

## Supporting Information

### Phenylglyoxaldehyde-functionalized Polymeric Sorbents for Urea Removal from Aqueous Solutions

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## 1. Pseudo-first order rate constants of the reactions of PGAH-analogues with urea

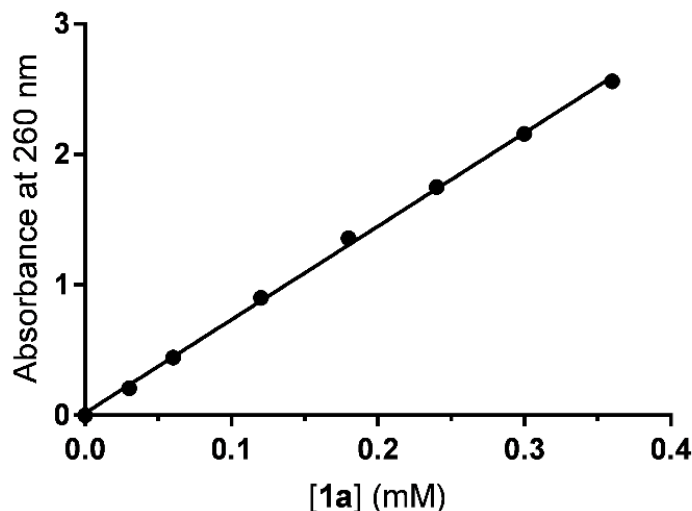


Figure S1: The absorbance at 260 nm versus the PGAH (**1a**) concentration in a 1:1 (v/v) mixture of PBS and DMSO used for calculation of the non-reacted PGA upon incubation with urea.

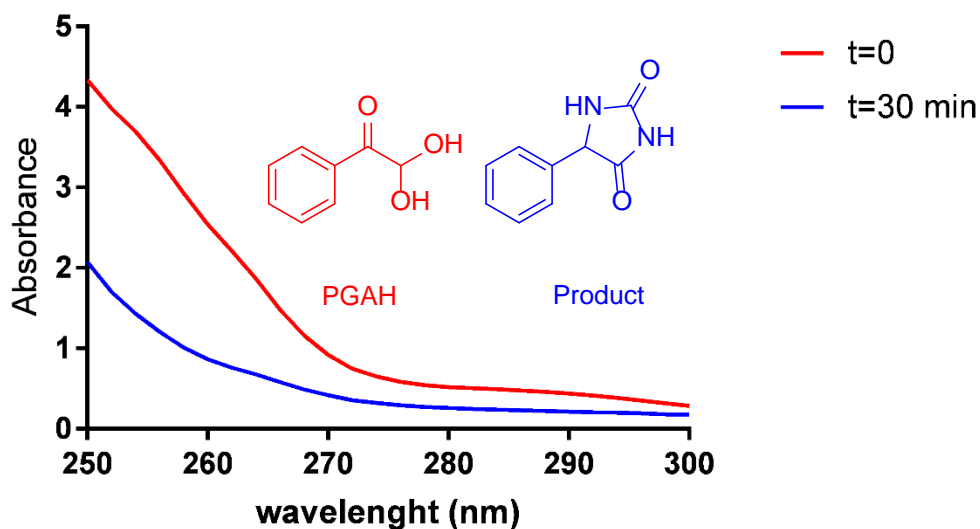


Figure S2: Absorbance spectrum of the reaction mixture of PGAH (**1a**, concentration = 0.30 mM) with 50 equivalents of urea in a 1:1 (v/v) mixture of PBS and DMSO.

Figure S2 shows that reaction of PGA with urea resulted in the formation of a product with a lower absorbance at 260 nm. Since the  $Ab_{\text{observed}}$  did not further decrease after  $t=60$ , it is assumed that PGAH was fully converted into the product at 60 minutes.

Thus,  $Abs_{t=0}$  is only due to the PGAH present in solution. This absorption corresponds to a [PGAH] of 27.7 mM according to figure S1.

$Abs_{t=60}$  is only due to the product present in solution, which concentration should thus be 27.7 mM as well.

The concentration of unreacted PGAH at different time points was calculated using the following equations:

**Equation S1:**  $Abs_t = Abs_{PGAH} + Abs_{product}$

**Equation S2:**  $Abs_{PGAH} = a[PGAH]$  (based on figure S1, in which a is the slope)

**Equation S3:**  $Abs_{product} = c[product]$  (in which  $c = (Abs_{t=60} - Abs_{solvent}) / ([product]_{t=60})$ )

**Equation S4:**  $[product]_t = [PGAH]_{t=0} - [PGAH]_t$

Substitution of S4 in S3 results in S5:

**Equation S5:**  $Abs_{product} = c[PGAH]_{t=0} - c[PGAH]_t$

Substitution of S5 and S2 in S1 results in S6.

**Equation S6:**  $[PGAH]_t = (Abs_t - c[PGAH]_{t=0}) / (a - c)$

Time (min)	Absorption	[1a] (mM)	ln[1a]
0	2.00	27.7	3.32
5	1.35	16.4	2.80
10	0.97	9.9	2.30
15	0.75	6.1	1.80
20	0.65	4.4	1.48
25	0.58	3.1	1.14
30	0.52	2.1	0.73

Table S1: The PGAH concentration in time during the reaction with 50 equivalents of urea in a 1:1 (v/v) mixture of PBS:DMSO at 50 °C.

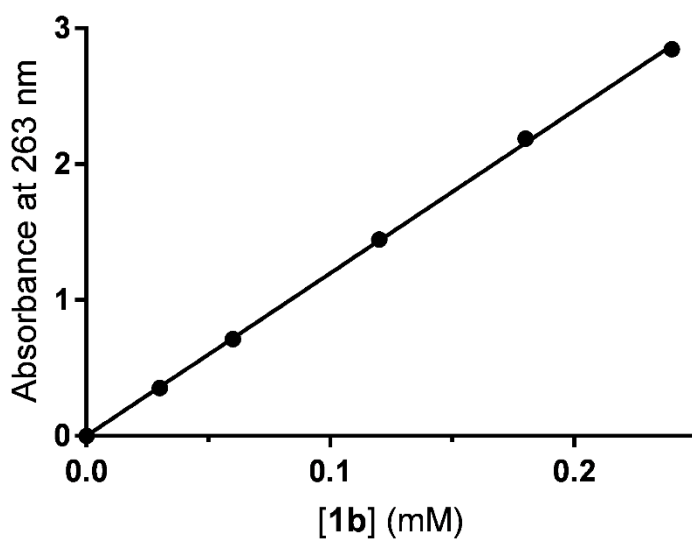


Figure S3: Absorbance at 263 nm versus the Me-PGAH (**1b**) concentration in a 1:1 (v/v) mixture of PBS and DMSO.

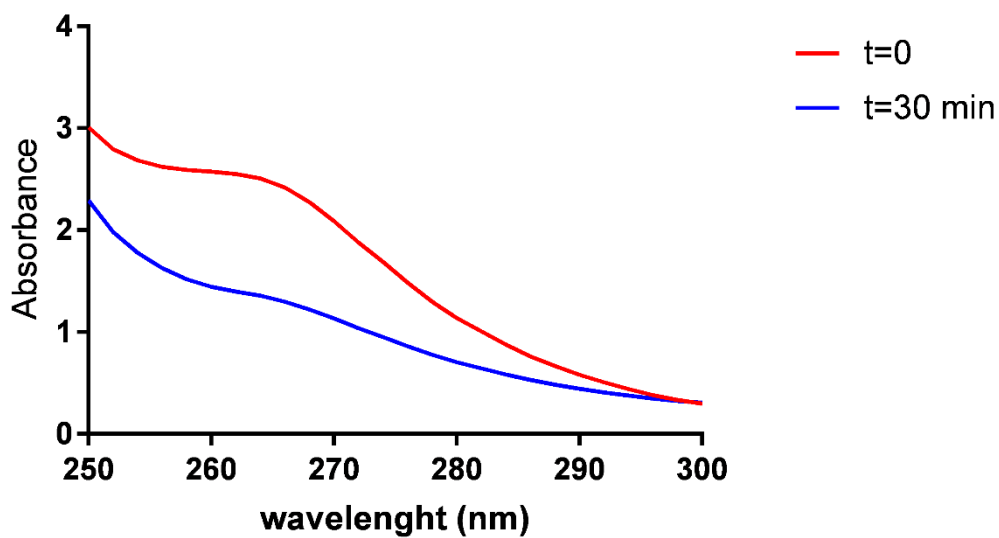


Figure S4: Absorbance spectrum of the reaction mixture of Me-PGAH (**1b**, concentration = 0.20 mM) with 50 equivalents of urea in a 1:1 (v/v) mixture of PBS and DMSO.

Time (min)	Absorption	[ <b>1b</b> ] (mM)	ln[ <b>1b</b> ]
0	2.17	27.2	3.30
5	1.95	20.2	3.00
10	1.84	16.7	2.82
15	1.71	12.4	2.52
20	1.64	10.3	2.33
25	1.54	6.9	1.93
30	1.52	6.2	1.83
40	1.38	2.0	0.68

Table S2: The concentration of **1b** in time during the reaction with 50 equivalents of urea in a 1:1 (v/v) mixture of PBS:DMSO at 50 °C. A similar correction was made to the [**1b**] using equation S6 as described above for **1a**.

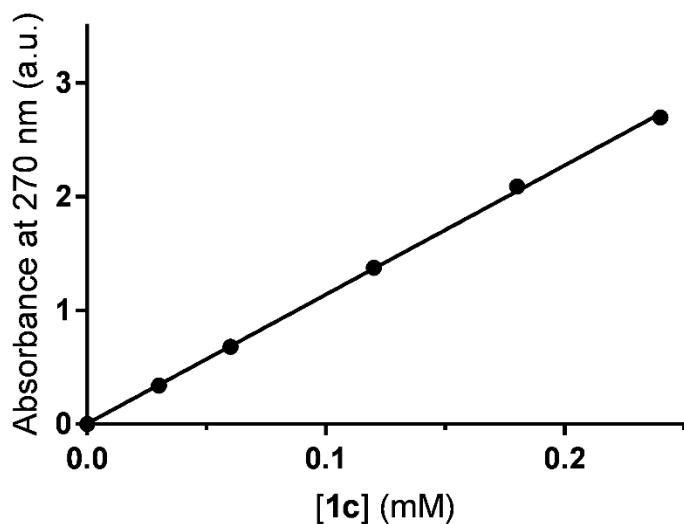


Figure S5: Absorbance at 270 nm versus the NO<sub>2</sub>-PGAH (**1c**) concentration in a 1:1 (v/v) mixture of PBS and DMSO.

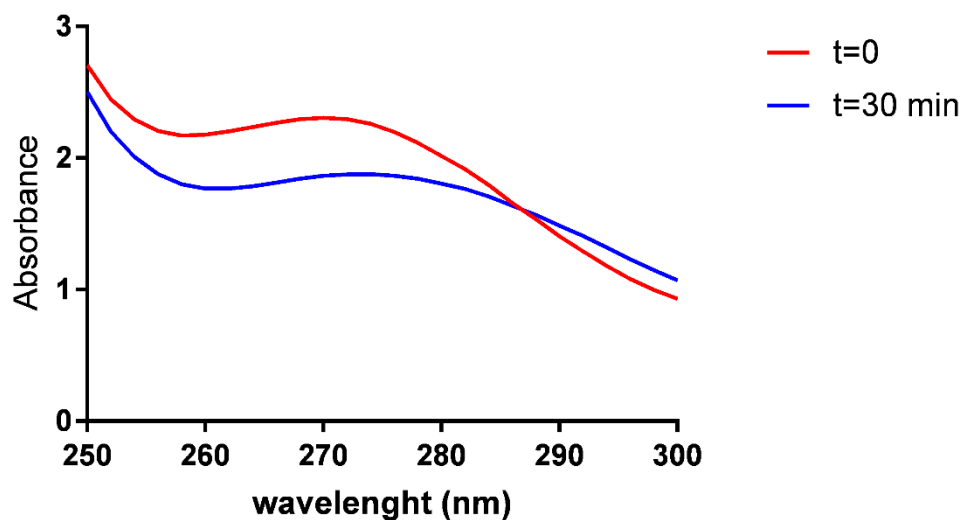


Figure S6: Absorbance spectrum of the reaction mixture of NO<sub>2</sub>-PGAH (**1c**, concentration = 0.20 mM) with 50 equivalents of urea in a 1:1 (v/v) mixture of PBS and DMSO.

Time (min)	Absorption	[ <b>1c</b> ] (mM)	ln[ <b>1c</b> ]
0	2.09	27.6	3.32
5	1.78	23.5	3.16
10	1.73	22.7	3.12
15	1.70	22.4	3.11
20	1.62	21.3	3.06
25	1.61	21.2	3.05
30	1.61	21.2	3.05
40	1.60	21.1	3.05

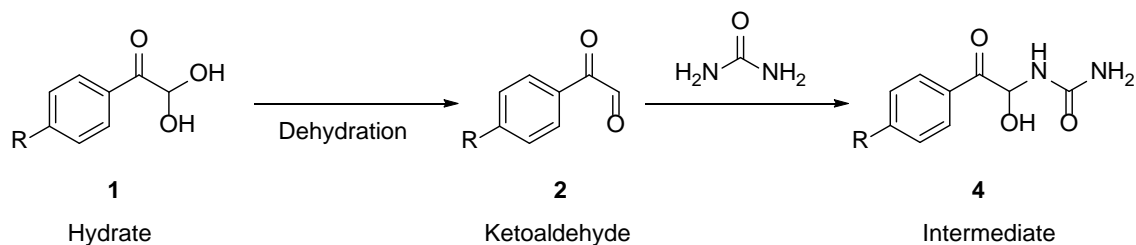
Table S3: The concentration of **1c** in time during the reaction with 50 equivalents of urea in a 1:1 (v/v) mixture of PBS:DMSO at 50 °C.

Entry	Substituent	$k_{PFO}$ (min <sup>-1</sup> )
<b>1a</b>	H	0.085 ± 0.003
<b>1b</b>	<i>p</i> -Me	0.061 ± 0.005
<b>1c</b>	<i>p</i> -NO <sub>2</sub>	0.006 ± 0.002

Table S4: Pseudo-first order rate constants of the reaction of PGAH(-analogues) with 50 eq. of urea in 1:1 (v/v) PBS:DMSO at 50 °C. The  $k_{PFO}$  was calculated from the negative slope divided by log(e) in the plot of log[**1a**, **1b**, **1c**] in time (figure 1C).

## 2. Computational data

### 2.1 Calculated G-values (Hartree)



Scheme S1: Dehydration of PGAH into PGA and subsequent reaction of PGA with urea.

Compound	$G_{\text{PGAH}}$ (Hartree)	$G_{\text{PGA}}$ (Hartree)	$G_{\text{intermediate}}$ (Hartree)	G (Hartree)
PGAH (1a)	-535.231654	-458.818308	-684.056086	
<i>p</i> -Me PGAH (1b)	-574.529475	-498.116566	-723.353774	
<i>p</i> -NO <sub>2</sub> PGAH (1c)	-739.734148	-663.319304	-888.557748	
Water				-76.423078
Urea				-225.24987

Table S5: Calculated G values of the optimized structures.

### 2.2 Calculated $\Delta G$ -values for the dehydration of PGAH and subsequent reaction with urea

Compound	$\Delta G_{\text{dehydration}}$ (kcal/mol)	$\Delta G_{\text{intermediate}}$ (kcal/mol)
PGAH (1a)	-6.11	7.59
<i>p</i> -Me PGAH (1b)	-6.38	7.95
<i>p</i> -NO <sub>2</sub> PGAH (1c)	-5.17	7.17

Table S6: Calculated  $\Delta G$ -values.

### 2.3 Calculated $\Delta\Delta G$ -values of dehydration of PGAH and subsequent reaction with urea

Compound	$\Delta\Delta G_{\text{dehydration}}$ (kcal/mol)	$\Delta\Delta G_{\text{intermediate}}$ (kcal/mol)
PGAH (1a)	0	0
<i>p</i> -Me PGAH (1b)	-0.27	0.35
<i>p</i> -NO <sub>2</sub> PGAH (1c)	0.94	-0.41

Table S7: Calculated  $\Delta\Delta G$ -values.



### 3. Suspension polymerization reactor

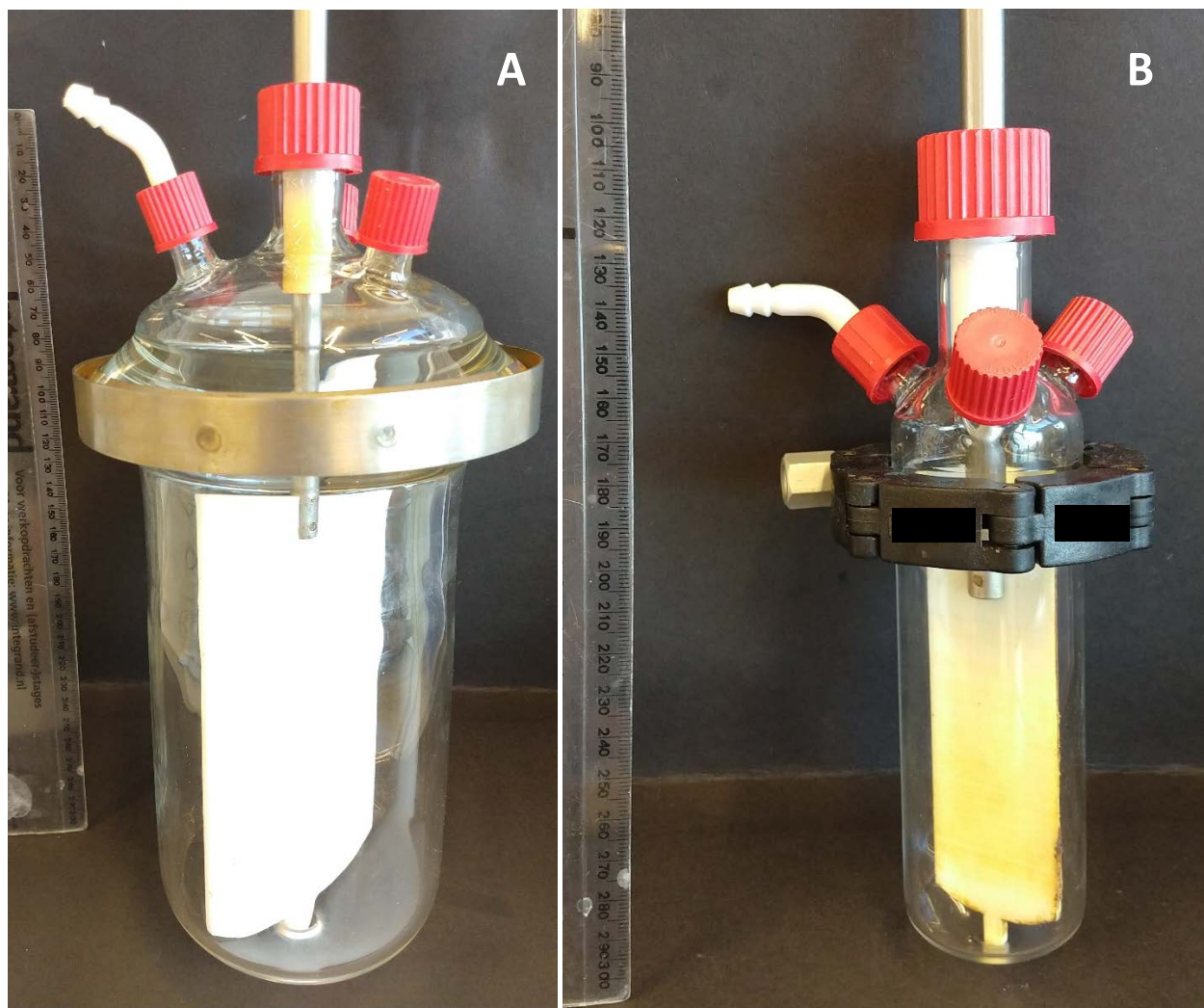


Figure S7: Photographs of the used reactor for suspension polymerization with a volume of A)  $\pm 1.0$  Liter and B)  $\pm 200$  mL.

## 4. DSC and TGA analysis of monomers and polymeric beads

### 4.1 Polystyrene-based materials

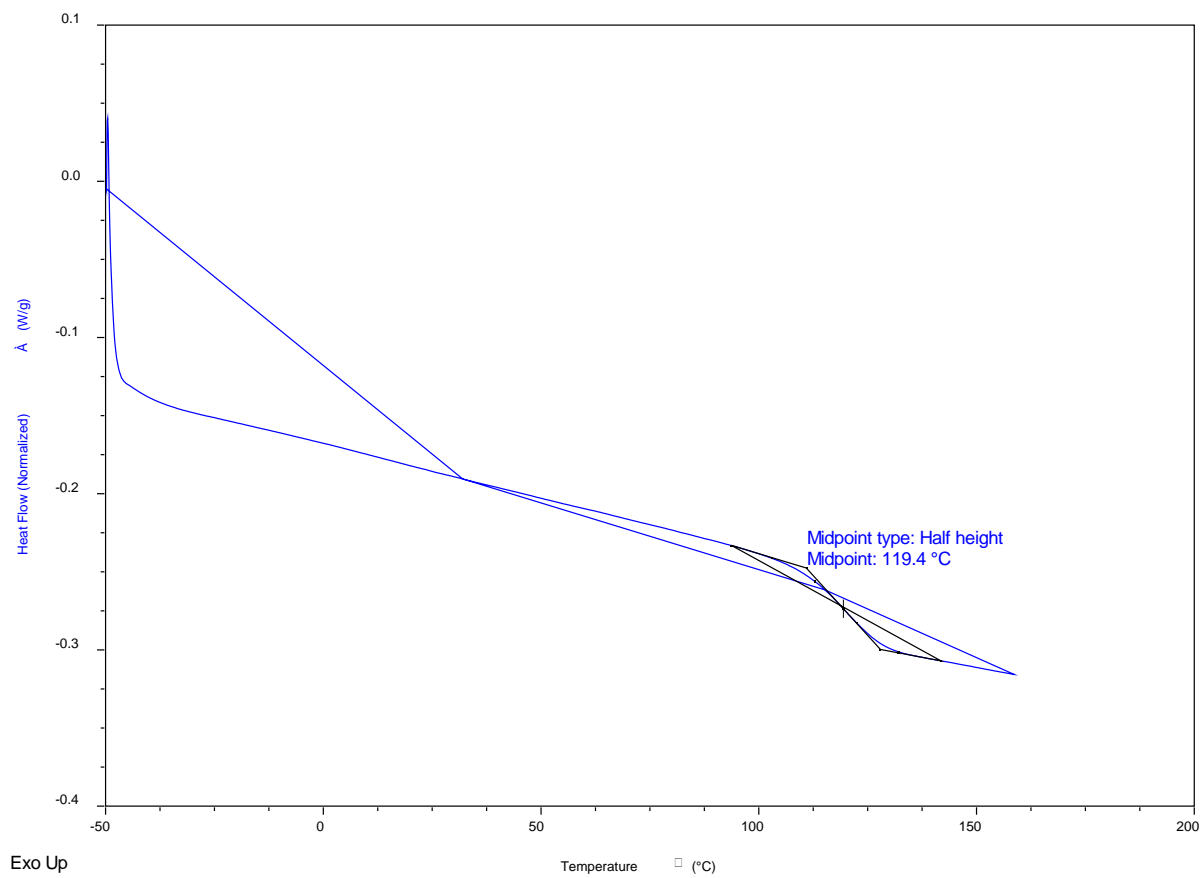


Figure S8: DSC thermogram of polystyrene beads (PS). Glass transition temperature ( $T_g$ ) is 119 °C.

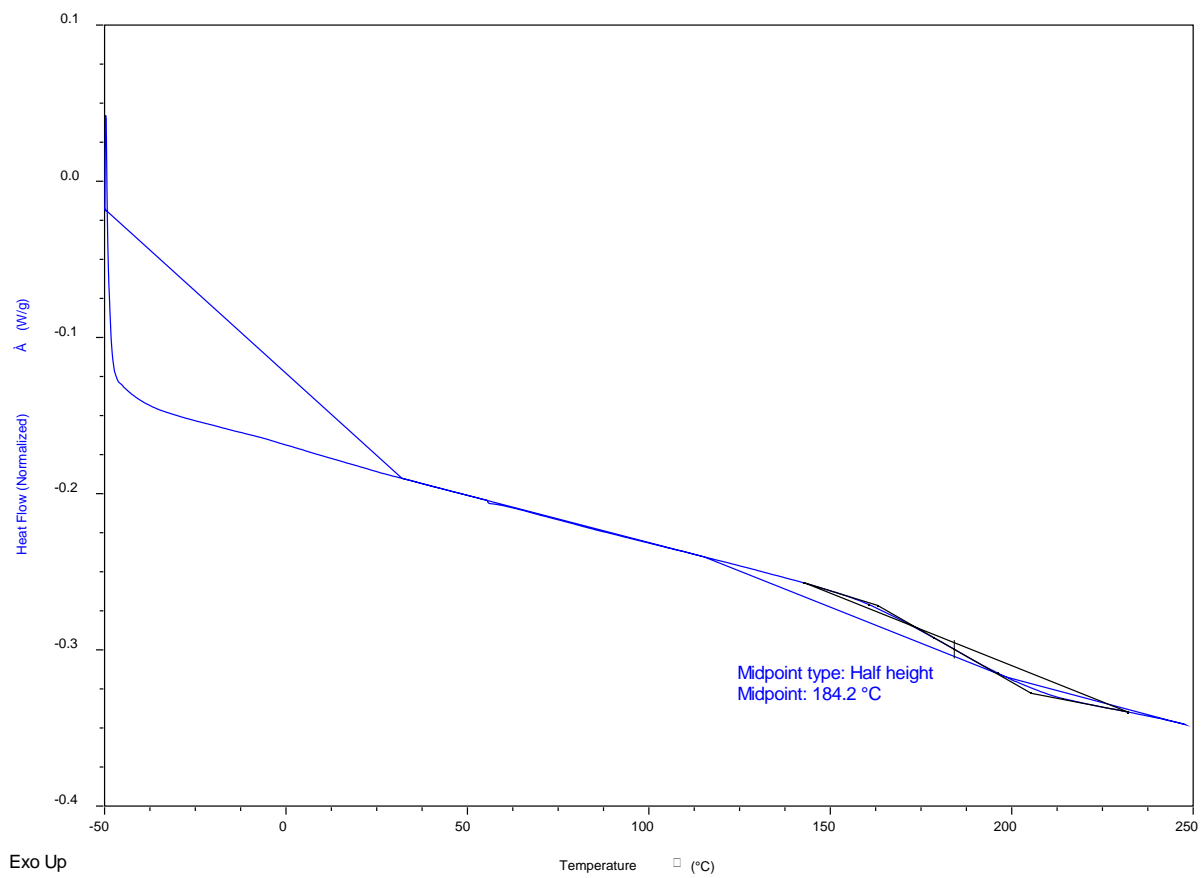


Figure S9: DSC thermogram of acetylated polystyrene beads (PS-Ac). Glass transition temperature ( $T_g$ ) is 184 °C.

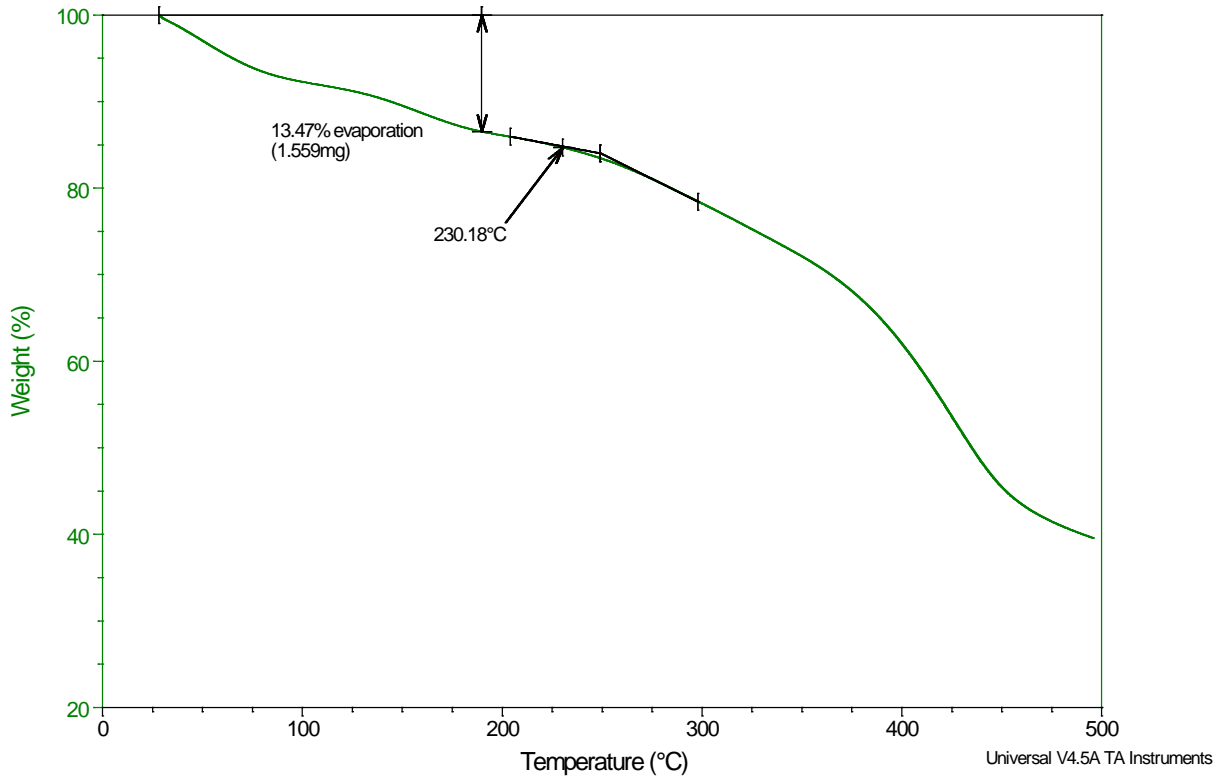


Figure S10: TGA plot of oxidized acetylated polystyrene beads (PS-Ac-Ox). Decomposition starts at ~230 °C; no glass transition temperature ( $T_g$ ) was observed below 230 °C by DSC analysis.

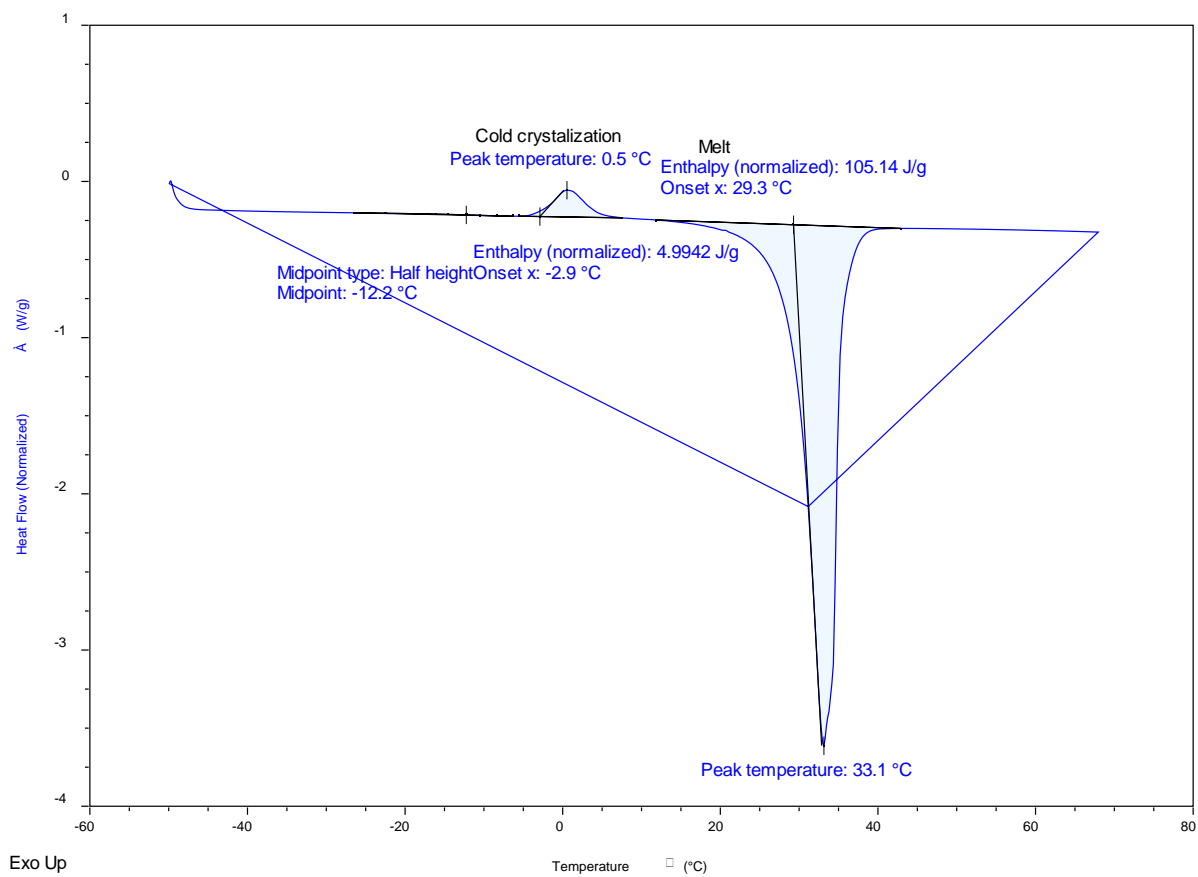


Figure S11: DSC thermogram of the VPE monomer. The melting temperature is 29 °C; Melting enthalpy 105 J/g.

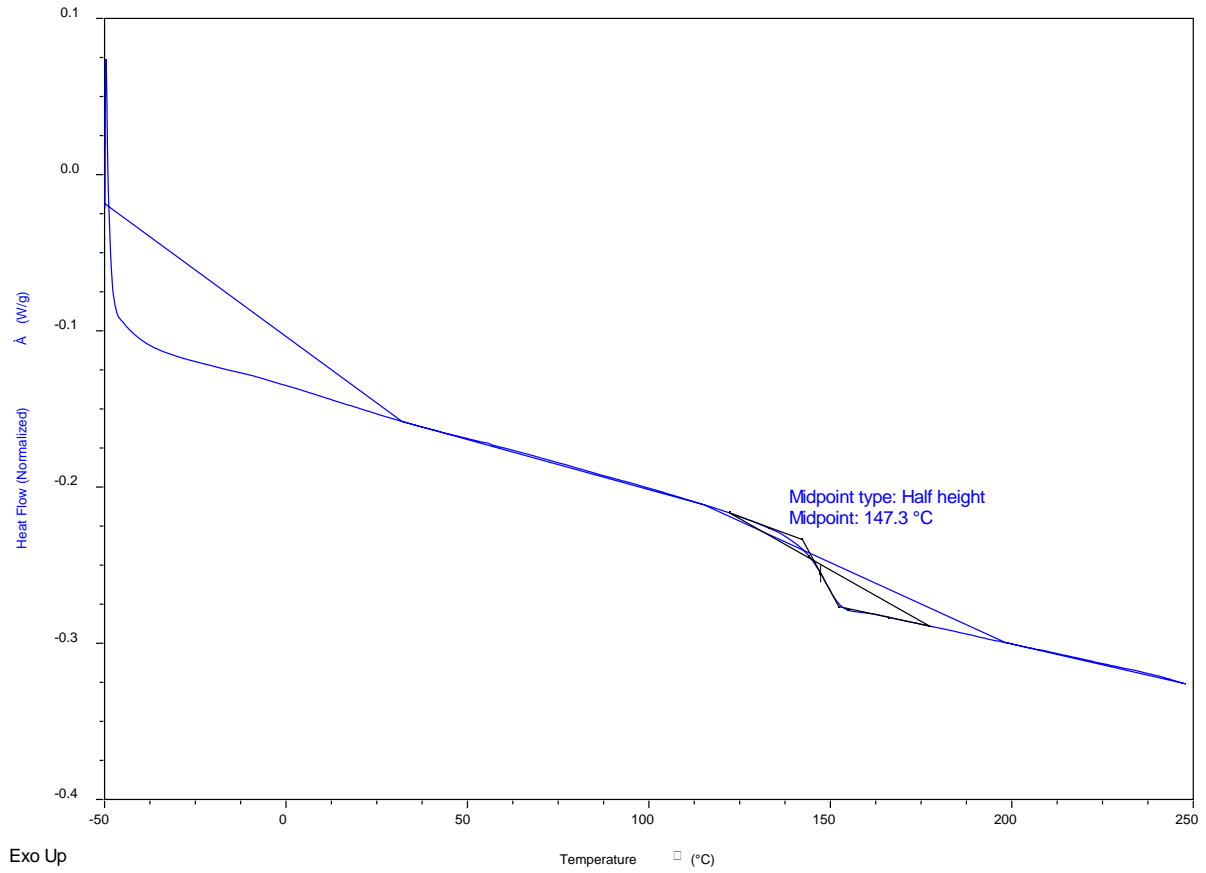


Figure S12: DSC thermogram of polyvinylphenylethanone (pVPE). Glass transition temperature ( $T_g$ ) is 147 °C.

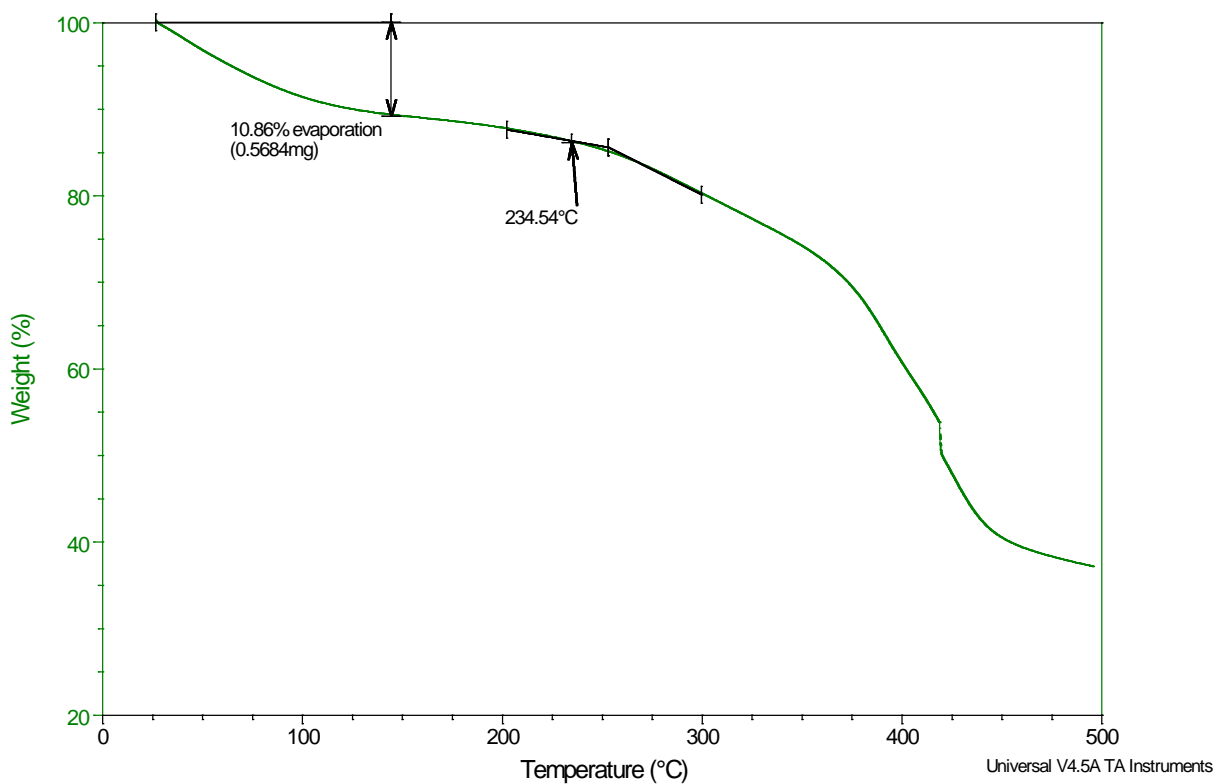
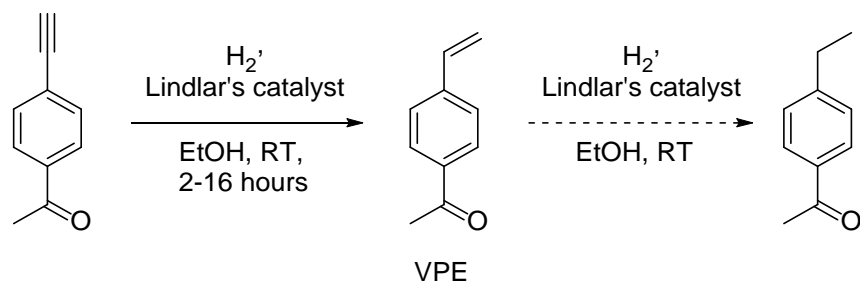


Figure S13: TGA plot of oxidized polyvinylphenylethanone (pVPE-Ox-(4)). Decomposition starts at ~230 °C; no glass transition temperature ( $T_g$ ) was observed below 235 °C by DSC.

## 5. VPE synthesis



Scheme S2: The synthesis of vinylphenylethanone (VPE).



## 6. IR Characterization of Sorbents

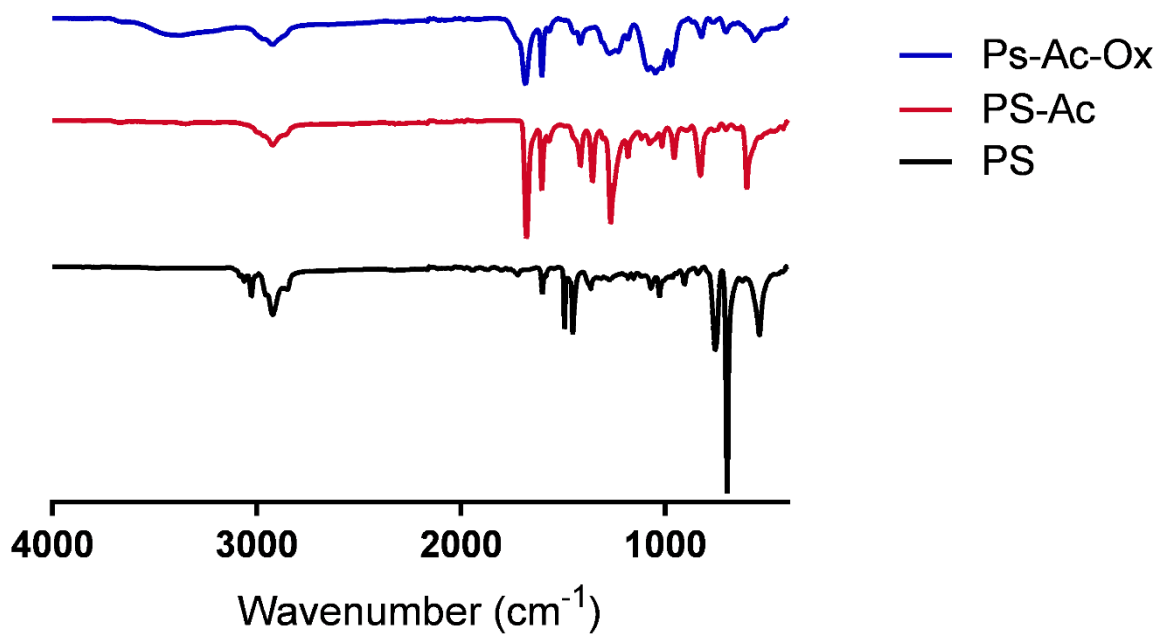


Figure S14: Full IR spectra of PS, PS-Ac and PS-Ac-Ox.

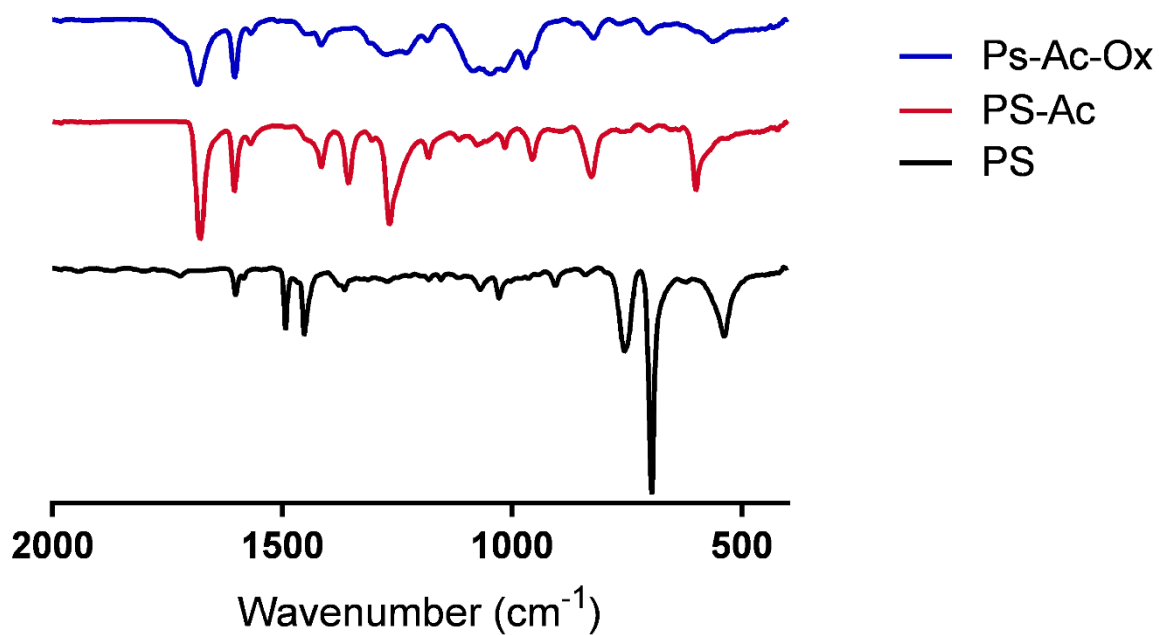


Figure S15: IR spectra of PS, PS-Ac and PS-Ac-Ox in the region of 2000-400 cm<sup>-1</sup>.

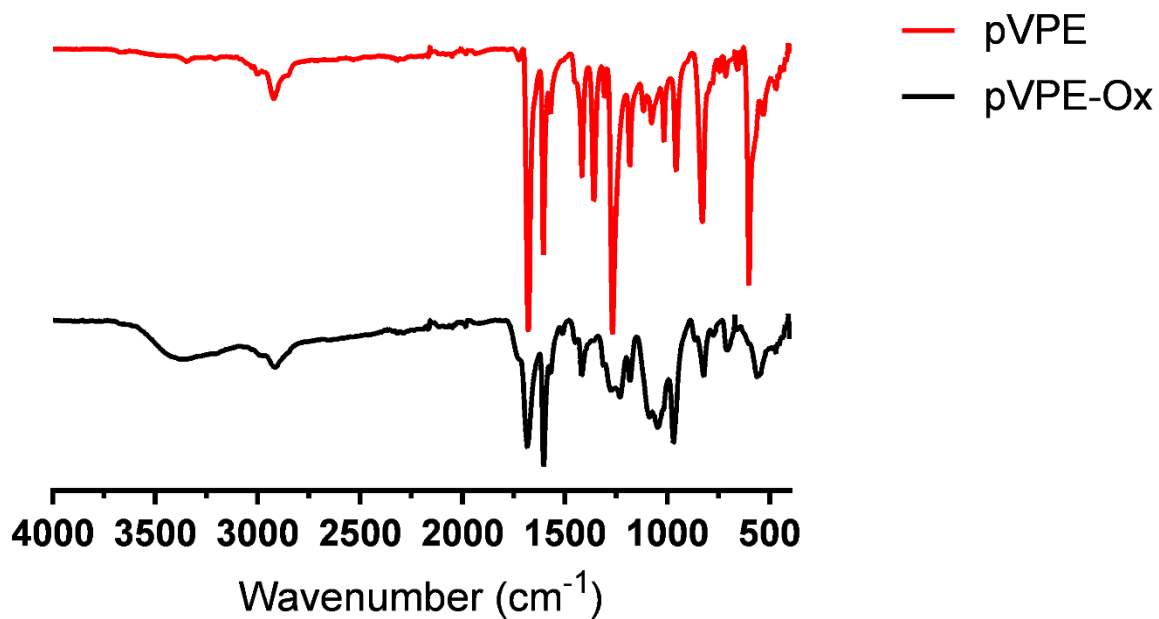


Figure S16: Full IR spectra of pVPE and pVPE-Ox.

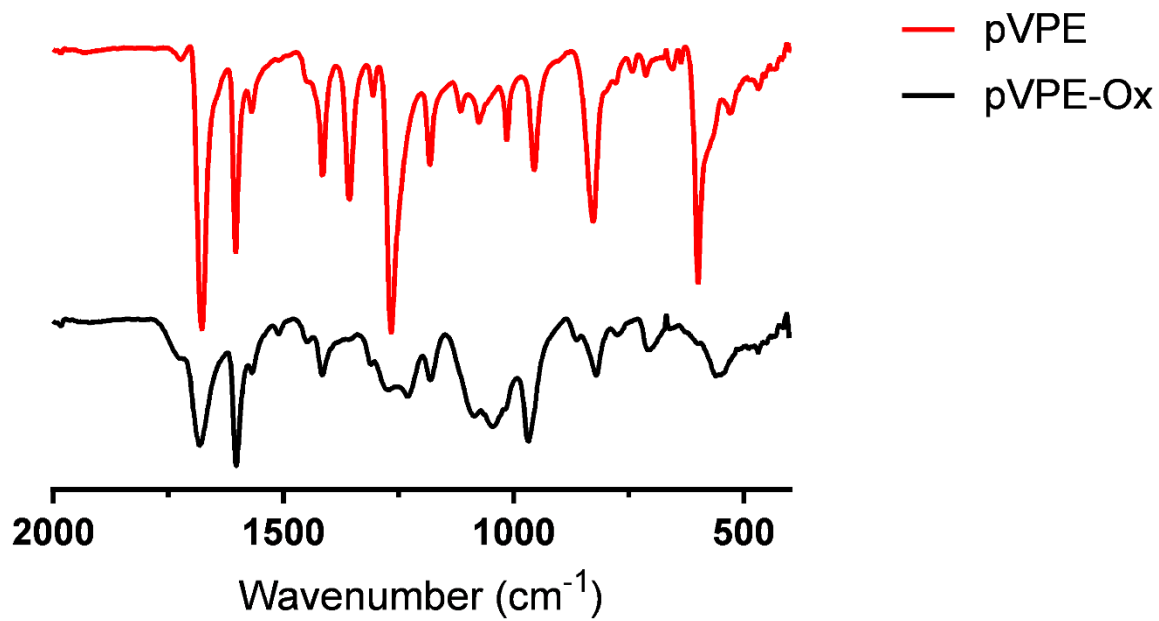


Figure S17: IR spectra of pVPE and pVPE-Ox in the region of 2000-400  $\text{cm}^{-1}$ .

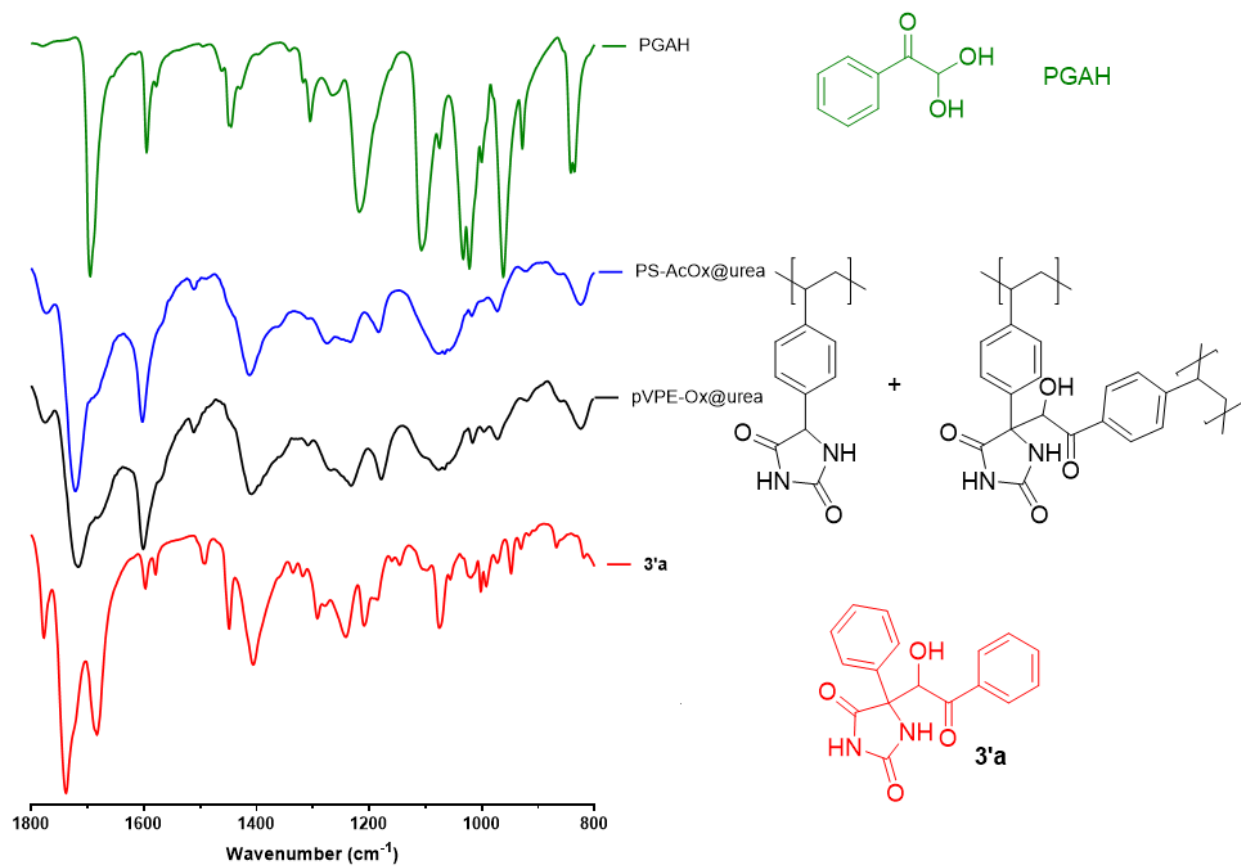


Figure S18: IR spectra of PGAH, PS-Ac-Ox@urea, pVPE-Ox-(4)@urea and the 2:1 addition product of PGAH and urea (**3'a**).

## 7. Quantitative $^{13}\text{C}$ - Solid State NMR Spectroscopy

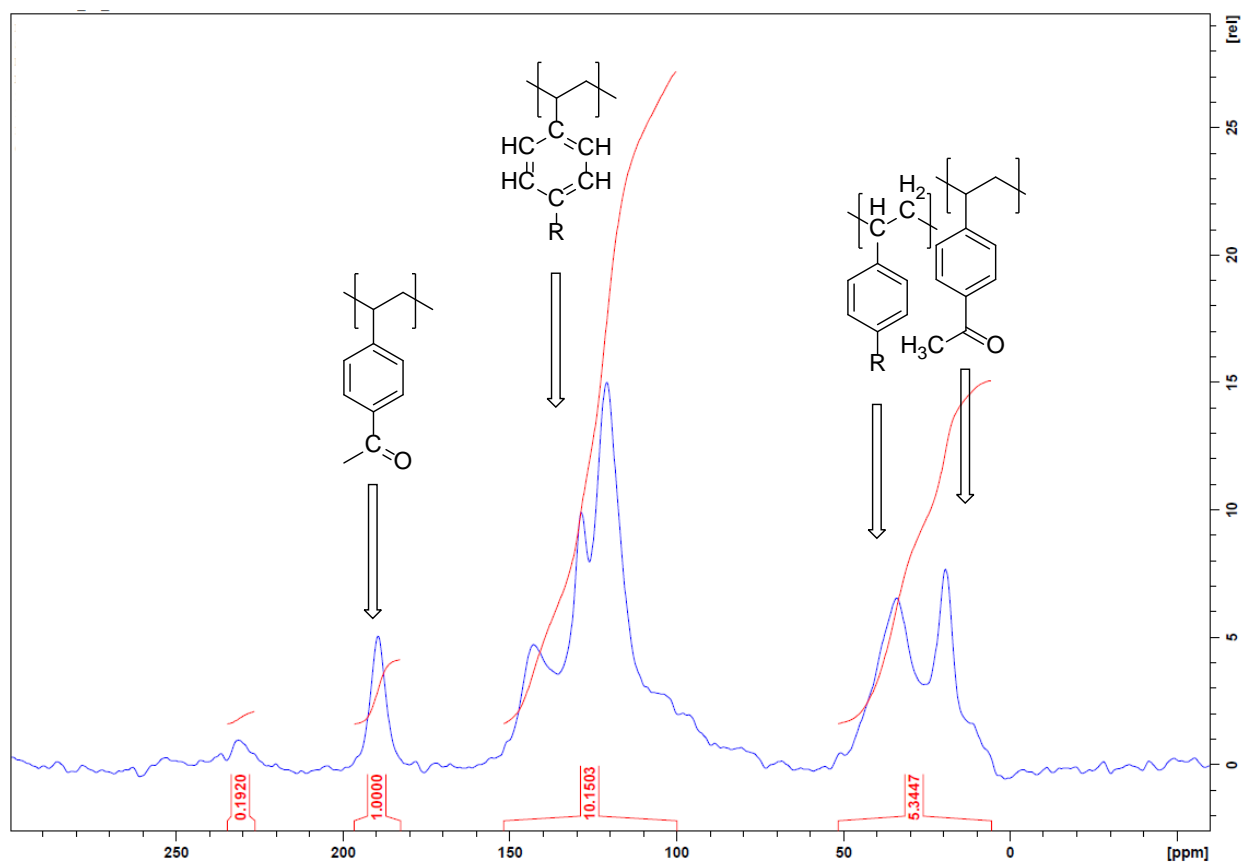


Figure S19: Quantitative  $^{13}\text{C}$  solid state NMR spectrum of PS-Ac. The spectrum was recorded on a Bruker 400 MHz spectrometer using a 100 s recycle delay, 20 ms acquisition time, 11 kHz MAS frequency and an accumulation of 4947 scans. Spinning sidebands, originating from the aromatic peak and indicated with a star (\*), were included in the integration of the aromatic and aliphatic peaks.

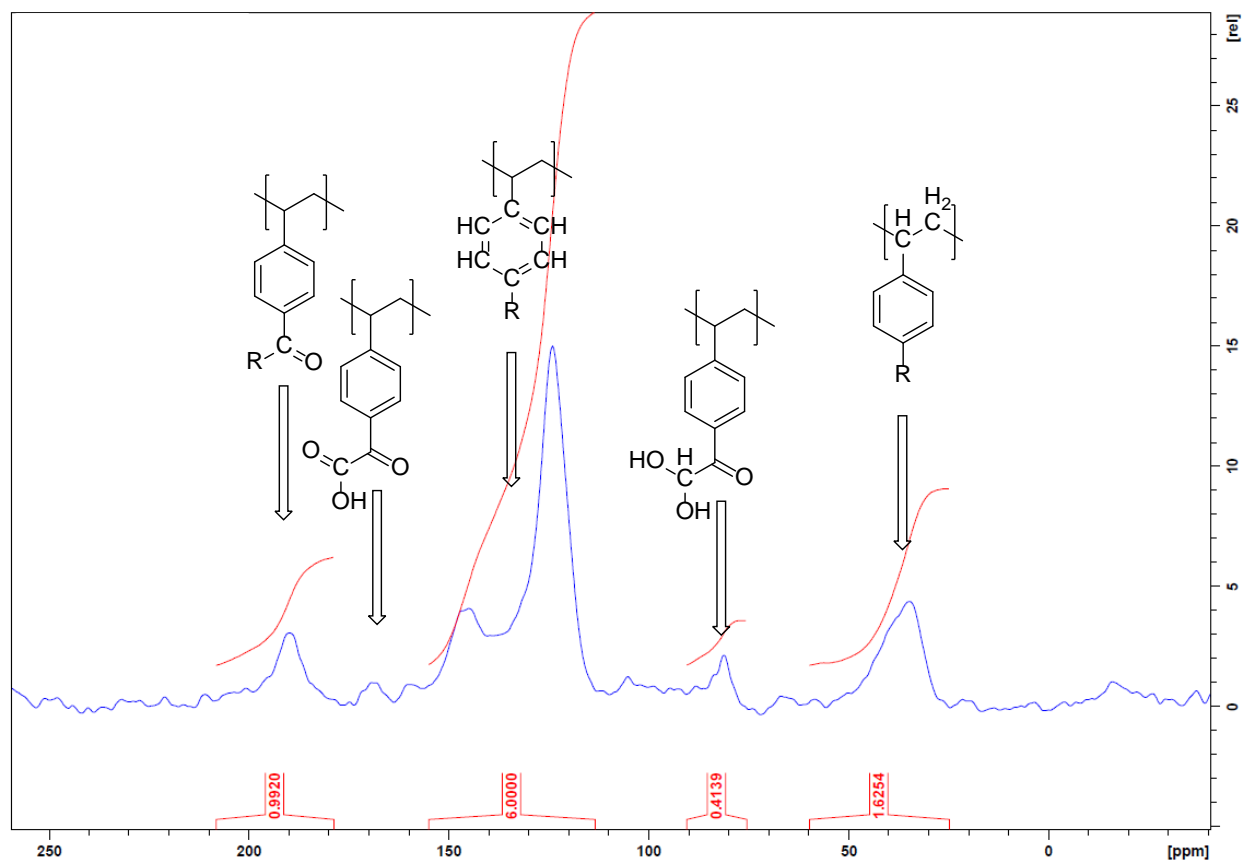


Figure S20: Quantitative  $^{13}\text{C}$  solid state NMR spectrum of PS-Ac-Ox (prepared at small scale (ca. 500 mg)). The spectrum was recorded on a Bruker 400 MHz spectrometer using a 150 s recycle delay, 20 ms acquisition time, 14 kHz MAS frequency and an accumulation of 3400 scans.

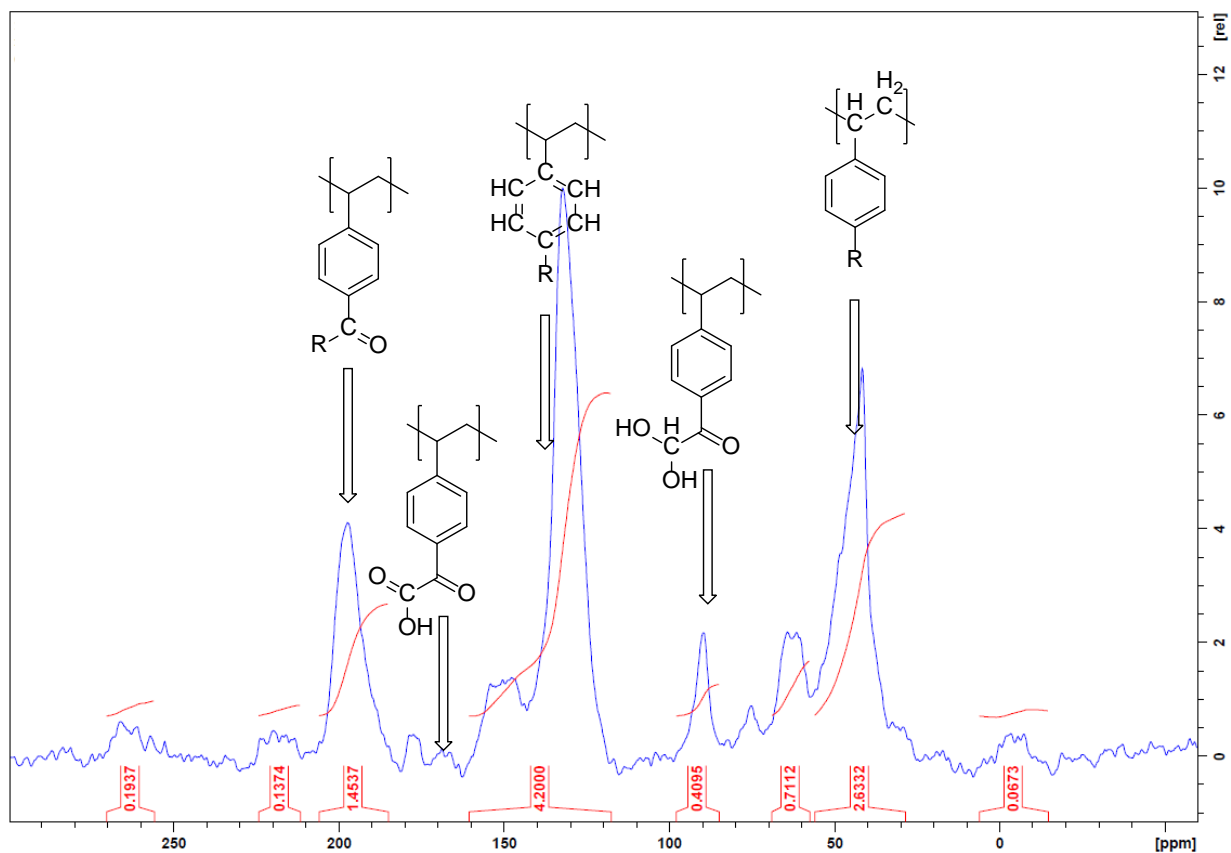


Figure S21: Quantitative  $^{13}\text{C}$  solid state NMR spectrum of PS-Ac-Ox (synthesized at large scale (60 grams)). The spectrum was recorded on a Bruker 700 MHz spectrometer using a 75 s recycle delay, 11 ms acquisition time, 12 kHz MAS frequency and an accumulation of 4482 scans. Spinning sidebands, originating from the aromatic peak and indicated with a star (\*), were included in the integration of the aromatic peak.

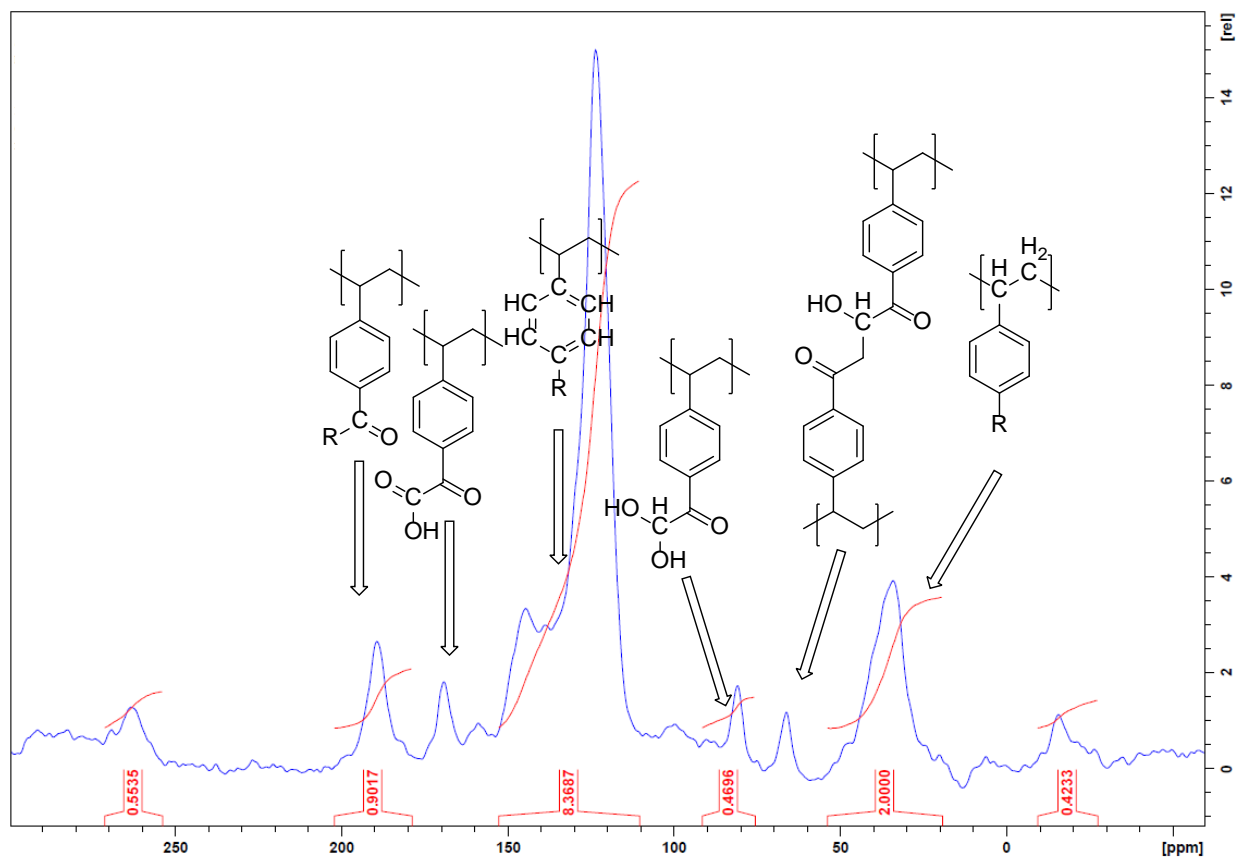


Figure S22: Quantitative  $^{13}\text{C}$  solid state NMR spectrum of pVPE-Ox-(2). The spectrum was recorded on a Bruker 700 MHz spectrometer using a 50 s recycle delay, 11 ms acquisition time, 13.5 kHz MAS frequency and an accumulation of 4771 scans. Spinning sidebands, originating from aromatic peak and indicated with a star (\*), were included in the integration of the aromatic peak.

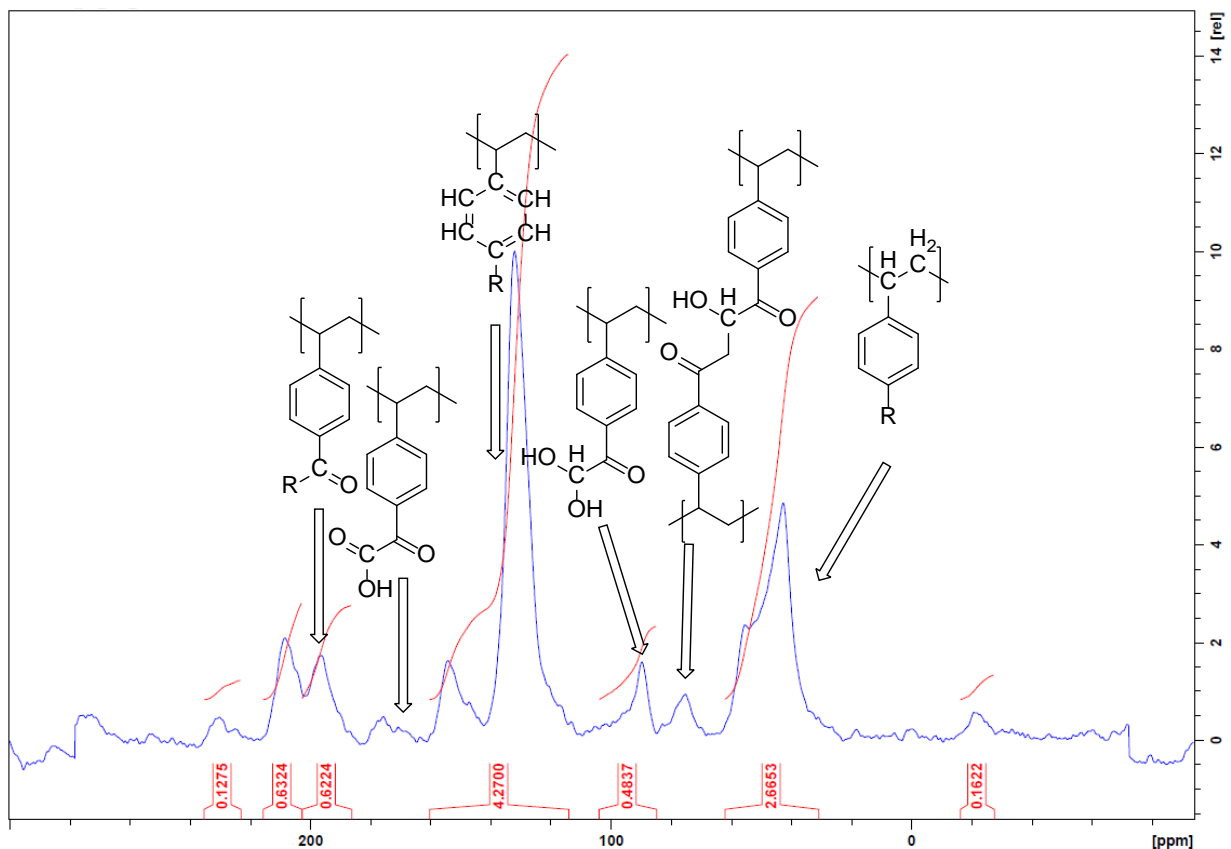


Figure S23: Quantitative  $^{13}\text{C}$  solid state NMR spectrum of pVPE-Ox-(4). The spectrum was recorded on a Bruker 400MHz spectrometer. The spectrum was recorded using a 150 s recycle delay, 20 ms acquisition time, 14 kHz MAS frequency and an accumulation of 5623 scans. Spinning sidebands, originating from aromatic peak and indicated with a star (\*), were included in the integration of the aromatic and carbonyl peaks.



## 8. Conditions to Determine the Maximum Urea Binding Capacity

Sorbent beads (PS-Ac-Ox, 15 mg) in an Eppendorf tube were dispersed in a urea solution (30 mM, 1.5 mL) and placed in a rotating oven at 70 °C. Per time point 2 Eppendorf tubes were removed and after sedimentation of the beads, the urea concentration was determined in the supernatant. It was found the urea concentration did not change after ~24 hours (table S8), indicating that under these conditions (24 hours reaction at 70 °C) all available PGAH groups have reacted with urea. Therefore for determination of the maximum binding capacity, the beads were incubated for 24 hours at 70 °C, after which the urea concentration was determined (table S9).

Time (h)	[Urea] <sub>t=24h</sub> (mM)		Urea bound (mmol/g)
	Duplicate#1	Duplicate#2	
0	31.4	31.1	0
16	18.6	19.0	1.25 ± 0.03
24	17.9	18.2	1.32 ± 0.02
32	17.2	18.1	1.36 ± 0.06

Table S8: Kinetics of urea sorption by PS-Ac-Ox in urea solution (30 mM) in PBS (10 mg/mL) at 70 °C under static conditions.

## 9. Oxidation of pVPE-Beads

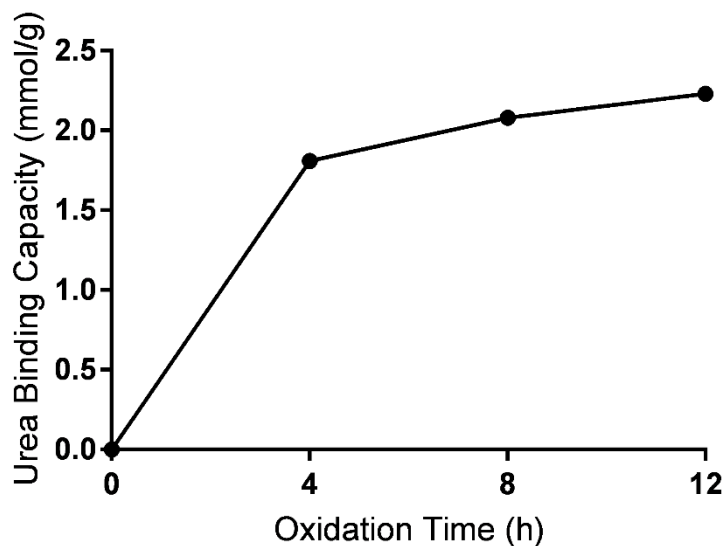


Figure S24: The urea binding capacity of pVPE beads (table 4 entry 2) as a function of oxidation time of pVPE. Conditions for oxidation: pVPE (500 mg) in DMSO (5.0 mL) and 48% aqueous HBr solution (1.45 mL) stirred with a Teflon blade stirrer at 80 °C for 4-12 hours. Per timepoint  $\pm$  150 mg beads was removed from the suspension and tested for urea binding according to the procedure described in supporting information section 7. Raw data are presented in table S8.

## 10. Maximum Binding Capacity Urea Sorbents

Sorbent	[Urea] <sub>t=0</sub> (mM)		[Urea] <sub>t=24h</sub> (mM)		Max Binding Capacity (mmol/g)
	Duplicate#1	Duplicate#2	Duplicate#1	Duplicate#2	
PS-Ac-Ox-1h	30.5	30.4	28.1	27.3	0.28 ± 0.06
PS-Ac-Ox-4h	30.5	30.4	17.4	17.6	1.30 ± 0.01
PS-Ac-Ox-8h	30.5	30.4	12.1	12.8	1.80 ± 0.05
PS-Ac-Ox-24h	30.5	30.4	16.2	16.6	1.41 ± 0.03
PS-Ac-Ox-32h	30.5	30.4	21.6	20.8	0.93 ± 0.06
PS-Ac-Ox-48h	30.5	30.4	27.0	27.5	0.32 ± 0.04
PS-Ac-Ox (60 g, 8h)	29.8	29.8	16.7	16.1	1.34 ± 0.04
PS-Ac-Ox (60 g, 8h)	46.1	43.4	30.6	30.8	1.41 ± 0.01
pVPE-Ox-(2)-4h	49.8	50.0	32.1	31.6	1.81 ± 0.04
pVPE-Ox-(2)-8h	49.8	50.0	29.0	29.2	2.08 ± 0.01
pVPE-Ox-(2)-12h	49.8	50.0	27.3	27.9	2.23 ± 0.04
pVPE-Ox-(4)	46.1	43.4	28.0	26.4	1.76 ± 0.11

Table S9: Urea sorption by the sorbent beads in urea solution in PBS (10 mg/mL) at 70 °C for 24 hours under static conditions.

## 11. Static Urea Sorption of PS-Ac-Ox and pVPE-Ox Beads

Time (h)	[Urea] (mM)				Urea removed (mmol/g)
	Duplicate#1	Duplicate#2	Duplicate#3	Duplicate#4	
0	27.7	27.7	29.3	29.3	0
1	26.1	25.8	28.2	28.8	0.13 ± 0.16
2	25.3	25.7	28.1	27.6	0.18 ± 0.05
4	24.2	24.2	27.9	27.8	0.25 ± 0.11
8	21.2	21.9	26.7	25.7	0.46 ± 0.16
16	22.9	23.1	23.9	24.2	0.50 ± 0.03
24	21.6	21.8	24.3	24.3	0.57 ± 0.04

Table S10: Urea sorption of PS-Ac-Ox sorbent beads (15 mg) in 1.5 mL urea solution (~30 mM) in PBS under static conditions.

Time (h)	[Urea] (mM)				Urea removed (mmol/g)
	Duplicate#1	Duplicate#2	Duplicate#3	Duplicate#4	
0	27.7	27.7	30.8	30.8	0
1	23.4	22.9	29.8	30.2	0.27 ± 0.19
2	24.4	25.0	29.1	29.1	0.26 ± 0.11
4	23.6	22.7	27.6	27.1	0.40 ± 0.07
8	22.5	20.7	27.5	25.8	0.51 ± 0.13
16	20.3	19.8	23.3	23.4	0.75 ± 0.02
24	18.5	19.1	22.8	22.5	0.85 ± 0.05

Table S11: Urea sorption of pVPE-Ox-(4) sorbent beads (15 mg) in 1.5 mL urea solution (~30 mM) in PBS under static conditions.

## 12. Optimized coordinates for compound 1, 2 and 4.

\*Also reported in ACS Omega, 2019, 47, 11928-11937.

### Optimized coordinates for PGAH (1a)\*

	X	Y	Z
C	-0.95253700	0.65075000	-0.00641900
O	-1.28404500	1.80954800	0.18897000
C	0.48192500	0.23827700	-0.01696500
C	0.89798900	-1.09646600	-0.16025900
C	1.45234800	1.24859400	0.10233600
C	2.25678000	-1.40831300	-0.18584300
H	0.16616700	-1.89233200	-0.22542500
C	2.80721800	0.93503100	0.07564000
H	1.12004300	2.27526900	0.21097800
C	3.21206800	-0.39594600	-0.07005700
H	2.56979600	-2.44214800	-0.29330700
H	3.54857600	1.72294300	0.16609000
H	4.26935300	-0.64260000	-0.09194400
C	-2.03182700	-0.42499200	-0.27344900
H	-1.77311700	-0.97892400	-1.18752400
O	-3.26034200	0.22664000	-0.42831600
H	-3.87033500	-0.38783600	-0.85933900
O	-1.99601200	-1.28930900	0.84880100
H	-2.45108300	-2.11101200	0.61491100

### Optimized coordinates for Me-PGAH (1b)

	X	Y	Z
C	-1.44369300	0.63809600	-0.02761500
O	-1.84851000	1.78013700	0.13181000
C	0.00967000	0.31439600	-0.02223200
C	0.51554000	-0.98654700	-0.18157100
C	0.92075200	1.37569600	0.12442800
C	1.89004900	-1.21116700	-0.19468500
H	-0.15953800	-1.82843800	-0.27547400
C	2.28963100	1.14384900	0.11216900
H	0.53076000	2.38108100	0.24139600
C	2.80082200	-0.15554900	-0.04629400
H	2.26326000	-2.22371500	-0.32070200
H	2.97723800	1.97800700	0.22321400
C	-2.45459300	-0.50922900	-0.26541200
H	-2.18050800	-1.04623100	-1.18527200

O	-3.72837300	0.05665100	-0.39279700
H	-4.30182400	-0.59533600	-0.81871600
O	-2.33699800	-1.36840100	0.85511800
H	-2.74733500	-2.21638200	0.63234100
C	4.28765000	-0.40684300	-0.03156300
H	4.83405700	0.40612100	-0.51857800
H	4.65927400	-0.47384300	0.99842000
H	4.54070800	-1.34456200	-0.53302900

Optimized coordinates for NO<sup>2</sup>-PGAH (**1c**)

	X	Y	Z
C	-2.11586100	0.62758400	-0.03642200
O	-2.53992500	1.76030900	0.10553300
C	-0.63966200	0.35010300	-0.01784100
C	-0.09737600	-0.94050400	-0.13097100
C	0.22088600	1.45507200	0.09571800
C	1.28193800	-1.12576100	-0.13461300
H	-0.74568500	-1.80458100	-0.19153900
C	1.59876000	1.28575100	0.09564100
H	-0.21086500	2.44526800	0.18083000
C	2.10632700	-0.00839600	-0.02204700
H	1.71715500	-2.11272200	-0.21910000
H	2.27383000	2.12698000	0.18190400
C	-3.08937700	-0.54893700	-0.27084600
H	-2.80739200	-1.06409000	-1.20117500
O	-4.37962100	-0.02281700	-0.37257000
H	-4.93681500	-0.67813600	-0.81477600
O	-2.92104500	-1.41203900	0.83894400
H	-3.30717000	-2.27204000	0.61825900
N	3.56359200	-0.20035800	-0.02521800
O	4.27879600	0.79769600	0.07629400
O	3.99654100	-1.34910600	-0.12940000

Optimized coordinates for PGA (**2a**)\*

	X	Y	Z
C	1.36529200	0.65257300	-0.00001600
C	2.54704800	-0.33874300	0.00000100
H	3.50633000	0.21680000	0.00001800
O	1.71341400	1.82969300	0.00000800
O	2.49468200	-1.54825000	0.00000900
C	-0.05403600	0.23235100	-0.00000900
C	-0.46103900	-1.11490100	-0.00000900

C	-1.02942200	1.24879600	-0.00000100
C	-1.81899200	-1.43026500	-0.00000300
H	0.28142800	-1.90136500	-0.00001400
C	-2.38088600	0.92729100	0.00000500
H	-0.70294500	2.28290100	-0.00000100
C	-2.77793900	-0.41510100	0.00000400
H	-2.12878000	-2.47049800	-0.00000300
H	-3.12682800	1.71577900	0.00001100
H	-3.83412900	-0.66717300	0.00000900

Optimized coordinates for Me-PGA (**2b**)

	X	Y	Z
C	1.87981200	0.58287500	0.00000700
C	2.97361100	-0.50413200	0.00256100
H	3.97634400	-0.03098900	0.00173000
O	2.32744100	1.72736200	0.00028800
O	2.82124300	-1.70540600	0.00590000
C	0.43493400	0.28142800	-0.00137900
C	-0.08808000	-1.02422200	-0.00593400
C	-0.46013200	1.37085900	-0.00029500
C	-1.46659100	-1.22396800	-0.00854100
H	0.58195300	-1.87341400	-0.00897300
C	-1.82963900	1.15967500	-0.00283100
H	-0.05519000	2.37697800	0.00090400
C	-2.35992300	-0.14416200	-0.00523600
H	-1.85680700	-2.23765800	-0.01406000
H	-2.50532700	2.01059800	-0.00392400
C	-3.85097800	-0.36275800	0.00848300
H	-4.10531100	-1.41088600	-0.16538000
H	-4.27718800	-0.06888800	0.97504300
H	-4.34603900	0.24503800	-0.75584400

Optimized coordinates for NO<sub>2</sub>-PGA (**2c**)

	X	Y	Z
C	2.55691100	0.55092700	0.00000000
C	3.60723500	-0.57763800	-0.00000200
H	4.62875300	-0.14993500	0.00000200
O	3.02932200	1.67957200	0.00000200
O	3.39382000	-1.76860900	-0.00000700
C	1.08747800	0.30343100	0.00000000
C	0.52511700	-0.98482000	0.00000100
C	0.24799600	1.43267900	-0.00000100

C	-0.85815400	-1.14175600	0.00000200
H	1.16534400	-1.85577500	0.00000200
C	-1.13169100	1.28749700	-0.00000100
H	0.69591100	2.41929400	-0.00000200
C	-1.66062700	-0.00391900	0.00000100
H	-1.31209600	-2.12384300	0.00000300
H	-1.79249500	2.14422900	-0.00000100
N	-3.12318800	-0.16909000	0.00000200
O	-3.81856400	0.84730200	-0.00000100
O	-3.57566500	-1.31435900	0.00000500

Optimized coordinates for PGA-urea intermediate compound (**4a**)\*

	X	Y	Z
C	0.19002300	0.80369100	0.01584800
O	-0.04672400	2.00143500	0.10360800
C	1.57503100	0.27214300	-0.02271200
C	1.86092000	-1.10366600	-0.06376400
C	2.63450600	1.19729800	-0.03546000
C	3.18327300	-1.54033600	-0.11918600
H	1.05823500	-1.83013800	-0.02490000
C	3.95219200	0.75741200	-0.09283900
H	2.40151800	2.25591600	-0.00397800
C	4.22827100	-0.61345700	-0.13615600
H	3.39855600	-2.60370600	-0.14699000
H	4.76440300	1.47734500	-0.10523600
C	-0.99516000	-0.19174800	-0.05482600
H	-0.84261700	-0.86076800	-0.91242100
O	-0.95553500	-0.93268000	1.15979800
H	-1.66925200	-1.58943500	1.10589600
N	-2.20631500	0.56707200	-0.24297200
H	-2.15476200	1.52753200	0.07809100
C	-3.46773800	0.01416700	-0.19611200
O	-4.46836000	0.68115000	0.05661400
N	-3.51770100	-1.35899700	-0.40451300
H	-4.46568500	-1.69495800	-0.51669300
H	-2.88224600	-1.75270600	-1.08872800
H	5.25700500	-0.95788000	-0.18156600

Optimized coordinates for Me-PGA-urea intermediate compound (**4b**)

	X	Y	Z
C	-0.28577900	0.87691200	0.01979800
O	-0.59094900	2.06143100	0.09181200



C	1.12172400	0.42101700	-0.00345600
C	1.48630800	-0.93562100	-0.03533500
C	2.13699900	1.39548000	-0.01480000
C	2.82919900	-1.30000300	-0.07982900
H	0.72695500	-1.70775200	-0.00135700
C	3.47274600	1.02300900	-0.06140800
H	1.85447400	2.44241400	0.00610900
C	3.84432400	-0.33269500	-0.09392200
H	3.09534200	-2.35281800	-0.10408500
H	4.24384200	1.78834800	-0.07626500
C	-1.41400200	-0.18359800	-0.04464500
H	-1.21732900	-0.85873400	-0.88823600
O	-1.34730400	-0.90013000	1.18364700
H	-2.02954200	-1.59008500	1.13741500
C	5.29804600	-0.73072500	-0.12051500
H	5.87890400	-0.07044800	-0.77136500
H	5.73645300	-0.66092700	0.88251000
H	5.42592000	-1.75960600	-0.46590700
N	-2.66291100	0.50400600	-0.25770900
H	-2.66597200	1.47190400	0.04485400
C	-3.89219800	-0.11646300	-0.21547200
O	-4.93187900	0.49829800	0.01125800

Optimized coordinates for NO<sub>2</sub>-PGA-urea intermediate compound (**4c**)

	X	Y	Z
C	-0.97435500	0.93454700	0.03012300
O	-1.30787000	2.10644800	0.09824300
C	0.46443500	0.53222200	0.02123400
C	0.87651700	-0.81035000	0.03451700
C	1.42547700	1.55669900	-0.02026700
C	2.23097600	-1.12756400	0.00340400
H	0.14753000	-1.60777800	0.09844900
C	2.77982200	1.25371500	-0.05373000
H	1.09303800	2.58794800	-0.02998600
C	3.15814600	-0.08897100	-0.04290600
H	2.56901200	-2.15520600	0.01661900
H	3.53363400	2.02907200	-0.08903900
C	-2.05709800	-0.16591300	-0.05192500
H	-1.83021700	-0.81180400	-0.91110800
O	-1.95007900	-0.90387000	1.16007100
H	-2.58637300	-1.63514600	1.09614900
N	-3.33428900	0.47008200	-0.24871600

H	-3.39220200	1.42374200	0.09010600
C	-4.53336900	-0.21315900	-0.22616800
O	-5.59863200	0.34352600	0.02583200
N	-4.43748600	-1.57922300	-0.45671200
H	-5.34377700	-2.01183300	-0.58164500
H	-3.75795800	-1.89542000	-1.13869100
N	4.59104100	-0.42069200	-0.07917000
O	5.39802900	0.50892500	-0.11684600
O	4.90969500	-1.61029300	-0.07034600