

Structure-performance correlations of cross-linked boronic acid polymers as adsorbents for recovery of fructose from glucose-fructose mixtures

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SUPPORTING INFORMATION

¹H- & ¹³C-NMR-spectra of iminodiethyl *p*-vinylphenylboronate

¹H-NMR, and ¹³C-NMR spectra were recorded at 400 and 100 MHz, respectively, using a Bruker AV400 spectrometer. Deuterated chloroform (CDCl₃) was used as NMR solvent and all measurements were performed at room temperature. The chemical shifts were references to the residual solvent signal (CDCl₃: δ = 7.26(s) ppm in ¹H-NMR, δ = 77.2 (t) ppm in ¹³C-NMR).

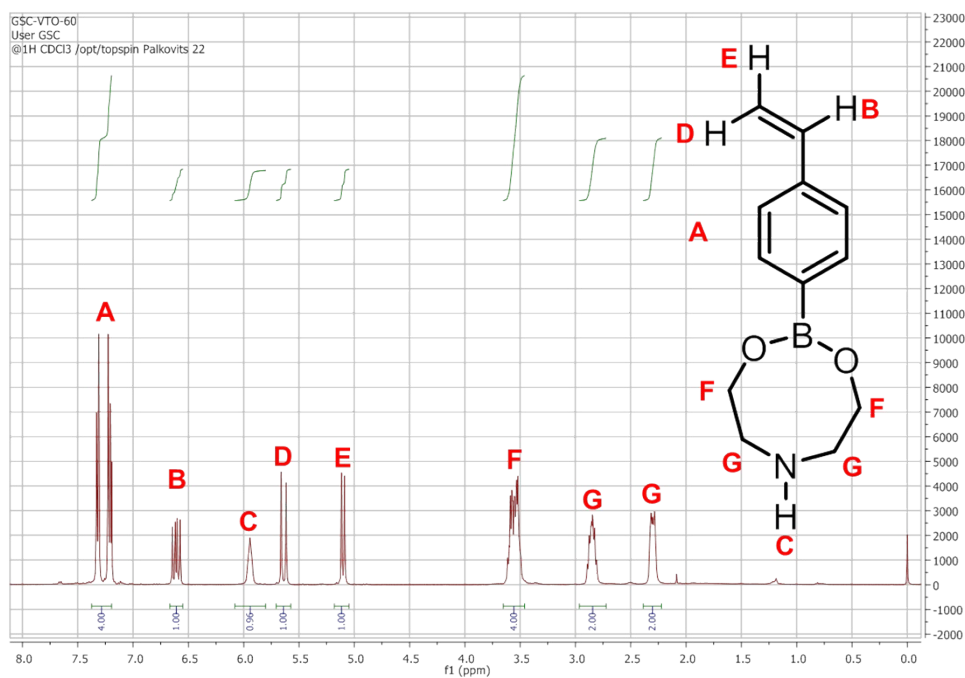


Fig. 1S: ¹H-NMR spectrum of *p*-vinylphenylboronic diethanolamine ester in CDCl₃.

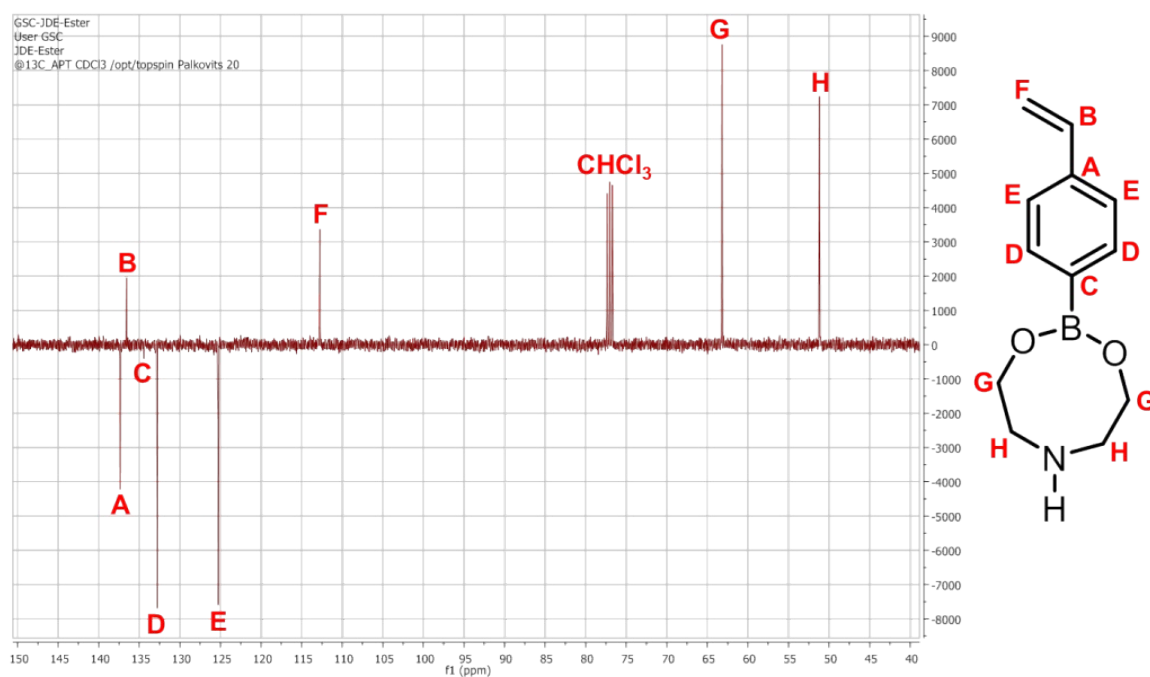


Fig. 2S: ¹³C-APT NMR spectrum of *p*-vinylphenylboronic diethanolamine ester in CDCl₃.

$^1\text{H-NMR}$ -spectra of 2,6-divinylnaphthalene

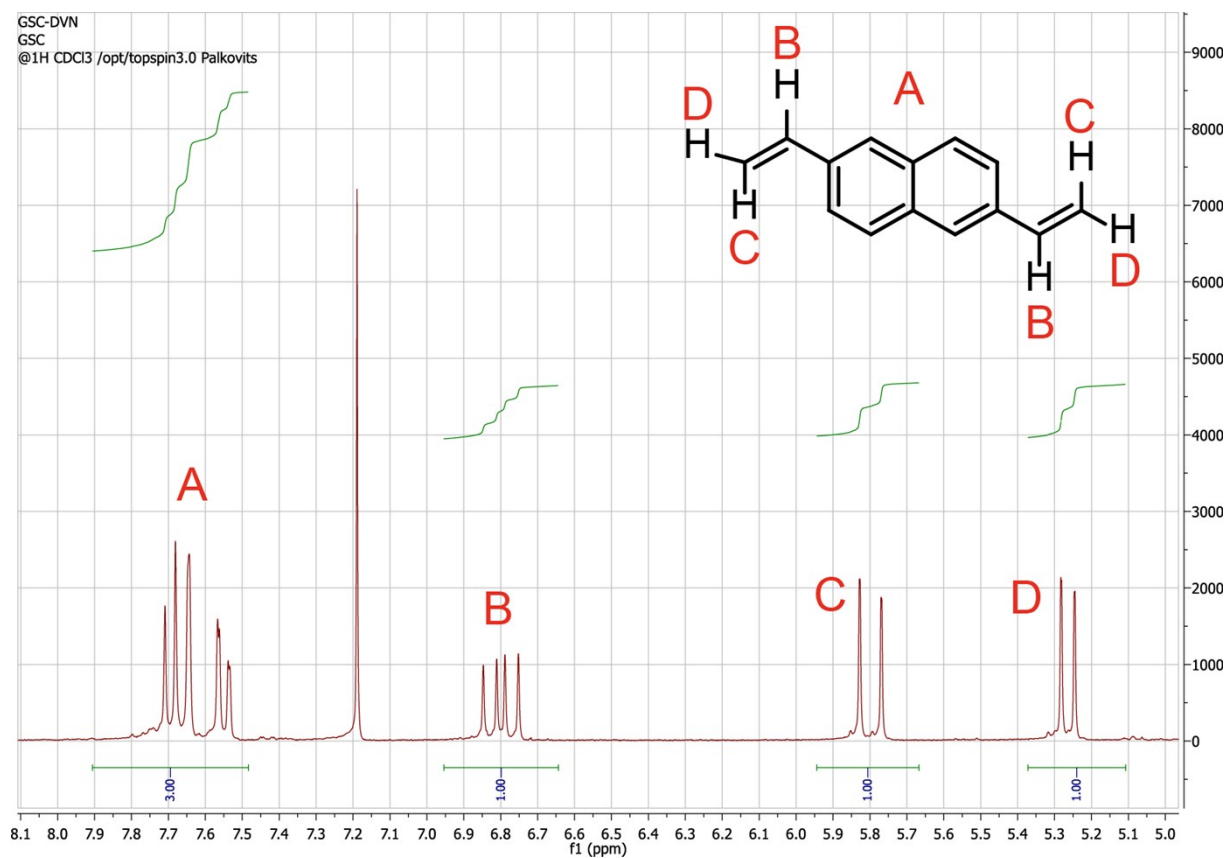


Fig. 3S: $^1\text{H-NMR}$ spectrum of 2,6-divinylnaphthalene in CDCl_3 .

Amount of cross-linker and polymer yields

Tab. 1S: Added amounts of cross-linker during polymer synthesis and polymer yields after washing with phosphate buffer, * - 3 g scale, +- amount in mg.

Entry	Cross-Linker	Amount [μ L]	Yield [%]
1	No-Cross-Linker	0	62
2	DVB, 5mol%	205	87
3	DVB, 20mol%	820	89
4	DVB, 40mol%	1639	86
5	EDMA, 5mol%	217	91
6	EDMA, 20mol%	870	97
7	EDMA, 40mol%	1739	91
8*	DVS, 20mol%	277	71
9*	TDMA, 20mol%	725	86
10*	PDMA, 20mol%	681 ⁺	93
11*	OD, 20mol%	408	53
12*	DD, 20mol%	509	70
13*	TD, 20mol%	703	61
14*	DVN, 20mol%	498 ⁺	71

Elemental analysis results

Tab. 2S: Calculated and found boron, carbon and hydrogen contents for the DVB and EDMA polymers with different amount of cross-linker. The polymers were analysed after washing with the phosphate buffer (pH 7.5).

Entry	Cross-Linker	B-content		C-content		H-content	
		[mg g ⁻¹]		[mg g ⁻¹]		[mg g ⁻¹]	
		calc.	found	calc.	found	calc.	found
1	No-Cross-Linker	72	51 (71%)	641	619 (97%)	74	64 (87%)
2	DVB, 5mol%	69	43 (62%)	656	642 (98%)	71	63 (88%)
3	DVB, 20mol%	59	38 (64%)	695	699 (101%)	72	67 (94%)
4	DVB, 40mol%	49	35 (71%)	732	739 (101%)	73	68 (94%)
5	EDMA, 5mol%	68	44 (65%)	638	610 (96%)	71	60 (85%)
6	EDMA, 20mol%	56	40 (71%)	633	621 (98%)	71	64 (90%)
7	EDMA, 40mol%	46	31 (67%)	628	642 (102%)	71	68 (96%)

Tab. 3S: Calculated and found boron for the polymers with different types of 20mol% of cross-linker. The polymers were analysed after washing with the phosphate buffer (pH 7.5).

Entry	Cross-Linker	B-content	
		[mg g ⁻¹]	
		calc.	found
1	DVS, 20mol%	61	45 (74%)
2	TDMA, 20mol%	51	37 (73%)
3	PDMA, 20mol%	53	35 (66%)
4	OD, 20mol%	61	47 (77%)
5	DD, 20mol%	59	52 (88%)
6	TD, 20mol%	55	46 (84%)
7	DVN, 20mol%	57	40 (71%)

Calculations

For both analytical methods sugar concentration was determined from the peak areas in mg g^{-1} . The amount of sugar in the samples was calculated following equation 1S.

$$n = \frac{c \cdot d \cdot V}{M} \quad (\text{Eq. 1S})$$

n – Amount of sugar [mmol]

c – Sugar concentration [mg g^{-1}]

d – Dilution factor []

V – Sample Volume [mL]

M – Molar mass [g mol^{-1}]

The equilibrium loading factor q was computed by dividing the amount of adsorbed sugar, calculated from the initial sugar amount n_0 and the sugar amount after adsorption n_1 , and either the amount of boron n_B (based on the ICP results, Eq. 2S) or the mass m_P of polymer used (Eq. 3S).

$$q = \frac{n_0 - n_1}{n_B} \quad (\text{Eq. 2S})$$

$$q = \frac{n_0 - n_1}{m_P} \quad (\text{Eq. 3S})$$

For the screening of the adsorption conditions, percentage of fructose sorption AE is calculated according as follows:

$$AE = \frac{n_0 - n_1}{n_0} \cdot 100\% \quad (\text{Eq. 4S})$$

Desorption efficiency DE was determined by dividing the amount of desorbed fructose n_D into the amount of adsorbed fructose n_A (Eq. 5S). The theoretical amount of n_A in 100 mg polymer with adsorbed fructose was calculated from adsorption results.

$$DE = \frac{n_D}{n_A} \cdot 100\%$$

(Eq. 5S)

Glucose conversion (X_{Glu}), fructose yield (Y_{Fru}) and selectivity (S_{Fru}) were computed by equations 6S-8S using the initial amount of glucose $n_{0, Glu}$ and amount of the respective sugar in the samples $n_{1, Glu}$ and $n_{1, Fru}$.

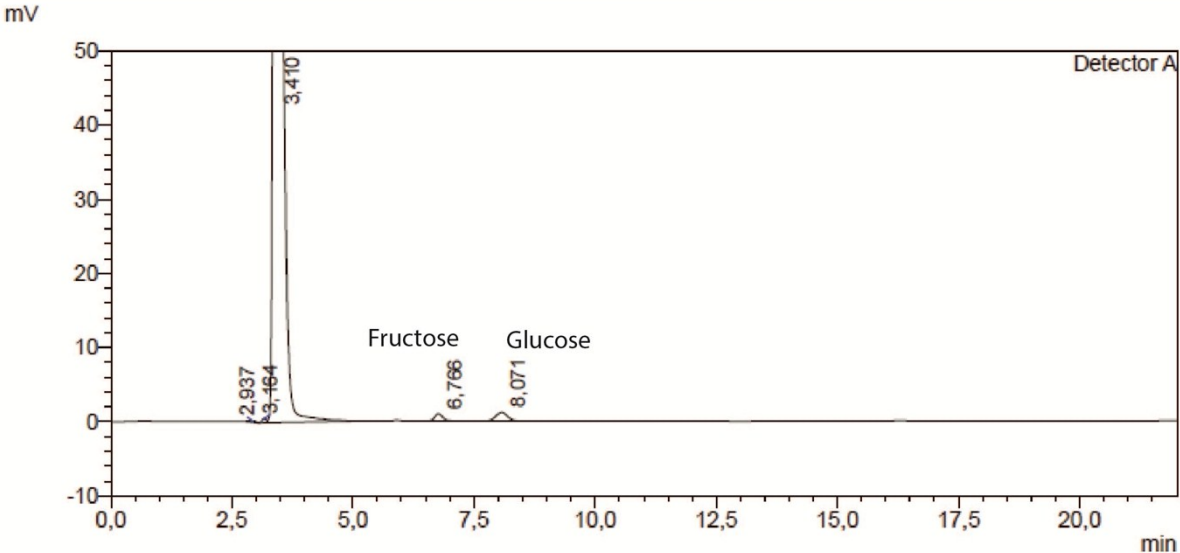
$$X_{Glu} = \frac{n_{0, Glu} - n_{1, Glu}}{n_{0, Glu}} \cdot 100\% \quad (\text{Eq. 6S})$$

$$Y_{Fru} = \frac{n_{1, Fru}}{n_{0, Glu}} \cdot 100\% \quad (\text{Eq. 7S})$$

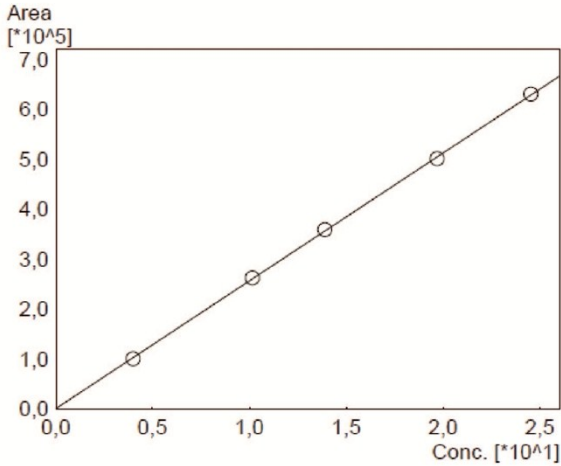
$$S_{Fru} = \frac{n_{1, Fru}}{n_{0, Glu} - n_{1, Glu}} \cdot 100\% \quad (\text{Eq. 8S})$$

HPLC analysis: example chromatogram and calibration curves

Chromatogram



Fructose: Standard Curve
 $f(x) = 25651.4 \cdot x + 0$
 $Rr1=0.9998971, Rr2=0.9997941$



Glucose: Standard Curve
 $f(x) = 24921.3 \cdot x + 0$
 $Rr1=0.9999771, Rr2=0.9999541$

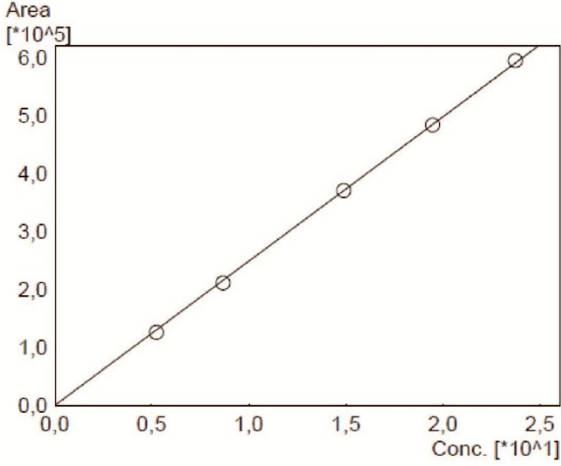


Fig. 4S: Example HPLC chromatogram of a sample containing glucose and fructose and corresponding calibration curves for glucose and fructose.

ATR-IR spectra of DVB, EDMA, PDMA and TDMA polymers

A Bruker Alpha-P FTIR spectrometer equipped with an ATR-IR diamond probe head was utilized to record solid-state IR data. A background spectrum was taken in the range of 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} prior to the sample measurement. Spectra were recorded in the same range and resolution. The obtained raw data was processed in the OPUS software.

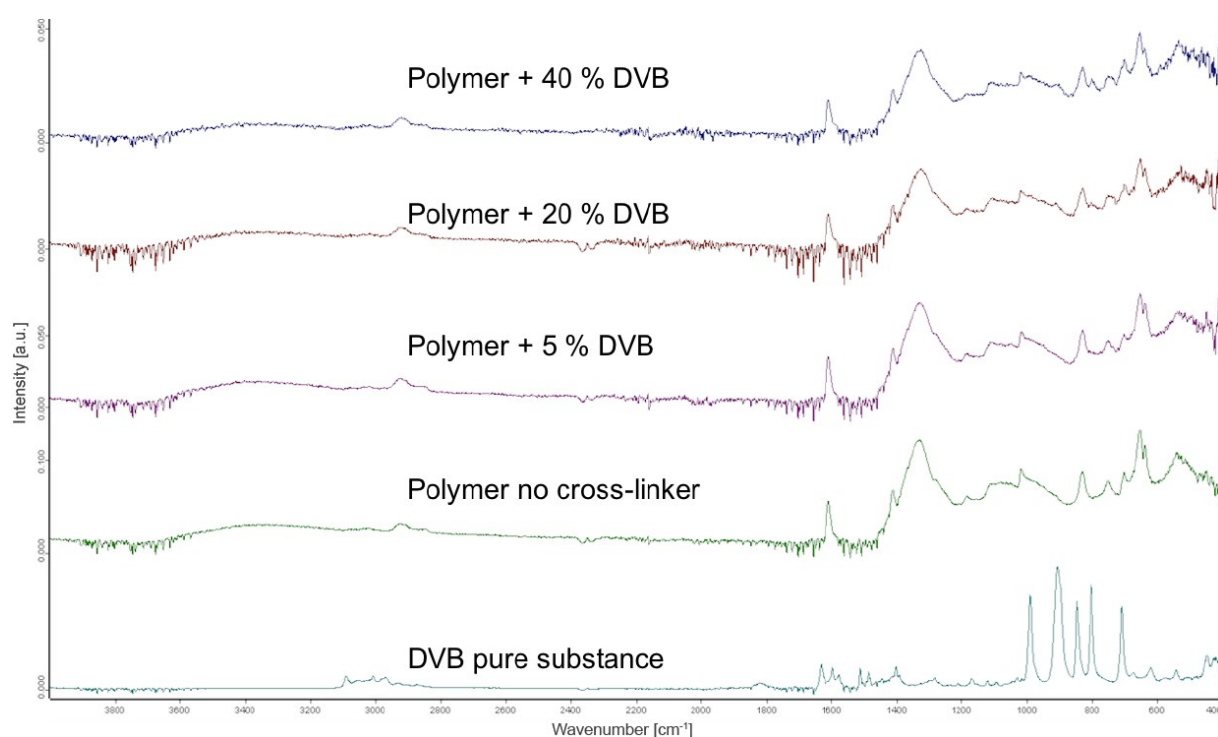


Fig. 5S: IR spectra of DVB and DVB cross-linked polymers.

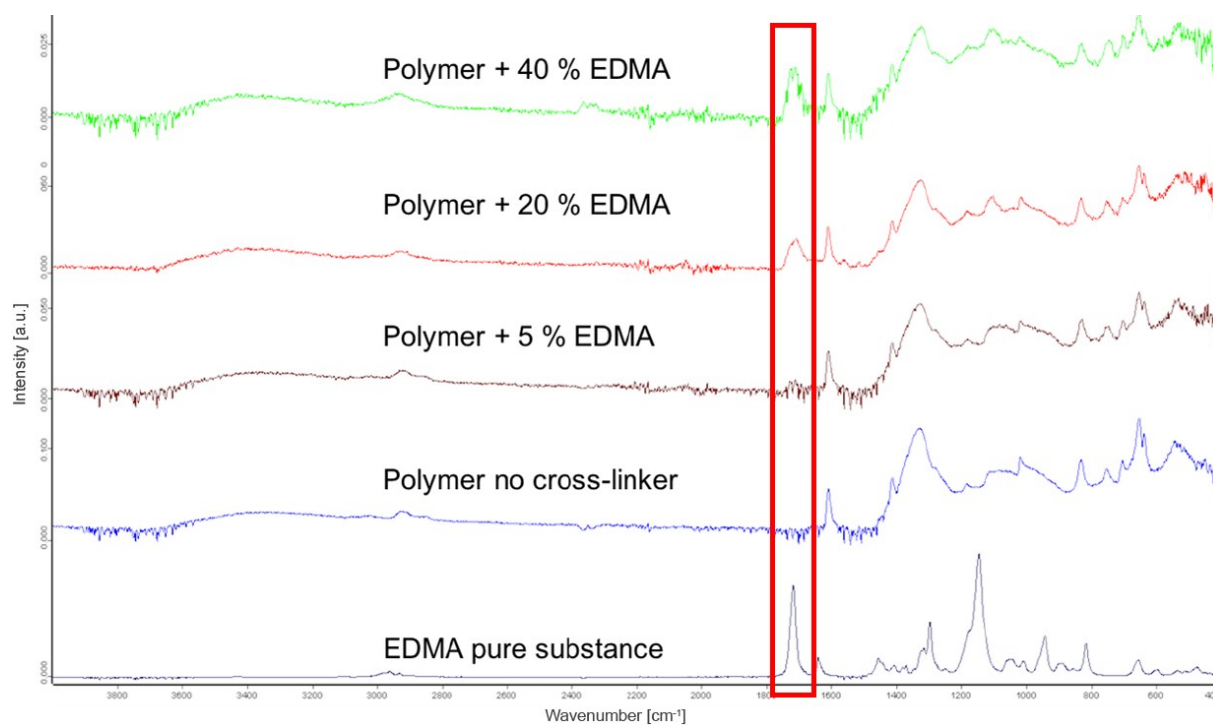


Fig. 6S: IR spectra of EDMA and EDMA cross-linked polymers.

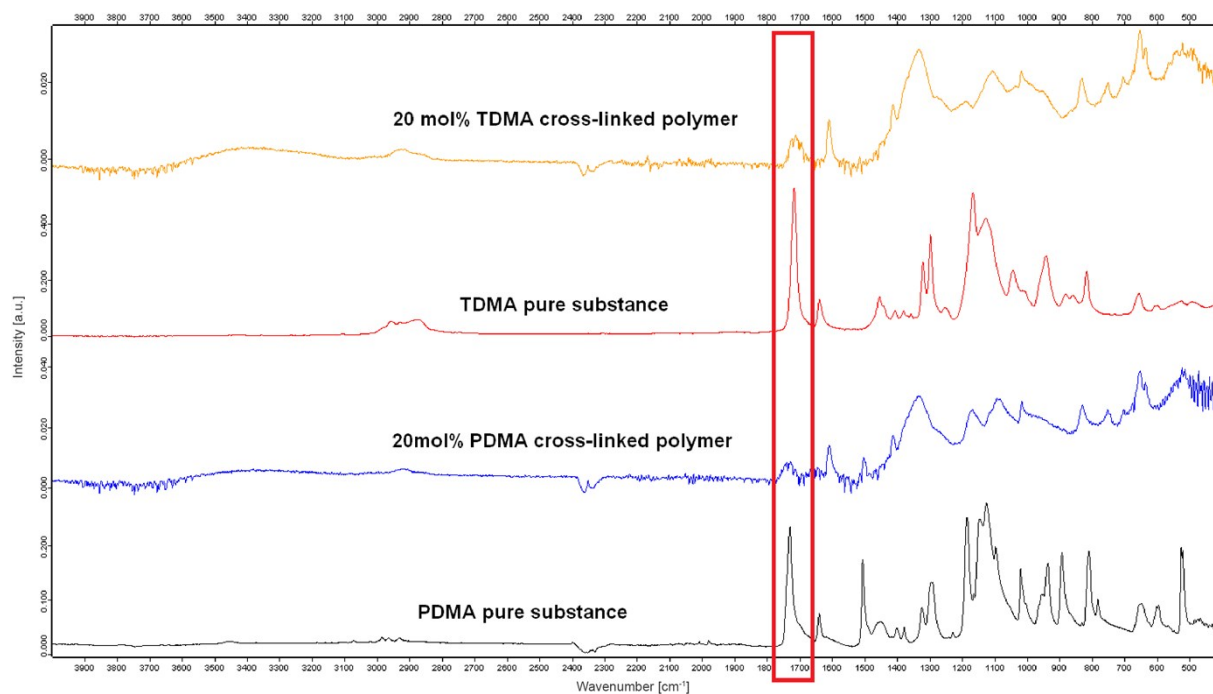


Fig. 7S: IR spectra of TDMA and PDMA cross-linked polymers.

Solid-State NMR spectra

Spectral Assignment (NMR in the solid state and in solution)

For spectral assignment, standard 1 and 2D NMR spectra in solution were recorded and compared to the respective data in the solid state.

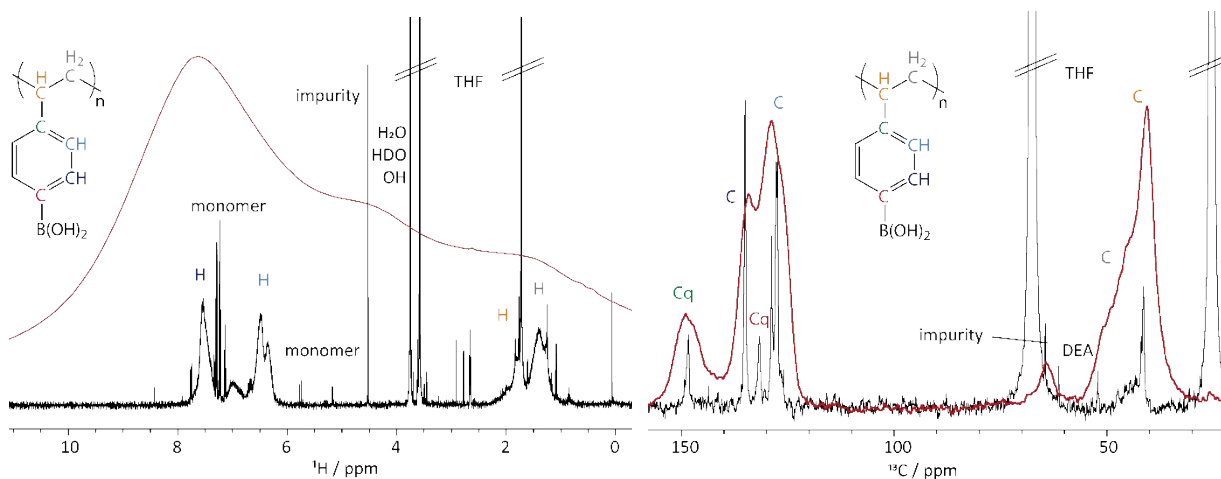


Fig. 8S: Comparison of the a) ^1H and b) ^{13}C NMR spectra of the neat polymer without cross-linker in the solid state (red, CP/MAS, 24 kHz) and dissolved in a 9:1 d_8 -THF: D_2O solution (black).

As can be seen in the comparison above, the solid-state NMR spectrum envelopes the one in solution and assignments can be transferred from the spectra in solution to the solid state.

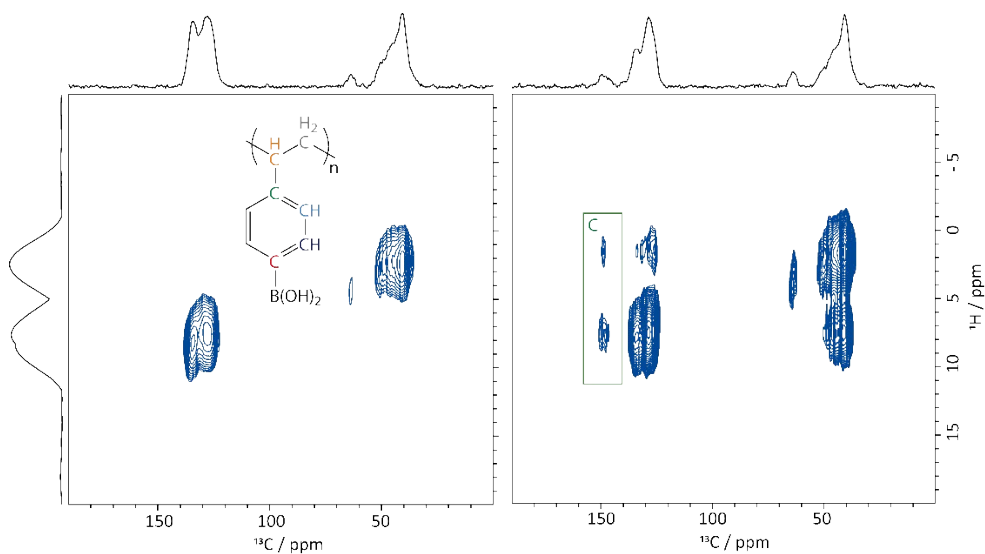


Fig. 9S: ^1H - ^{13}C CP/MAS HETCOR NMR spectra of the neat polymer without cross-linker. The left spectrum was recorded with a short contact time of 50 μs , the right spectrum with 1000 μs .

The assignment from the spectra in solution is also confirmed by the ^1H - ^{13}C HETCOR NMR spectra in the solid state recorded with two different contact times (short: 50 μs and long: 1000 μs). In the HETCOR using a short contact time, only direct CH contacts appear, while with longer contact times, proximities to adjacent moieties are also showing as cross peaks. This confirms the quaternary carbon highlighted in green due to weak interactions with the polymer backbone signals. While all signals belonging to the polymer show contacts to both ^1H resonances, the peak at 64 ppm in the carbon dimension has no contact to any of the two indicating that this is an impurity (benzyl alcohol from the synthesis) and not part of the polymer itself.

Comparison of different polymeric materials

In the following, ^1H , ^{13}C and ^{11}B NMR spectra of the initial *p*-VPBA polymer and the two materials cross-linked using 20 mol% of either DVB or EDMA are compared.

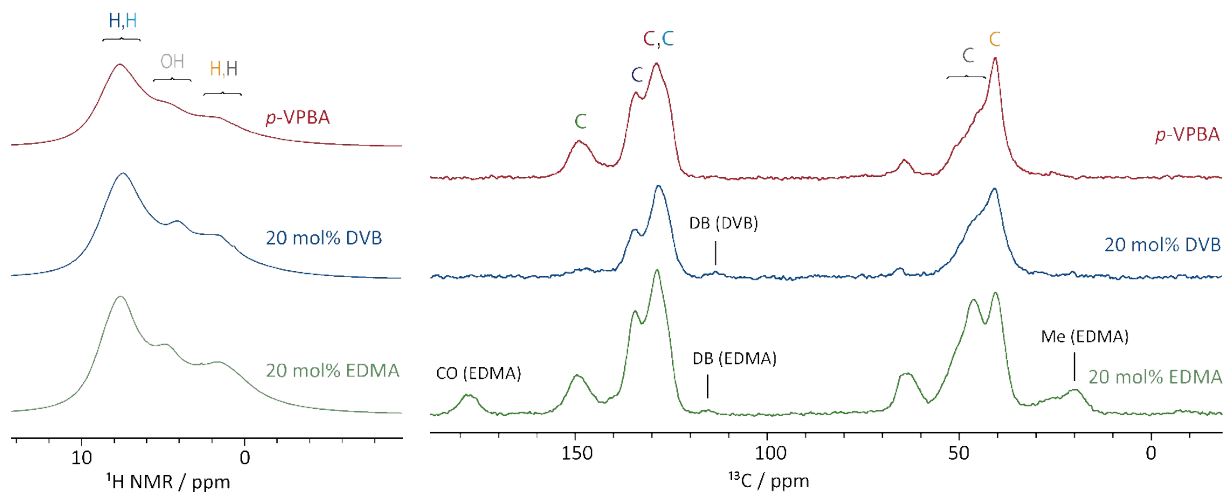


Fig. 10S: ^1H and ^{13}C solid-state NMR spectra of the neat polymer without cross-linker (red) and the polymer materials cross-linked with 20 mol% DVB and 20 mol% EDMA, respectively. Additional peaks due to incorporated or unused (DB) cross-linker are indicated.

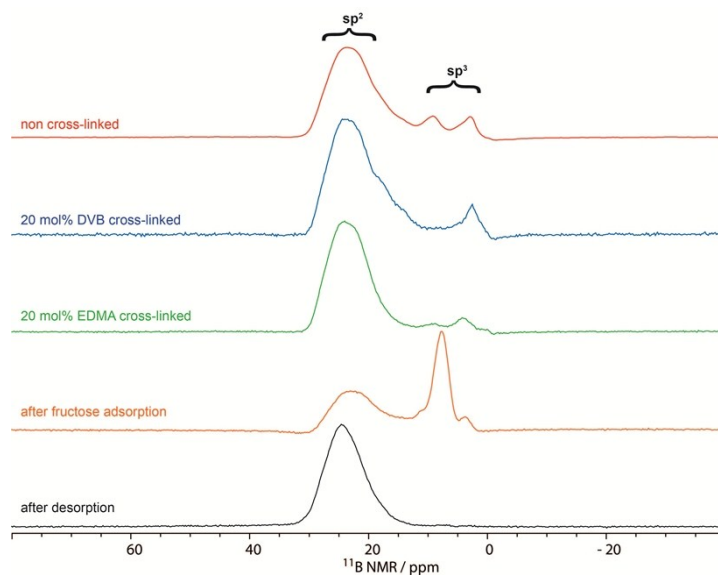


Fig. 11S: ^{11}B Hahn-Echo solid-state NMR spectra of the polymer without cross-linker (red), the polymer materials cross-linked with 20 mol% DVB (blue) and 20 mol% EDMA (green), the 20mol% DVB% cross-linked polymer after fructose adsorption (yellow) and after desorption with 0.5M H_2SO_4 .

In the ^{11}B Hahn-Echo spectra for the same set of samples, broad signals corresponding to three-coordinate boron (sp^2) were observed around 20-30 ppm, while four-coordinate (sp^3) boron resulted in resonances at lower ppm values.

Measurement of zeta potentials

Polymers were dispersed either in water at pH 10 adjusted with 4M NaOH, or a 50:50 wt% mixture of water (pH 10) and ethanol, or pure ethanol for zeta potential measurements. Fresh polymer without adsorbed substrate, polymer with adsorbed glucose, and polymer with adsorbed fructose were examined. For polymers with adsorbed glucose and fructose, respectively, adsorption was performed (0.1 g polymer, 2.625 mL sorption solution (stock solution: 0.5 g sugar in 18.75 mL carbonate buffer), 3 h, RT) and polymers dried under HV. Unfortunately, the dispersion of the polymers was insufficient to perform reliable measurements. Measurements in the 50:50 wt% EtOH:H₂O mixture also gave an error during sampling. In pure ethanol, measurements were possible, but the accuracy was very poor, and a high fluctuation around zeta potentials of 0 mV was noted for all three samples.

Optimization of Adsorption Conditions

Tab. 4S: Influence of solvent and solvent mixture on the fructose adsorption, conditions: RT, 3 h, 100 mg polymer, 2.100 mL stock solution + vol.% of added solvent, stock solution: 0.500 g fructose in 15 mL 0.5M aqueous phosphate buffer.

Entry	Adsorption Solution	Adsorption Efficiency [%]
1	Pure Buffer	11.8
2	Buffer + 5% EtOH	12.9
3	Buffer + 10% EtOH	16.0
4	Buffer + 20% EtOH	21.2
5	Buffer + 5%MeOH	12.3
6	Buffer + 10%MeOH	13.5
7	Buffer + 20% MeOH	16.5
8	Buffer + 10%DMSO	11.5
9	Buffer +20%H ₂ O	13.5

Tab. 5S: Influence of pH value of the phosphate and carbonate buffers on fructose adsorption, conditions: RT, 3 h, 100 mg polymer, 2.625 mL stock solution, stock solution: 0.500 g fructose in 18.75 mL buffer with 20wt% EtOH, additionally the pH after adsorption was measured.

Entry	Buffer Solution	q [mol _{Fructose} /mol _{Boron}]	pH
1	Phosphate buffer at pH 7.5	0.099	7.34
2	Carbonate buffer at pH 7.5	0.128	7.72
3	Phosphate buffer at pH 10	0.154	8.33
4	Carbonate buffer at pH 10	0.357	9.65

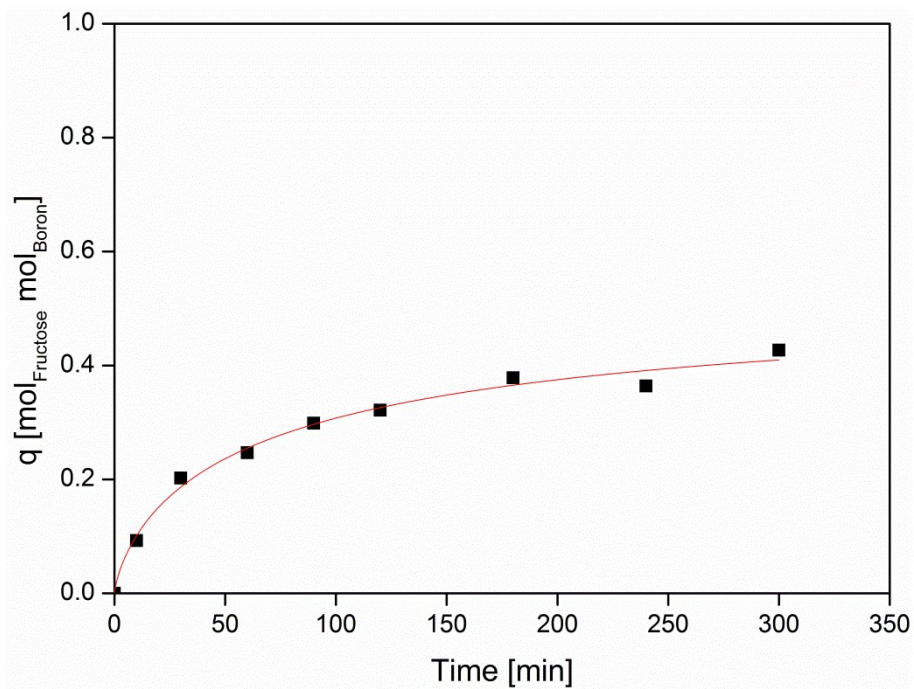


Fig. 12S: Influence of time on the fructose adsorption, equilibrium reached after approx. 3 h, conditions: RT, 100 mg polymer, 2.625 mL stock solution, stock solution: 0.500 g fructose in 15 mL carbonate buffer.

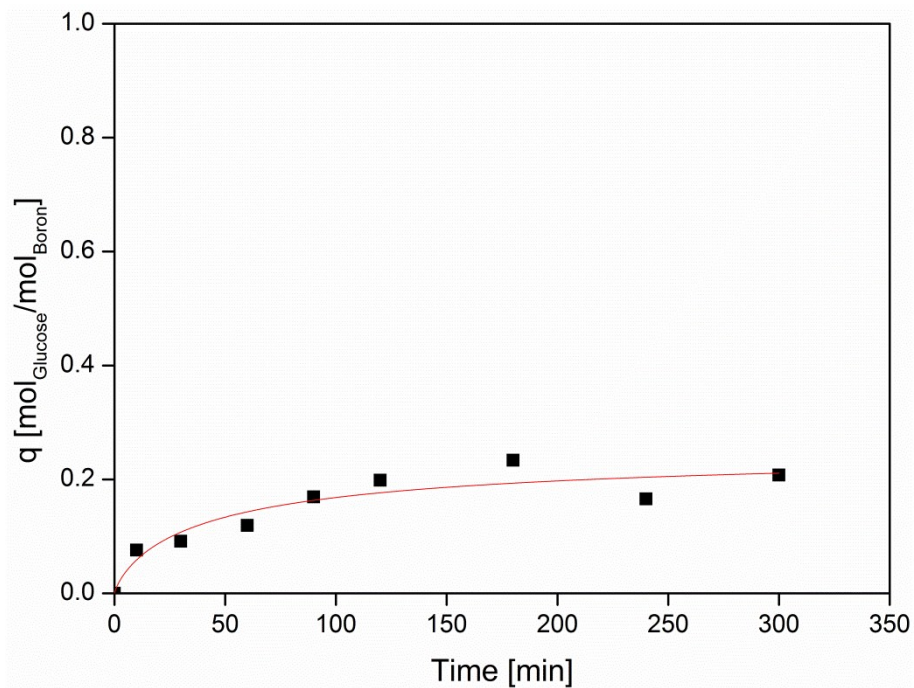


Fig. 13S: Influence of time on the glucose adsorption, equilibrium reached after approx. 90 minutes, conditions: RT, 100 mg polymer, 2.625 mL stock solution, stock solution: 0.500 g glucose in 15 mL carbonate buffer.

Interactions of phosphates and carbonates with phenylboronic acid moieties of the polymer

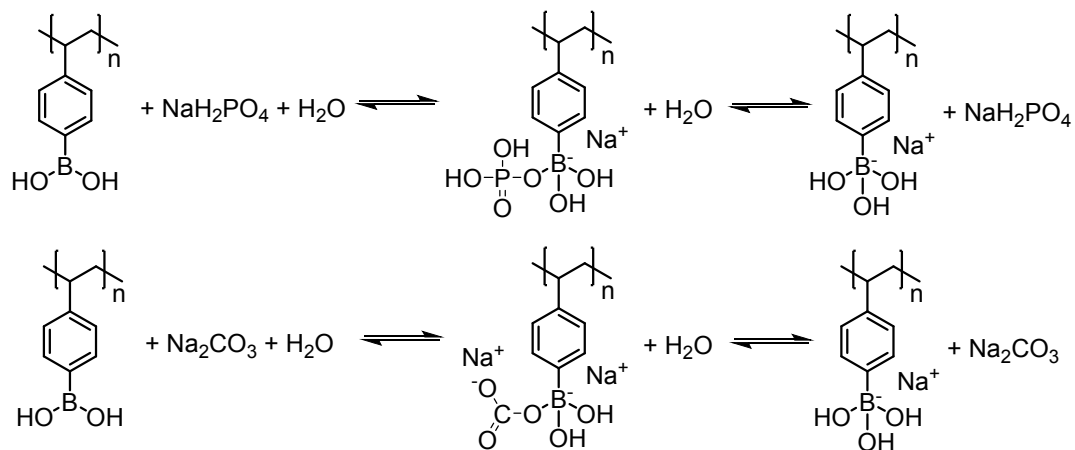


Fig. 14S: Interactions of phosphates and carbonates with phenylboronic acid moieties of the polymer according to Bosch et al..¹

Tab. 6S: Influence of the pre-treatment procedures on the swelling degree. The polymer cross-linked with 20% DVB was used. Swelling degree was measured in the carbonate buffer solution.

Entr y	Pre-treatment	Swelling Degree [%]		
		Pure Buffer	In presence of Fructose	In presence of Glucose
1	Phosphate buffer	68	212	68
2	Phosphate buffer , dialyzed	63	104	91
3	Carbonate buffer	61	94	64
4	Carbonate buffer, dialyzed	59	73	59

Sorption Isotherms of DVB and EDMA cross-linked polymers

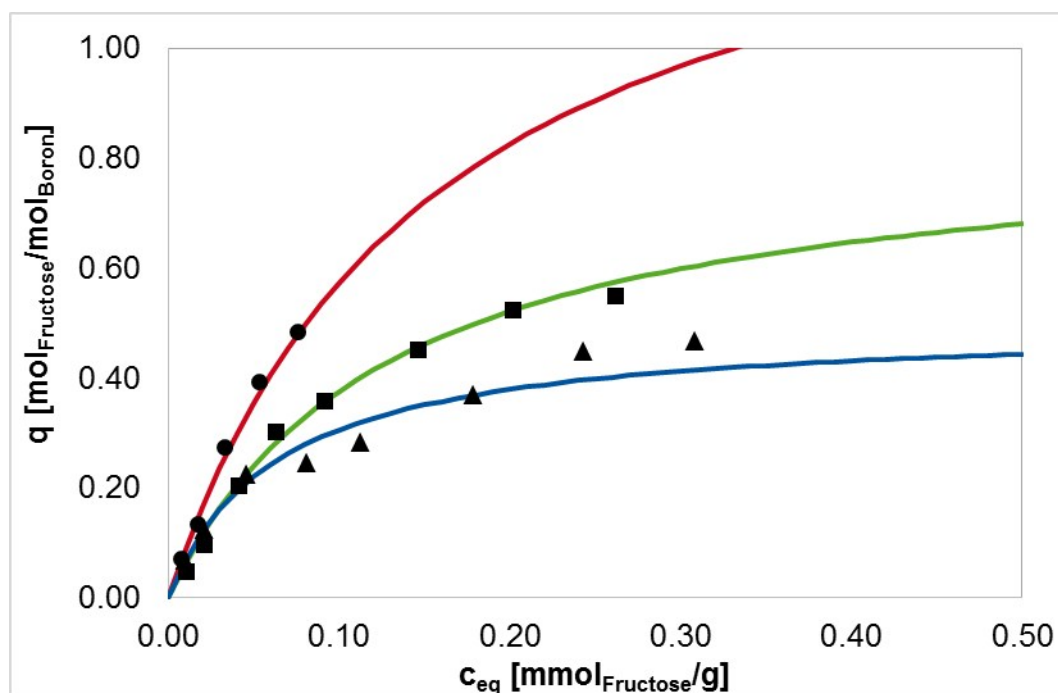


Fig. 15S: Adsorption isotherms for fructose adsorption on DVB cross-linked polymers: a) 5mol% DVB (circles: data points, red line: Langmuir-fit), b) 20mol% DVB (squares: data points, green line: Langmuir-fit), c) 40mol% DVB (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

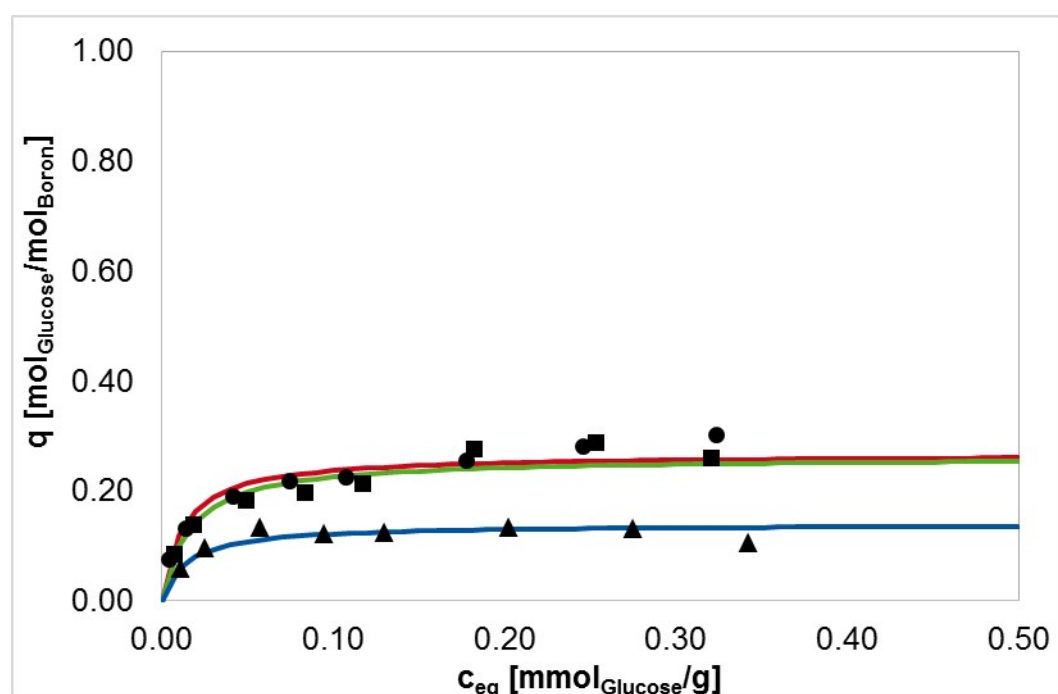


Fig. 16S: Adsorption isotherms for glucose adsorption on DVB cross-linked polymers: a) 5mol% DVB (circles: data points, red line: Langmuir-fit), b) 20mol% DVB (squares: data points, green line: Langmuir-fit), c) 40mol% DVB (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

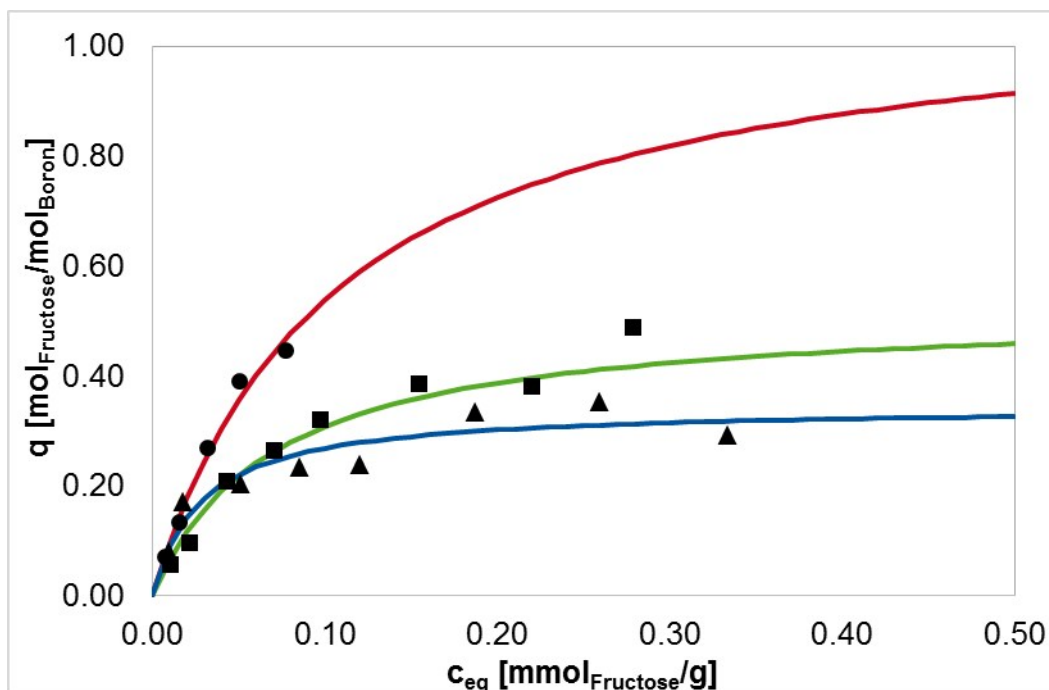


Fig. 17S: Adsorption isotherms for fructose adsorption on EDMA cross-linked polymers: a) 5mol% EDMA (circles: data points, red line: Langmuir-fit), b) 20mol% EDMA (squares: data points, green line: Langmuir-fit), c) 40mol% EDMA (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

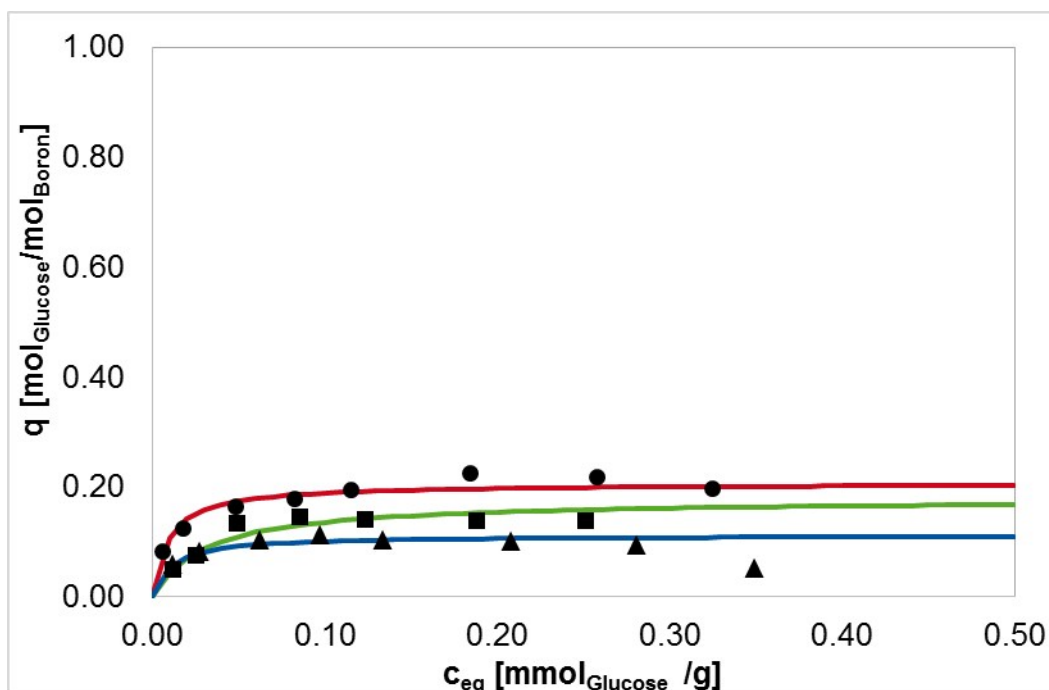


Fig. 18S: Adsorption isotherms for glucose adsorption on EDMA cross-linked polymers: a) 5mol% EDMA (circles: data points, red line: Langmuir-fit), b) 20mol% EDMA (squares: data points, green line: Langmuir-fit), c) 40mol% EDMA (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

The used Langmuir-fit function is expressed in equation 9S. Results of the fit are summarized in Tab.7S and Tab.8S.

$$q = q_{max} \frac{k \cdot c_{eq}}{1 + k \cdot c_{eq}} \quad (\text{Eq. 9S})$$

Tab. 7S: Summary of the Langmuir-Fit for fructose adsorption on DVB and EDMA cross-linked polymers.

Entry	Cross-Linker	q_{max} [mol _{Fructose} /mol _{Boron}]	Langmuir constant [g/mmol _{Fructose}]	Fit-Accuracy [R ²]
1	DVB, 5mol%	1.478	6.3	0.993
2	DVB, 20mol%	0.854	7.8	0.991
3	DVB, 40mol%	0.499	15.8	0.944
4	EDMA, 5mol%	1.108	9.5	0.983
5	EDMA, 20mol%	0.523	14.3	0.954
6	EDMA, 40mol%	0.344	35.3	0.861

Tab. 8S: Summary of the Langmuir-fit for glucose adsorption on DVB and EDMA cross-linked polymers.

Entry	Cross-Linker	q_{max} [mol _{Glucose} /mol _{Boron}]	Langmuir constant [g/mmol _{Glucose}]	Fit-Accuracy [R ²]
1	DVB, 5mol%	0.266	79.6	0.919
2	DVB, 20mol%	0.201	62.1	0.881
3	DVB, 40mol%	0.139	69.0	0.706
4	EDMA, 5mol%	0.206	109.8	0.909
5	EDMA, 20mol%	0.178	32.5	0.841
6	EDMA, 40mol%	0.111	92.7	0.847

Adsorption solution after adsorption at high fructose concentration

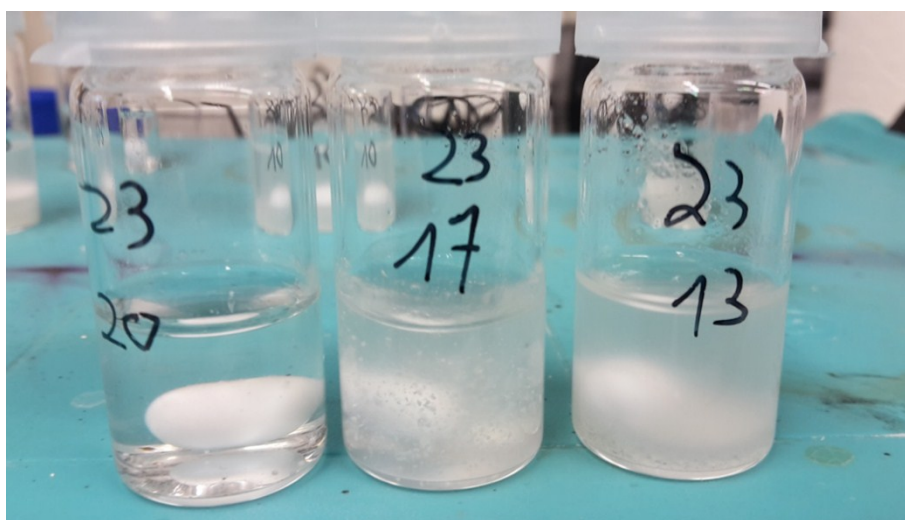


Fig. 19S: Adsorption of fructose, pictures of solutions after adsorption for 3 h: a) 23-20: not cross-linked polymer, b) 23-17: 5% DVB cross-linked polymer and c) 23-13 40% EDMA cross-linked polymer.

Sorption Isotherms of 20mol% cross-linked polymers

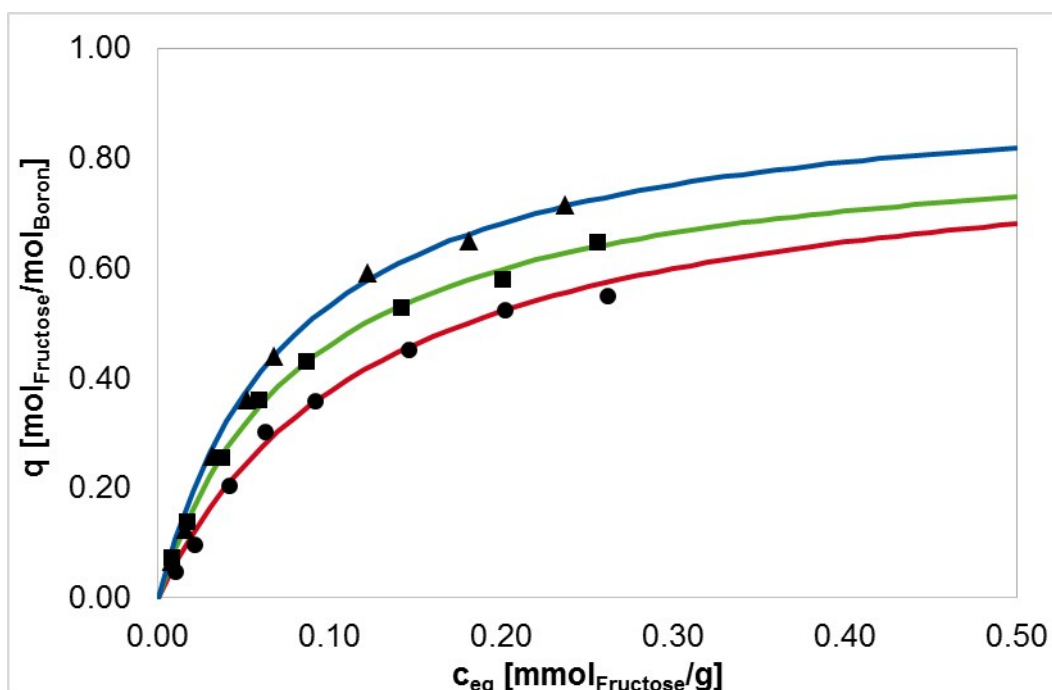


Fig. 20S: Adsorption isotherms for fructose adsorption on polymers with aromatic cross-linkers: a) 20mol% DVB (circles: data points, red line: Langmuir-fit), b) 20mol% PDMA (squares: data points, green line: Langmuir-fit), c) 20mol% DVN (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

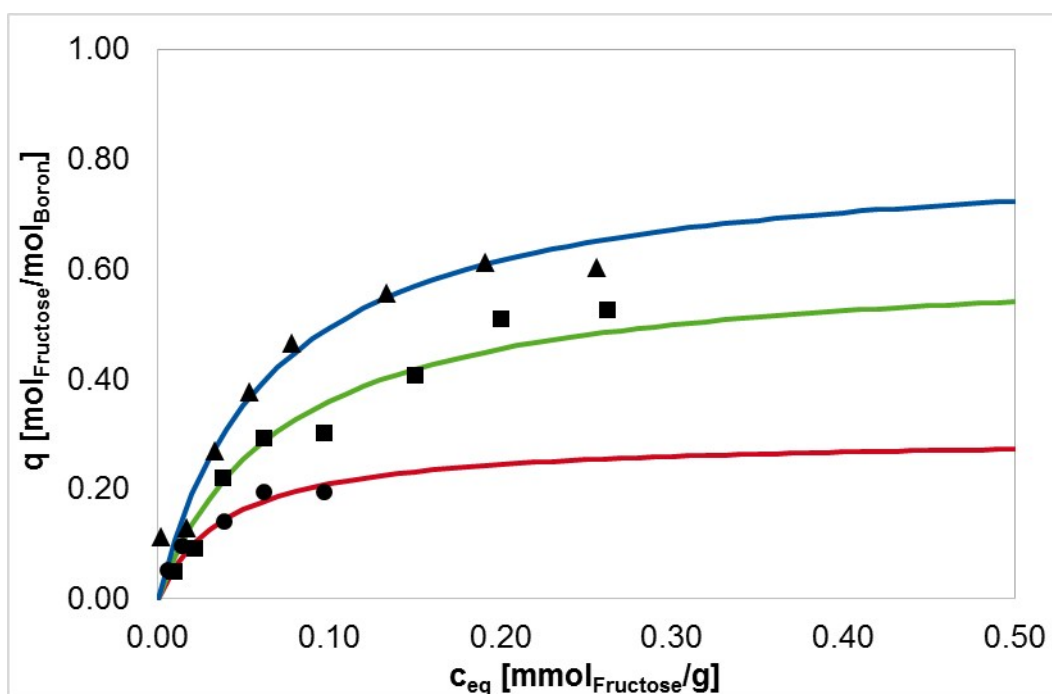


Fig. 21S: Adsorption isotherms for fructose adsorption on polymers with polar aliphatic cross-linkers: a) 20mol% DVS (circles: data points, red line: Langmuir-fit), b) 20mol% EDMA (squares: data points, green line: Langmuir-fit), c) 20mol% TDMA (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

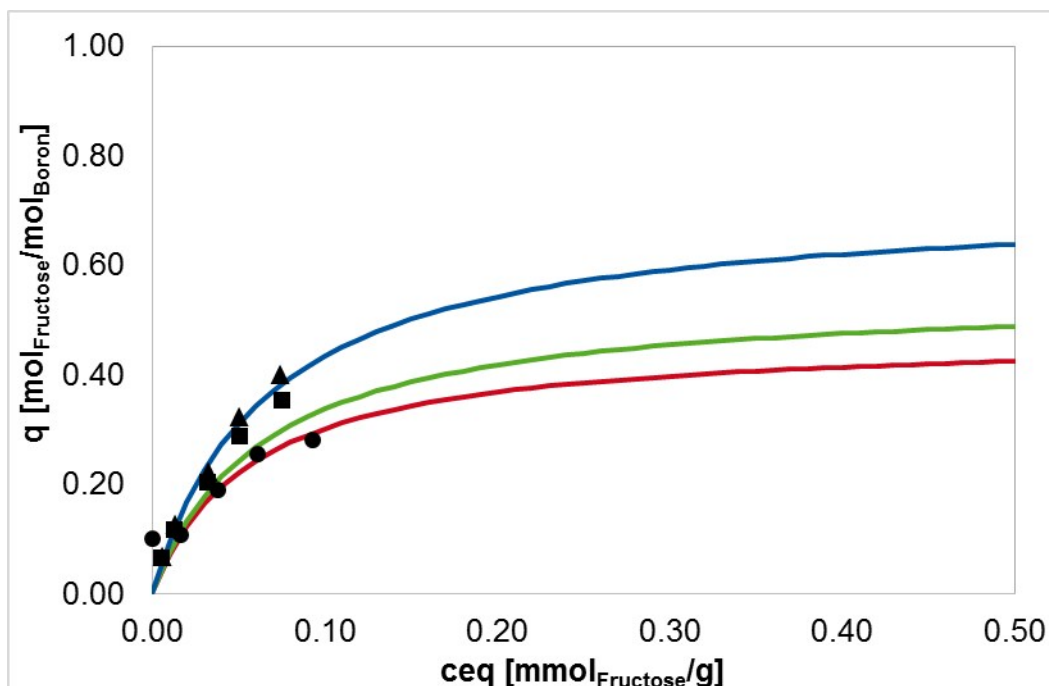


Fig. 22S: Adsorption isotherms for fructose adsorption polymers with aliphatic low-polar cross-linkers: a) 20mol% OD (circles: data points, red line: Langmuir-fit), b) 20mol% DD (squares: data points, green line: Langmuir-fit), c) 20mol% TD (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

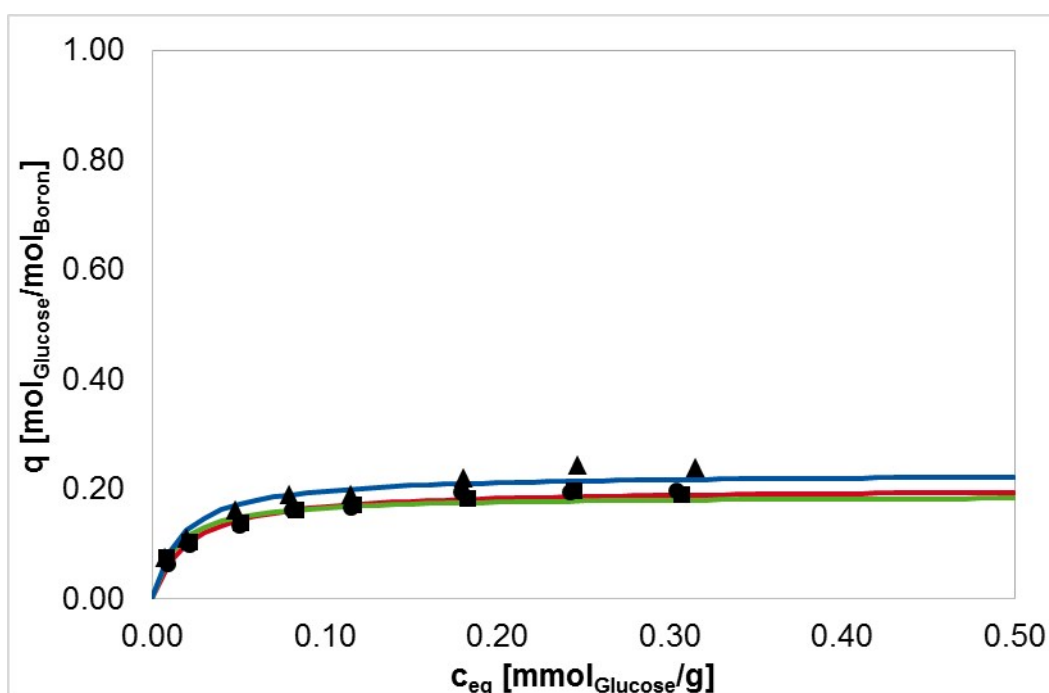


Fig. 23S: Adsorption isotherms for glucose adsorption on polymers with aromatic cross-linkers: a) 20mol% DVB (circles: data points, red line: Langmuir-fit), b) 20mol% PDMA (squares: data points, green line: Langmuir-fit), c) 20mol% DVN (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

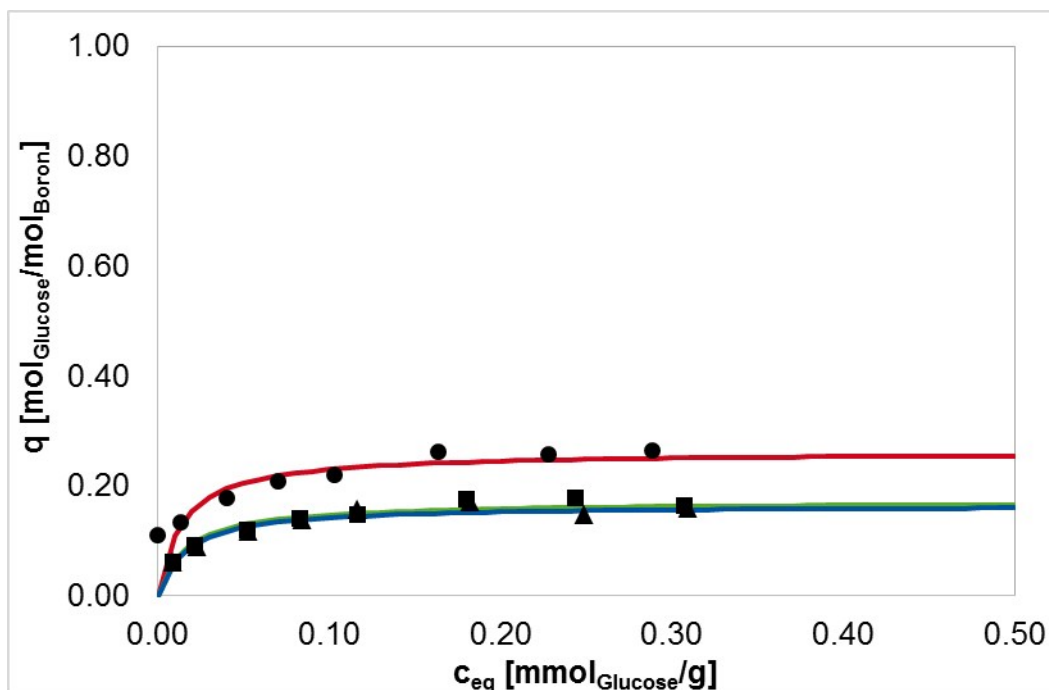


Fig. 24S: Adsorption isotherms for glucose adsorption on polymers with polar aliphatic cross-linkers: a) 20mol% DVS (circles: data points, red line: Langmuir-fit), b) 20mol% EDMA (squares: data points, green line: Langmuir-fit), c) 20mol% TDMA (triangles: data points, blue line: Langmuir-fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

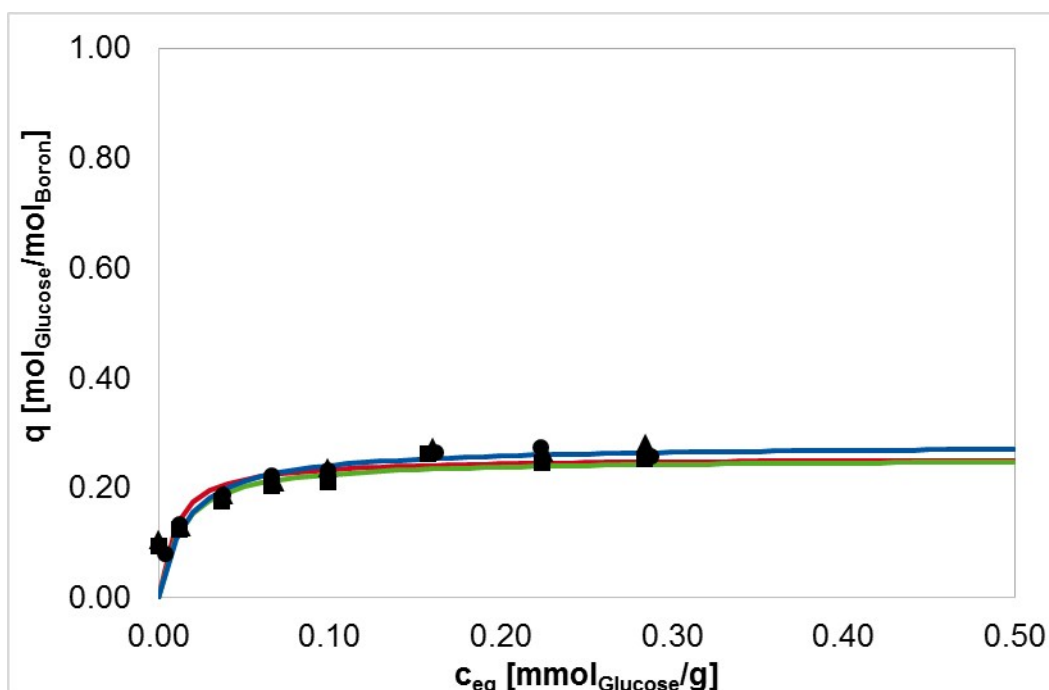


Fig. 25S: Adsorption isotherms for glucose adsorption on polymers with low-polar aliphatic cross-linkers: a) 20mol% OD (circles: data points, red line: Langmuir-Fit), b) 20mol% DD (squares: data points, green line: Langmuir-Fit), c) 20mol% TD (triangles: data points, blue line: Langmuir-Fit), RT, 3 h, 100 mg polymer, 2.625 mL solution in the carbonate buffer.

The used Langmuir-fit function is expressed in equation 9S. Results of the fit are summarized in Tab.9S and Tab.10S.

Tab. 9S: Summary of the Langmuir-Fit for fructose adsorption on 20mol% cross-linked polymers.

Entry	Cross-Linker	qmax [mol _{Fructose} /mol _{Boron}]	Langmuir constant [g/mmol _{Fructose}]	Fit-Accuracy [R ²]
1	DVB, 20mol%	0.854	7.8	0.992
2	DVN, 20%	0.947	12.8	0.992
3	PDMA, 20mol%	0.879	11.0	0.997
4	DVS, 20mol%	0.294	24.4	0.968
5	EDMA, 20mol%	0.618	13.9	0.950
6	TDMA, 20mol%	0.819	15.1	0.958
7	OD, 20mol%	0.472	17.6	0.994
8	DD, 20mol%	0.550	15.8	0.928
9	TD, 20mol%	0.722	15.1	0.993

Tab. 10S: Summary of the Langmuir-Fit for glucose adsorption on 20mol% cross-linked polymers.

Entry	Cross-Linker	qmax [mol _{Glucose} /mol _{Boron}]	Langmuir constant [g/mmol _{Glucose}]	Fit-Accuracy [R ²]
1	DVB, 20mol%	0.201	48.5	0.972
2	DVN, 20mol%	0.228	60.1	0.927
3	PDMA, 20mol%	0.187	75.0	0.917
4	DVS, 20mol%	0.262	71.7	0.921
5	EDMA, 20mol%	0.171	61.2	0.929
6	TDMA, 20mol%	0.165	61.5	0.924
7	OD, 20mol%	0.255	108.9	0.942
8	DD, 20mol%	0.253	78.1	0.917
9	TD, 20mol%	0.278	62.8	0.948

In-Situ-¹³C-MAS NMR results

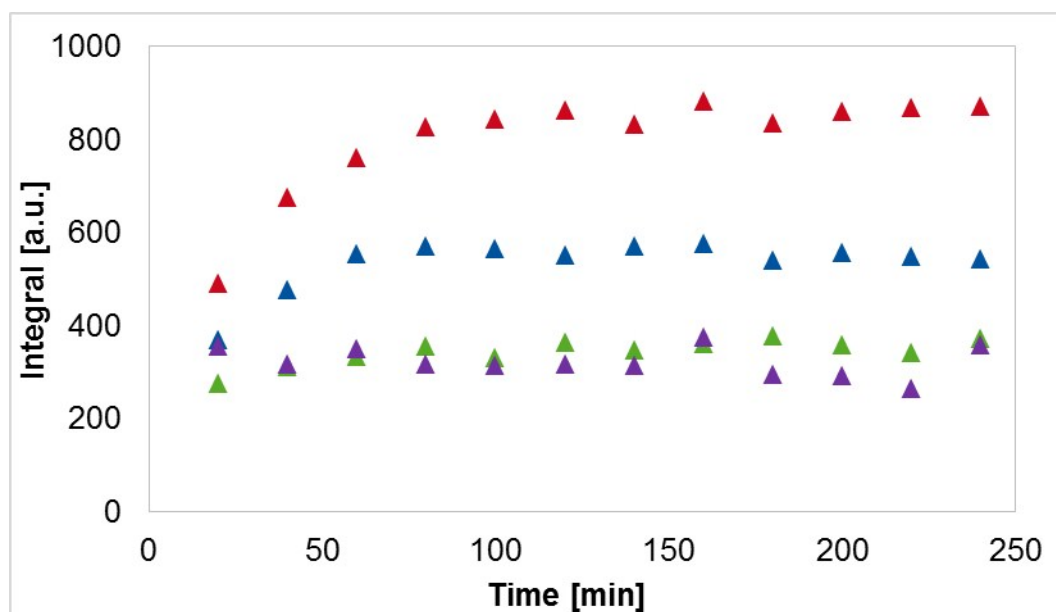


Fig. 26S: Time-resolved plots of direct polarization ¹³C-MAS-NMR spectra of fructose sorption on 20mol% DVB cross-linked phenylboronic acid polymer at RT: fructose-boronate esters (numbers refer to paper Fig.5): a) 2,3-exo monoboronate ester with β-Fru^p (1a, red triangles), b) 2,3,6 tridentate monoboronate ester with β-Fru^p (2, blue triangles), c) 2,3-endo monoboronate ester with β-Fru^p (1b, green triangles) and d) diboronate esters with β-Fru^p (3, purple triangles), conditions: 80%:20% 0.5 mol L⁻¹ NaHCO₃-buffer in D₂O (pH adjusted to 10 with 4 mol L⁻¹ NaOH):EtOH mixture.

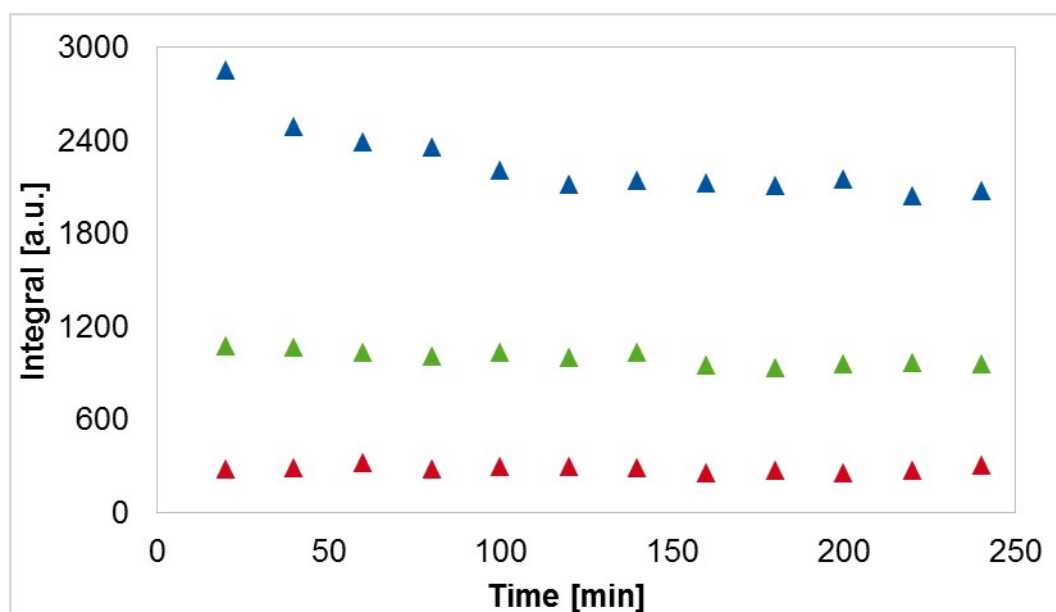


Fig. 27S: Time-resolved plots of direct polarization ¹³C-MAS-NMR spectra of fructose sorption on 20mol% DVB cross-linked phenylboronic acid polymer at RT: free fructose tautomers: a) β-fructopyranose (β-Fru^p, blue triangles), b) α-fructofuranose (α-Fru^f, green triangles) and c) β-fructofuranose (β-Fru^f, red triangles), conditions: 80%:20% 0.5 mol L⁻¹ NaHCO₃-buffer in D₂O (pH adjusted to 10 with 4 mol L⁻¹ NaOH):EtOH mixture.

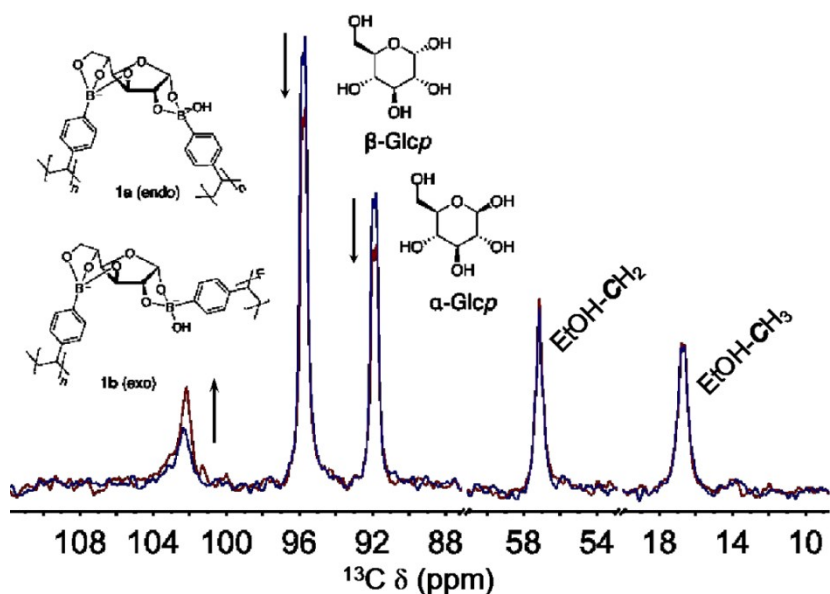


Fig. 28S: *In situ* direct polarization ^{13}C -MAS-NMR spectra upon mixing $1\text{-}^{13}\text{C}$ -marked glucose with 20mol% DVB cross-linked phenylboronic acid polymer at RT, after 20 min (blue) and 4 h (red), conditions: 80%:20% 0.5 mol L^{-1} NaHCO_3 -buffer in D_2O (pH adjusted to 10 with 4 mol L^{-1} NaOH):EtOH mixture.

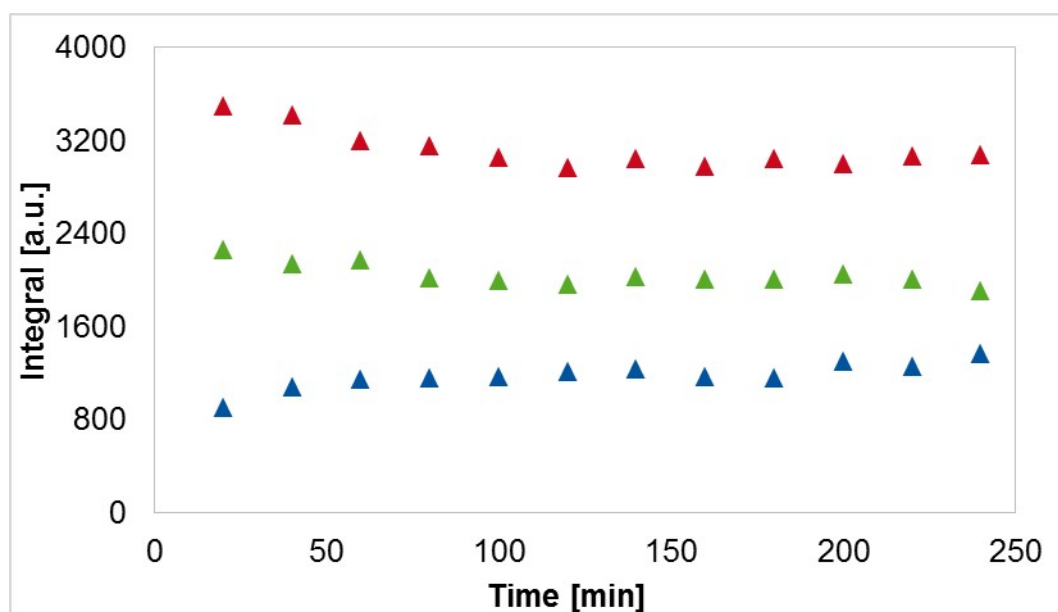


Fig. 29S: Time-resolved plots of direct polarization ^{13}C -MAS-NMR spectra of glucose sorption on 20mol% DVB cross-linked phenylboronic acid polymer at RT: free glucose tautomers and glucose-borante esters: a) β -glucopyranose ($\beta\text{-Glc}^p$, red triangles), α -glucopyranose ($\alpha\text{-Glc}^p$, green triangles) and endo- and exo diboronate esters with glucofuranose (1a and 1b, Fig. 27S, blue triangles), conditions: 80%:20% 0.5 mol L^{-1} NaHCO_3 -buffer in D_2O (pH adjusted to 10 with 4 mol L^{-1} NaOH):EtOH mixture.

Optimization and screening of desorption conditions

Tab. 11S: Influence of time on the desorption efficiency (DE), conditions: RT, 100 mg 20mol% DVB cross-linked polymer with adsorbed fructose, 2.625 mL 80%:20% 0.5M sulfuric acid:EtOH mixture, amount of adsorbed fructose $n_A = 0.157$ mmol.

Entry	Time [min]	C_{Fructose} [g L ⁻¹]	$n_{\text{D,Fructose}}$ [mmol]	DE [%]
1	120	0.81	0.118	75.0
2	180	0.93	0.136	86.1
3	240	0.95	0.138	88.0
4	360	0.94	0.137	87.0

Tab. 12S: Influence of temperature on the desorption efficiency, conditions: RT, 4 h, 100 mg 20mol% DVB cross-linked polymer with adsorbed fructose, 2.625 mL 80%:20% 0.5M sulfuric acid:EtOH mixture, amount of adsorbed fructose $n_A = 0.157$ mmol.

Entry	Temperature [°C]	C_{Fructose} [g L ⁻¹]	$n_{\text{D,Fructose}}$ [mmol]	DE [%]
1	RT	0.95	0.138	88.0
2	50 °C	0.93	0.136	86.1
3	70 °C	0.91	0.133	84.3

Tab.13S: Fructose desorption efficiency in various acidic solutions, from polymers cross-linked with 20 mol% EDMA (extent of table 5). Repetitive desorption (entries 9a-9c) was performed with the 20 mol% DVB cross-linked polymer, conditions: 100 mg polymer, 2.63 mL desorption solution, 4 h, RT. a: Measured using half the amount of desorption solution (1.32 mL), b: Measured using double the amount of desorption solution (5.25 mL), c: The polymer used in 9a was reused for a 2nd desorption, d: The polymer used in 9b was reused for a 3rd desorption, e: desorption performed in larger scale, amounts of adsorbed fructose: $n_A = 0.157$ mmol (for entries 1-8) and $n_A = 1.253$ mmol (for entries 9).

Entry	Desorption Solution	C_{Fructose} [g L ⁻¹]	$n_{\text{D,Fructose}}$ [mmol]	DE [%]
1	0.5 M H ₂ SO ₄ + 20 vol% EtOH ^a	1.92	0.140	89
2	0.5 M H ₂ SO ₄ + 20 vol% EtOH	0.95	0.138	88
3	0.5 M H ₂ SO ₄ +20 vol% EtOH ^b	0.49	0.143	91
4	1 M Formic Acid	0.97	0.141	90
5	1 M Acetic Acid	1.00	0.146	93
6	1 M Acetic Acid+20 vol% EtOH	0.95	0.138	88
7	1 M Acetic acid/acetate buffer	0.85	0.124	79
8	CO ₂ desorption, 30 bar, 50 °C	0.98	0.142	92
9a	0.5 M H ₂ SO ₄ + 20 vol% EtOH	1.52 ^e	1.107	88
9b	0.5 M H ₂ SO ₄ + 20 vol% EtOH ^c	0.18 ^e	0.094	9
9c	0.5 M H ₂ SO ₄ + 20 vol% EtOH ^d	0.04 ^e	0.016	2

Utilization of pressurized CO₂ for desorption of glucose and fructose

Tab.14S: Results for the desorption of glucose and glucose-fructose from model solutions and a mixture after glucose isomerization, conditions: adsorption: 0.1 g 20mol% EDMA cross-linked polymer, 2.63 mL sorption solution, 3 h, RT, stock solution for model solutions (entries 1-3): 0.500 g sugar in 18.75 mL carbonate buffer, desorption: dispersion of polymer in 80%:20% water-EtOH mixture, 30 bar CO₂, 50 °C, 4 h, for isomerization: 10wt% glucose solution in carbonate buffer, isomerization for 1 h at 63 °C.

Entry	Adsorption Solution/Substrate	$n_{D,Sugar}$ [mmol]	DE [%]
1	Fructose	0.142	89
2	Glucose	0.042	51
3	70%:30% Glucose-Fructose Mixture:		
	Glucose	0.021	60
	Fructose	0.012	71
4	Isomerization Mixture:		
	Glucose	0.013	32
	Fructose	0.017	51

Recycling of polymers in consecutive adsorption-desorption cycles

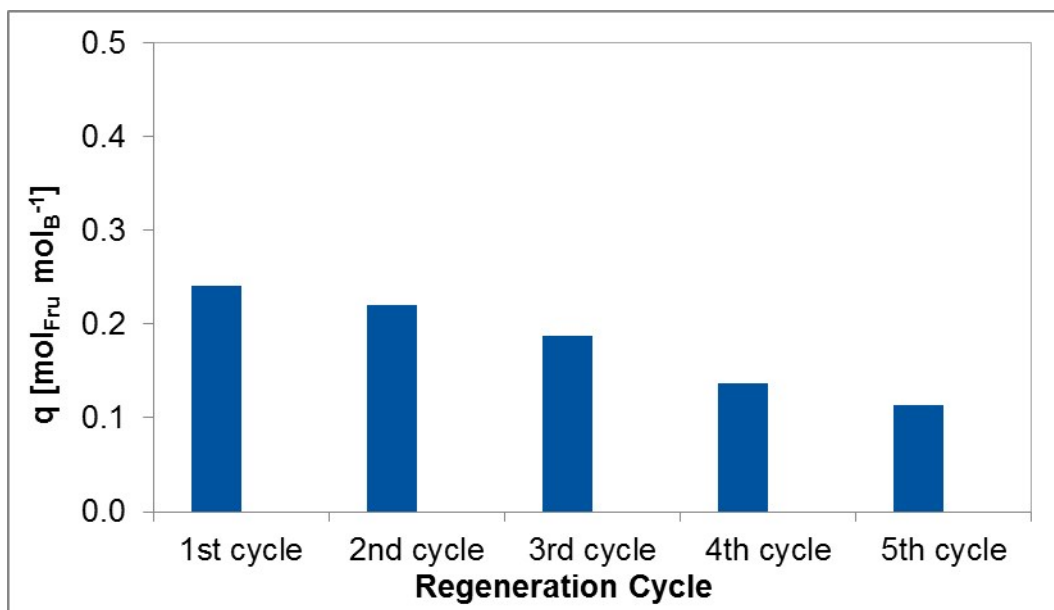


Fig. 30S: Recycling of polymer using 0.5M H₂SO₄ for desorption, conditions: start with two 0.5 g scale adsorption experiments: 0.5 g 20mol% EDMA cross-linked polymer, 13.13 mL sorption solution, 3 h, RT, desorption: 0.5M H₂SO₄ + 20% EtOH, 4 h; RT, amounts were adjusted to the polymer amount and the two batches combined after the third cycle.

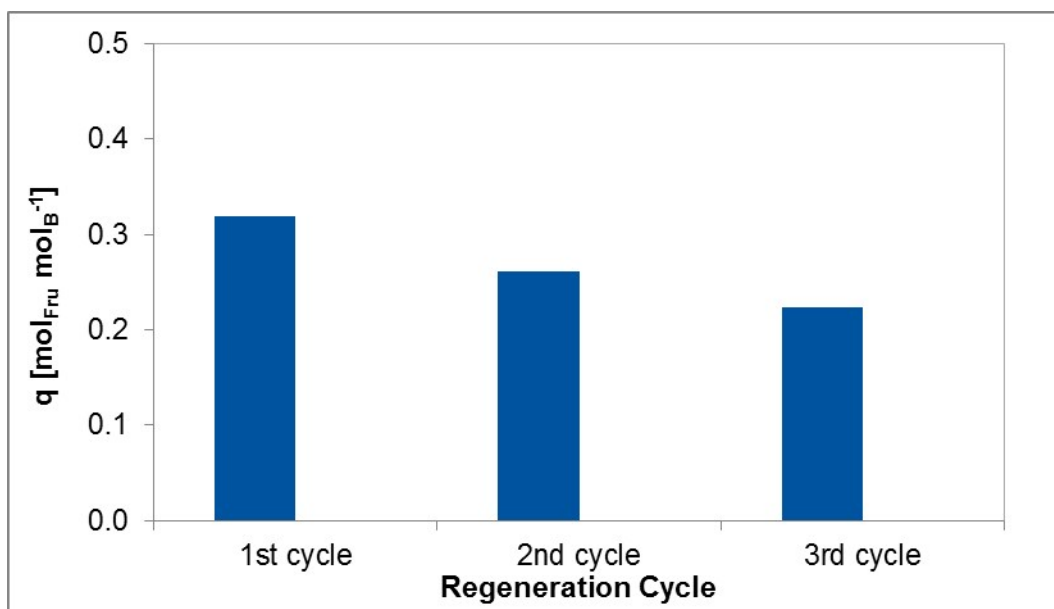


Fig. 31S: Regeneration of polymer using pressurized CO₂ for desorption, conditions: start with two 0.1 g scale adsorption experiments: 0.1 g 20mol% DVB cross-linked polymer, 2.63 mL sorption solution, 3 h, RT, desorption: dispersion of polymer in 80%:20% water-EtOH mixture, 30 bar CO₂, 50 °C, 4 h, amounts were adjusted to the polymer amount and the two batches combined after the first cycle.

Polymer leaching was studied by liquid-phase ICP-analysis of the adsorption and desorption solutions after the experiments. Boron contents of 13 ppm and 5 ppm were detected correlating to a loss of 0.0034% and 0.0012%, respectively. The measured amounts are within the measurement error. The polymers are thus stable against leaching under reaction conditions. Nonetheless, a notable weight loss of polymer during the work-up upon recycling, particularly during drying and filtration, has to be mentioned. Additionally, a minor colouring of the polymer after the third adsorption-desorption cycle using 0.5M H₂SO₄ was observed.

Swelling degrees during fructose sorption for polymers cross-linked with aromatic cross-linkers

Tab. 15S: Swelling degree in the presence and absence of fructose for polymers cross-linked with 20 mol% of aromatic cross-linker, measured in the carbonate buffer solution.

Entry	Cross-linker	Swelling Degree [%]	
		In Pure Buffer	In Presence of Fructose
1	DVB, 20mol%	68	212
2	DVN, 20mol%	70	217
3	PDMA, 20mol%	71	182

Results of glucose isomerization in absence and presence (*in situ* adsorption-assisted glucose isomerization) of polymer

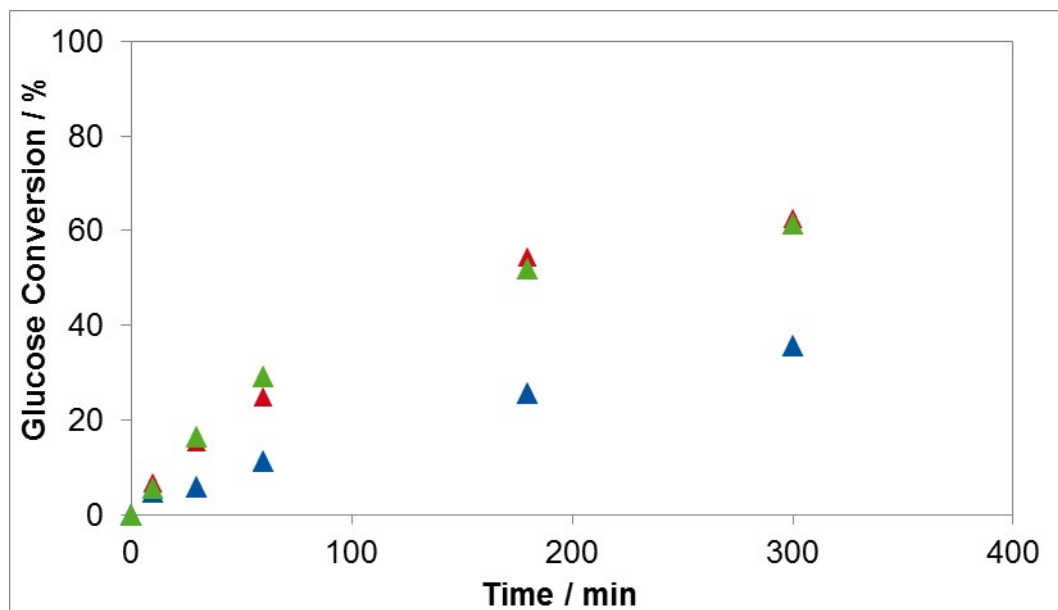


Fig. 32S: Glucose isomerization in absence of polymer: glucose conversion at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) oil bath temperature: 70 °C (data points: red triangles), conditions: 10wt% glucose solution in the carbonate buffer.

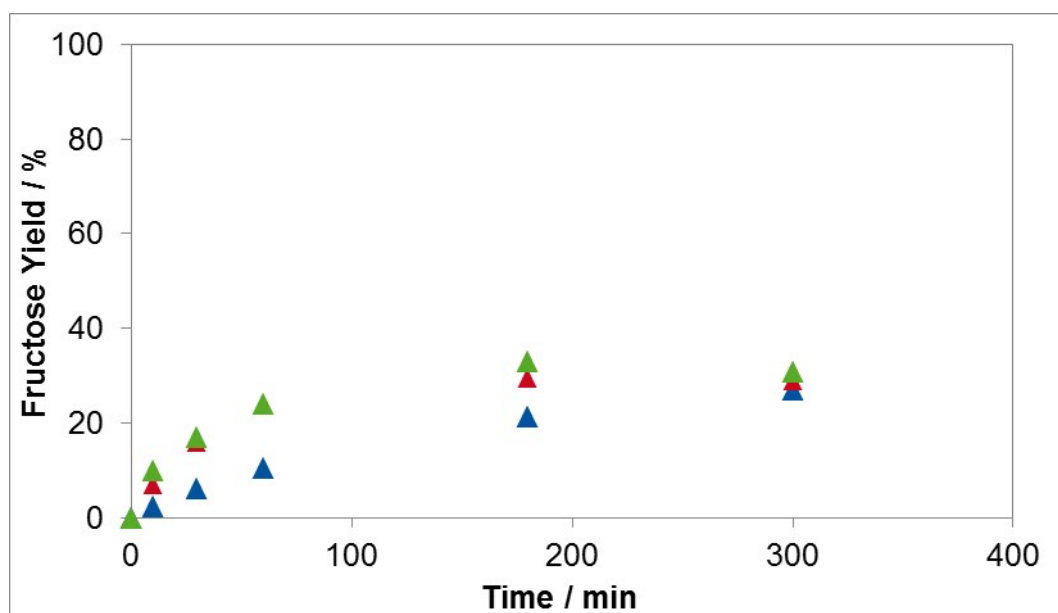


Fig. 33S: Glucose isomerization in absence of polymer: fructose yield at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), conditions: 10wt% glucose solution in the carbonate buffer.

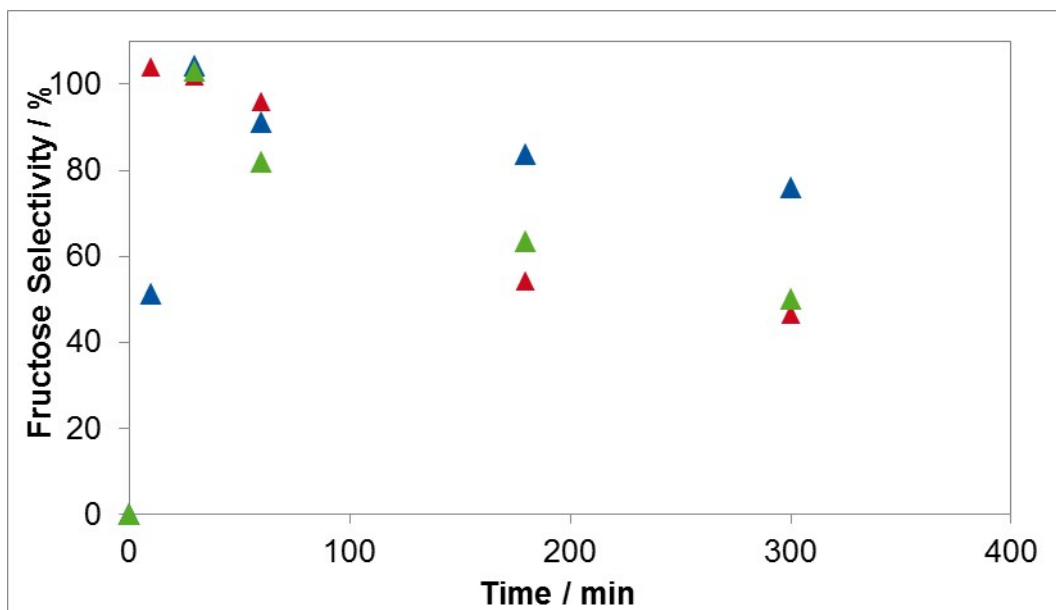


Fig. 34S: Glucose isomerization in absence of polymer: fructose selectivity at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), conditions: 10wt% glucose solution in the carbonate buffer.

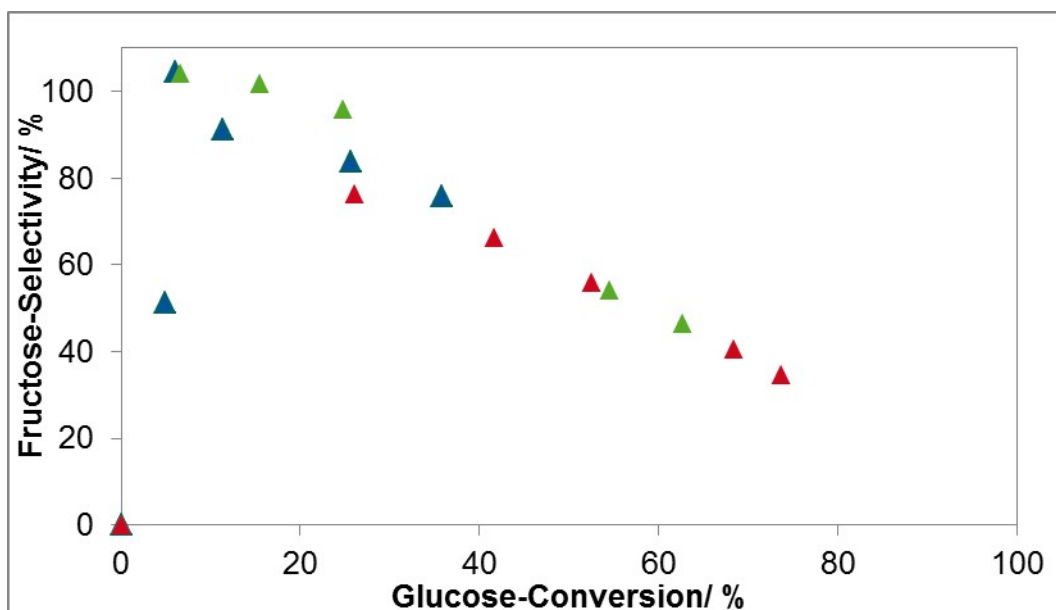


Fig. 35S: Glucose isomerization in absence of polymer: fructose selectivity in dependence of glucose conversion at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), conditions: 10wt% glucose solution in the carbonate buffer.

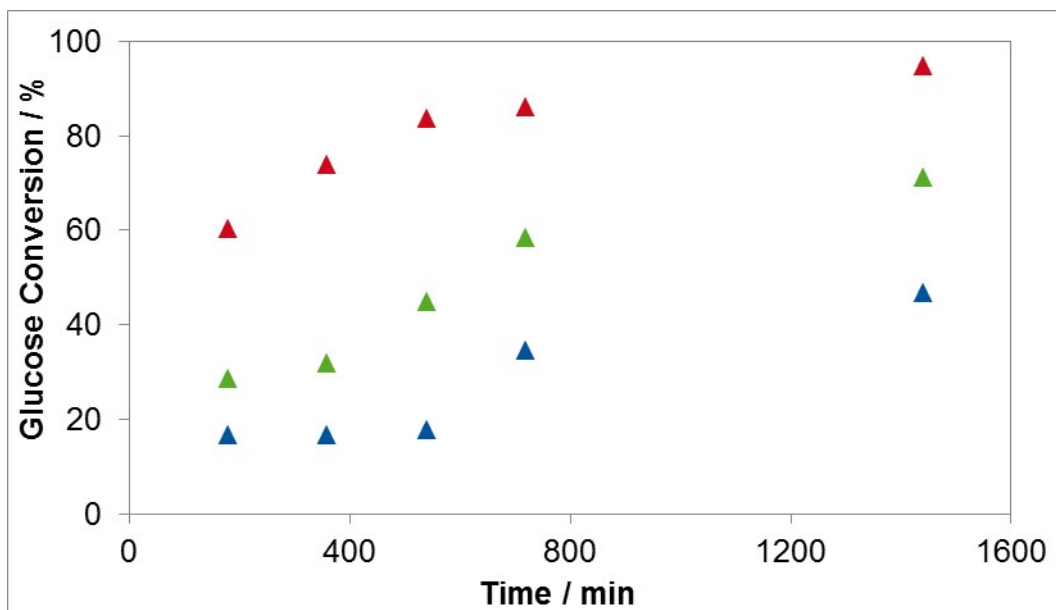


Fig. 36S: Glucose Isomerization in presence of polymer: glucose conversion at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), conditions: 2.625 mL 10wt% glucose solution in the carbonate buffer, 100 mg polymer.

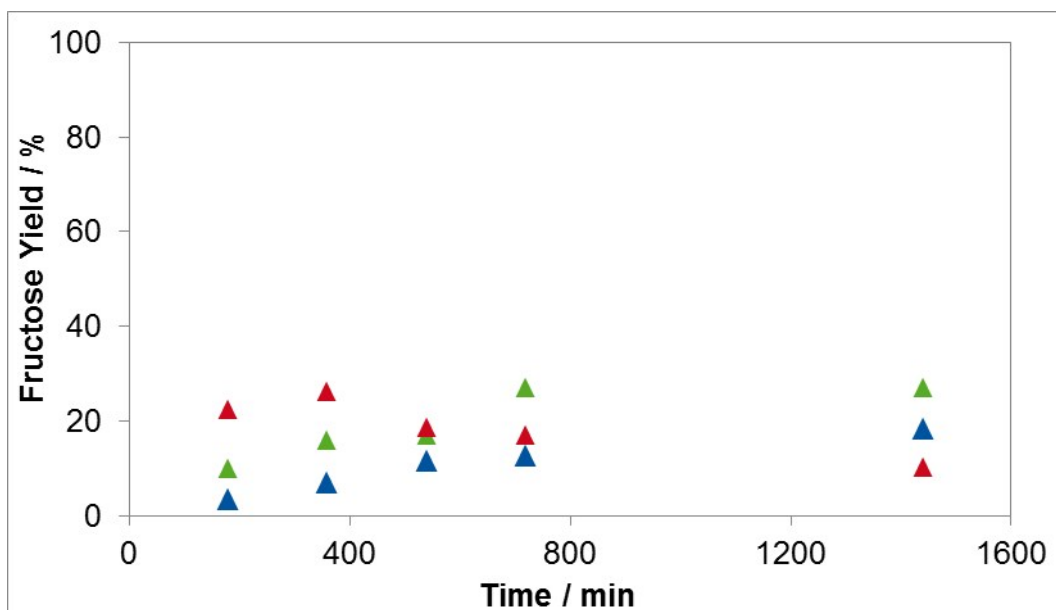


Fig. 37S: Glucose isomerization in presence of polymer: fructose yield at different temperatures a) oil bath temperature: a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), conditions: 2.625 mL 10wt% glucose solution in the carbonate buffer, 100 mg polymer.

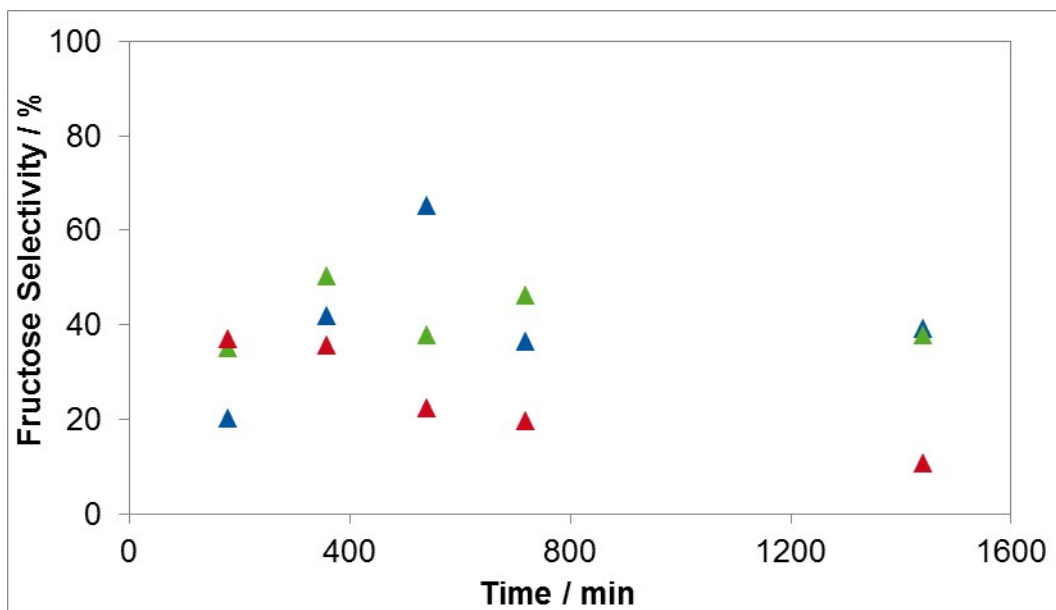


Fig. 38S: Glucose isomerization in presence of polymer: fructose selectivity at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), conditions: 2.625 mL 10wt% glucose solution in the carbonate buffer, 100 mg polymer.

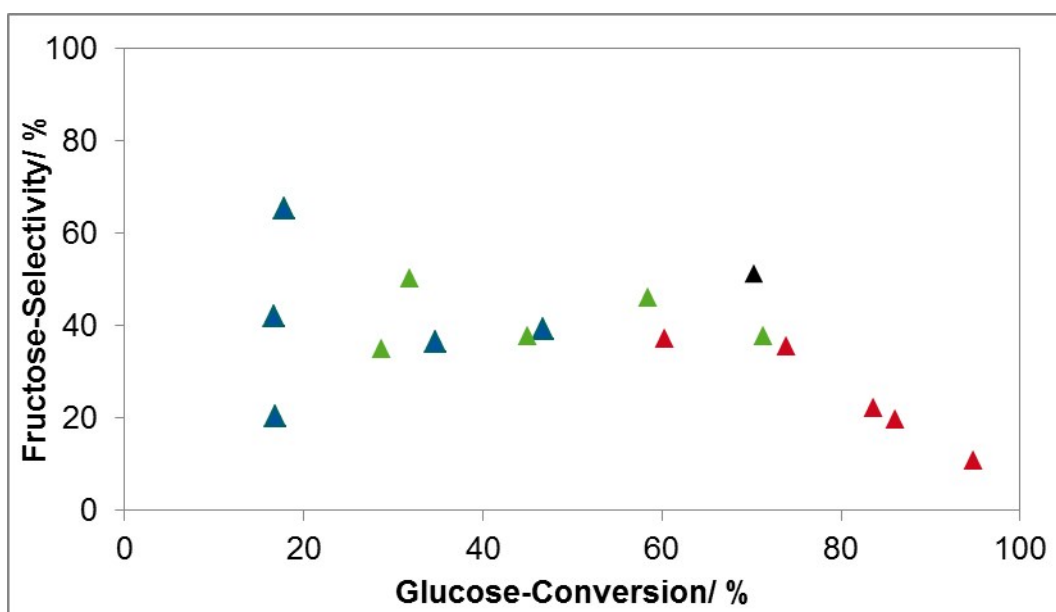


Fig. 39S: Glucose Isomerization in presence of polymer: fructose selectivity in dependence of glucose conversion at different temperatures a) 52 °C (data points: blue triangles), b) 63 °C (data points: green triangles), c) 70 °C (data points: red triangles), d) re-production of Barker conditions (data point: black triangle), conditions: 2.625 mL 10wt% glucose solution in the carbonate buffer, 100 mg polymer.

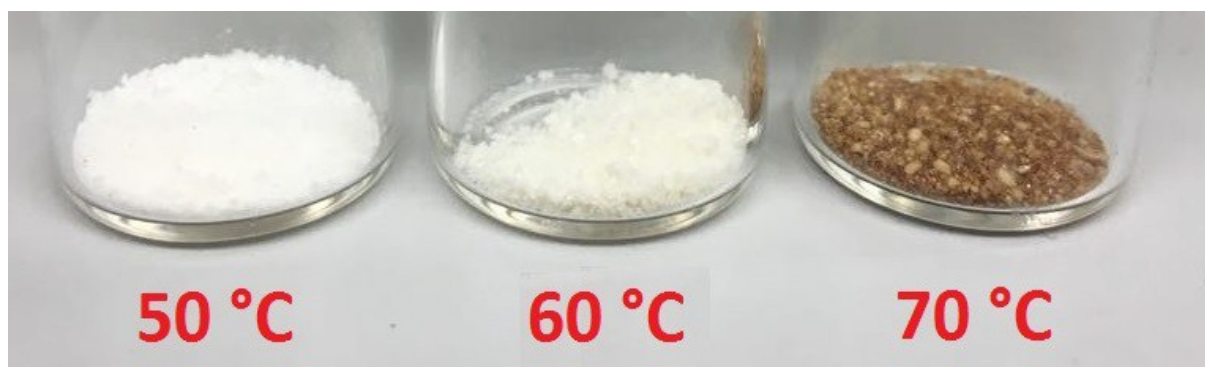


Fig. 40S: Pictures of polymers after in-situ application during glucose isomerization after 9 h reaction time, degradation products adsorb on the polymer leading to colouring of the polymer.

Calculations and results of adsorption-assisted isomerization

Tab. 16S: Adsorption-assisted isomerization: molar amounts of glucose and fructose prior to experiment, after isomerization and adsorption as well as calculated amounts of glucose conversion, isolated fructose yield, adsorbed amounts of glucose and fructose, selectivity for fructose adsorption and overall fructose yield, conditions: glucose isomerization: 10 mL of 10wt% glucose solution in the carbonate buffer, 1 h at 63 °C, adsorption: 2.625 mL isomerization solution added to 0.100 g polymer, 3 h at RT.

Isomerization						
Run	[Glu] ₀ [M]	[Fru] ₀ [M]	[Glu] ₁ [M]	[Fru] ₁ [M]	Conversion of Glu [%]	Isolated yield of Fru [%]
1	0.541	0	0.342	0.139	37	6
2	0.488	0.032	0.339	0.133	34	8
3	0.489	0.033	0.343	0.130	32	9
4	0.482	0.031	0.350	0.124	31	10
5	0.459	0.018	0.390	0.109	28	11
6	0.504	0.029	0.362	0.130	28	12
7	0.484	0.031	0.370	0.117	28	12
8	0.497	0.032	0.365	0.124	27	12

Adsorption						
Run	[Glu] ₂ [M]	[Fru] ₂ [M]	Adsorbed Glu [%]	Adsorbed Fru [%]	Selectivity for Fru [%]	Overall Fru Yield [%]
1	0.348	0.109	-1.8	22	100	26
2	0.341	0.107	-0.5	20	100	35
3	0.342	0.108	0.4	17	94	41
4	0.348	0.103	0.4	17	94	45
5	0.386	0.088	1.2	19	82	48
6	0.361	0.103	0.3	21	96	52
7	0.378	0.099	-2.2	15	100	54
8	0.369	0.111	-1.1	11	100	56

[Glu]₀ and [Fru]₀ are the initial molar glucose and fructose concentrations prior to isomerization of the respective run. [Glu]₁ and [Fru]₁ are the molar glucose and fructose concentrations after isomerization and [Glu]₂ and [Fru]₂ are the concentrations after adsorption of the respective run. Glucose conversion, isolated fructose yield, extracted amounts of glucose and fructose, selectivity for fructose adsorption and overall fructose yield are calculated according to equations 10S to 15S.

$$X_{Glu} = \frac{\sum_0^i [Glu]_{0_i} - [Glu]_{1_i}}{\sum_0^i [Glu]_{0_i}} \cdot 100\% \quad (\text{Eq. 10S})$$

$$Y_{Fru,isolated} = \frac{\sum_0^i [Fru]_{1_i} - [Fru]_{2_i}}{\sum_0^i [Glu]_{0_i} - [Glu]_{2_{i-1}}} \cdot 100\% \quad (\text{Eq. 11S})$$

$$Ad_{Glu} = \frac{[Glu]_{1_i} - [Glu]_{2_i}}{[Glu]_{1_i}} \cdot 100\% \quad (\text{Eq. 12S})$$

$$Ad_{Fru} = \frac{[Fru]_{1_i} - [Fru]_{2_i}}{[Fru]_{1_i}} \cdot 100\% \quad (\text{Eq. 13S})$$

$$S_{Fru, ad.} = \frac{[Fru]_{1_i} - [Fru]_{2_i}}{([Fru]_{1_i} - [Fru]_{2_i}) + ([Glu]_{1_i} - [Glu]_{2_i})} \cdot 100\% \quad (\text{Eq. 14S})$$

$$Y_{Fru,overall} = \frac{\sum_0^i [Fru]_{0_i} - [Fru]_{1_i}}{\sum_0^i [Glu]_{0_i} - [Glu]_{2_{i-1}}} \cdot 100\% \quad (\text{Eq. 15S})$$

References

1. L. Bosch, T. Fyles and T. D. James, *Tetrahedron*, 2004, **60**, 11175-11190.