}$	17.10	12.21	10.99
PVAM-eBIS$_{10}$	16.80	12.00	10.80

PVAM-eBIS$_{20}$	17.20	12.28	11.05

[a] Results from elemental analysis. [b]Calculated from elemental analysis

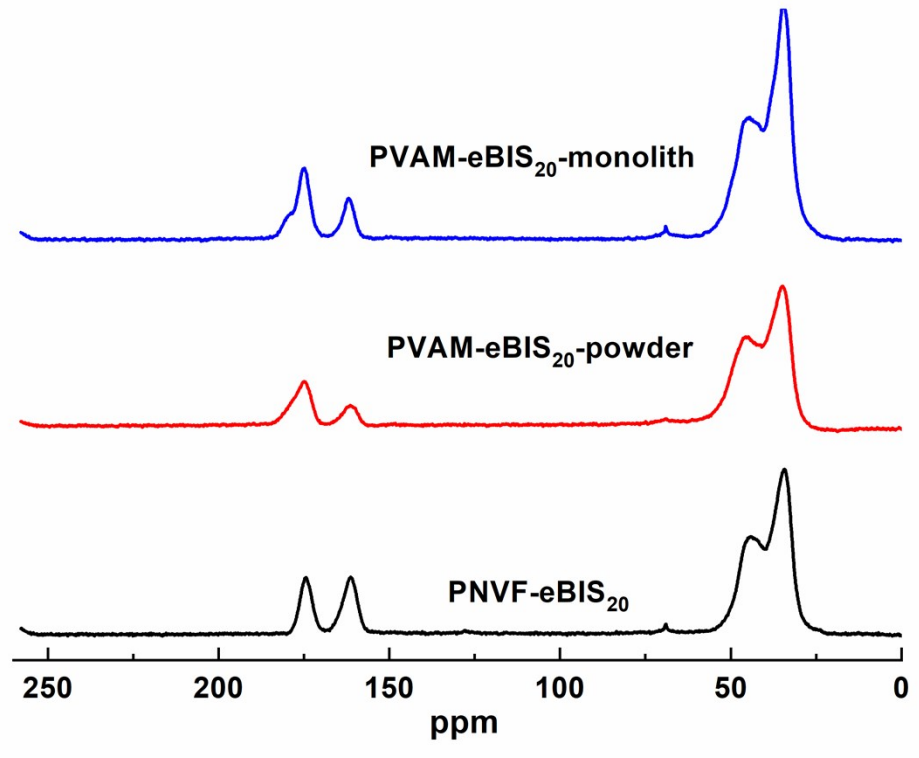


Figure S2. Solid-state ^{13}C CP/MAS NMR spectra of PNVF-eBIS$_{20}$ sample

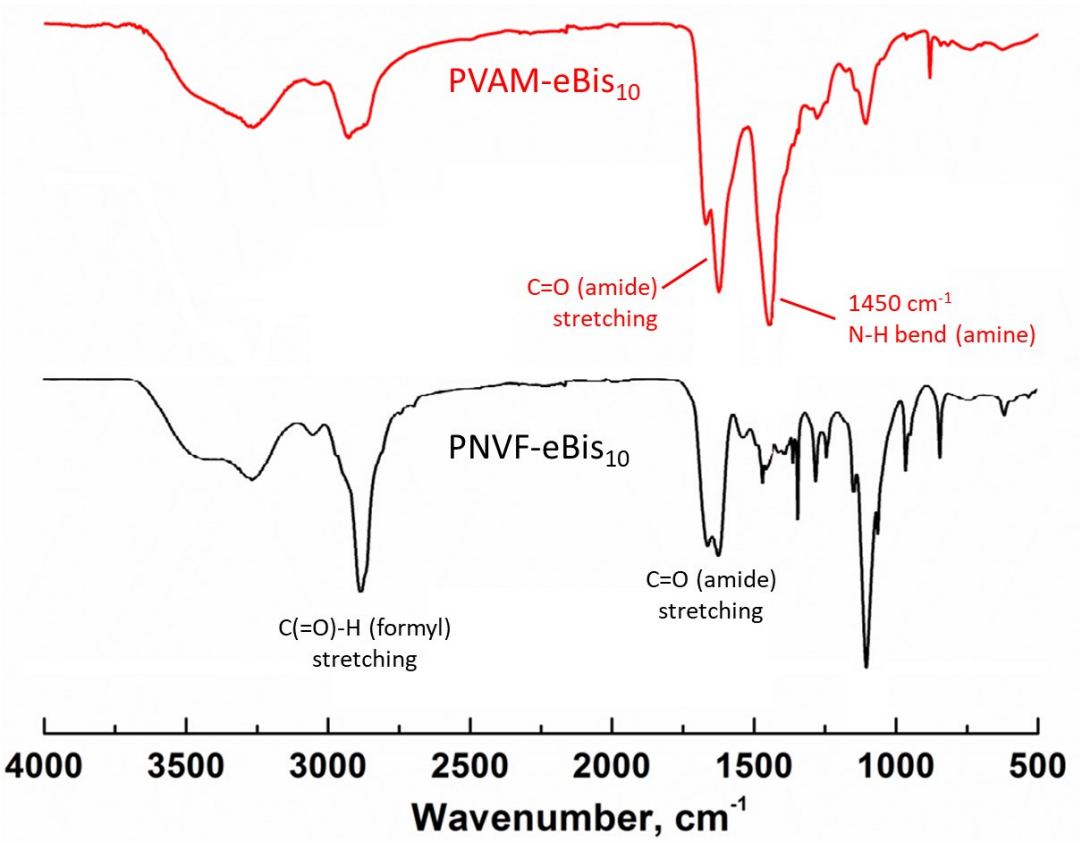


Figure S3. FT-IR spectra (ATR) of $PNVF_{eBIS10}$ polyHIPE before (black curve) and after (red curve) base hydrolysis.

Porosity

The total porosity ($P_{PH\text{-}T}$) of PNVF-eBIS$_{10}$ and PNVF-eBIS$_{20}$ hydrogel polyHIPEs can be subdivided into the porosity from the polyHIPE voids ($P_{PH\text{-}V}$) and the porosity within the polyHIPE void walls ($P_{PH\text{-}HG}$) that is derived from the total bulk hydrogel porosities ($P_{HG\text{-}T}$).[1]

The polyHIPE's porosity components were calculated using following equations:

Equation S1
$$P_{PH-T} = 1 - \frac{\rho_{PH}}{\rho_P}$$

Equation S2
$$P_{HG-T} = 1 - \frac{\rho_{HG}}{\rho_P}$$

Equation S3
$$P_{PH-HG} = \left(\frac{\rho_{PH}}{\rho_{HG}}\right) P_{HG-T}$$

Equation S4
$$P_{PH-V} = P_{PH-T} - P_{PH-HG} = 1 - \frac{\rho_{PH}}{\rho_{HG}}$$

There are two contributions to the total porosity of a dry PNVF polyHIPEs ($P_{PH\text{-}T;}$ Eq S1): (1) the porosity originating in the polyHIPE voids ($P_{PH\text{-}V}$; Eq S4); (2) the porosity originating in the porous hydrogel walls ($P_{PH\text{-}HG}$; Eq S3) (derived from the total HG-R porosity ($P_{HG\text{-}T}$; Eq S2)). These four porosity values were calculated using Equation S1 through Equation S4. As expected, The $P_{PH\text{-}T}$ values, calculated from the polyHIPE densities (being 0.13 and 0.15 g·cm^{-3}) were around 87 and 85 % for PNVF-eBIS$_{10}$ and PNVF-eBIS$_{20}$, respectively. The bulk hydrogel porosities ($P_{HG\text{-}T}$), from the bulk hydrogel densities (being 0.37 and 0.41 g·cm^{-3}), were found around 63 and 59 % for PNVF-eBIS$_{10}$ and PNVF-eBIS$_{20}$ bulk hydrogels, respectively. $P_{PH\text{-}HG}$ (the porosity originating in the porous void walls and based upon $P_{HG\text{-}T}$) was relatively small, around 22 and 21 % for PNVF-eBIS$_{10}$ and PNVF-eBIS$_{20}$, respectively. Therefore, based on these results, we can conclude that the dominant contribution, by far, to the total porosity ($P_{PH\text{-}T}$) of hydrogel polyHIPEs is the porosity originating from the highly interconnected void structure ($P_{PH\text{-}V}$), which is around 65 and 64 % for PNVF-eBIS$_{10}$ and PNVF-eBIS$_{20}$, respectively.

[1] (a) S. Kovačič and M. S. Silverstein, *Macromol. Rapid Commun.*, **2016**, 37, 1814; (b) D. Pahovnik, J. Majer, E. Žagar and S. Kovačič, *Polym. Chem.*, **2016**, 7, 5132; (c) M. Ovadia and M. S. Silverstein, *Polym. Int.*, **2016**, 65, 280.