SUPPORTING INFORMATION

Adsorption Microcalorimetry of CO$_2$ in Confined Aminopolymers

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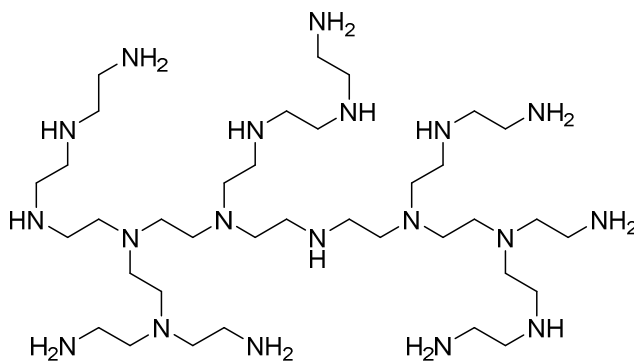
Figure S1: Graphical representation of low molecular weight PEI used in this study.
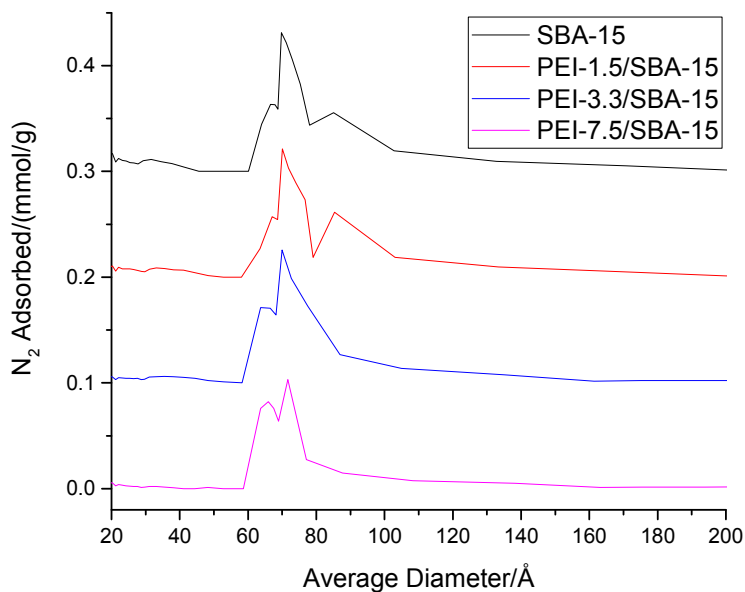

Figure S2: Pore size distribution showing primarily pore with diameters between 70 – 80 Å calculated using the BdB-FHH model.
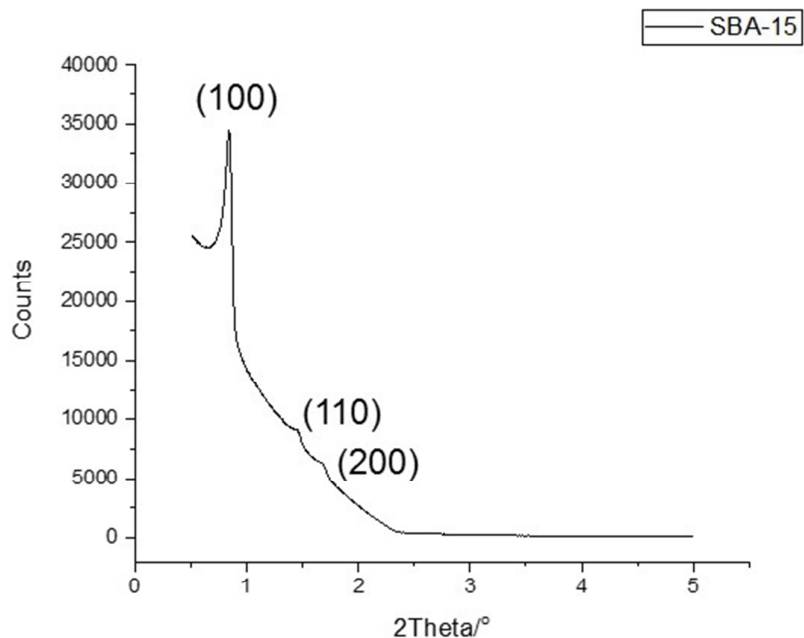
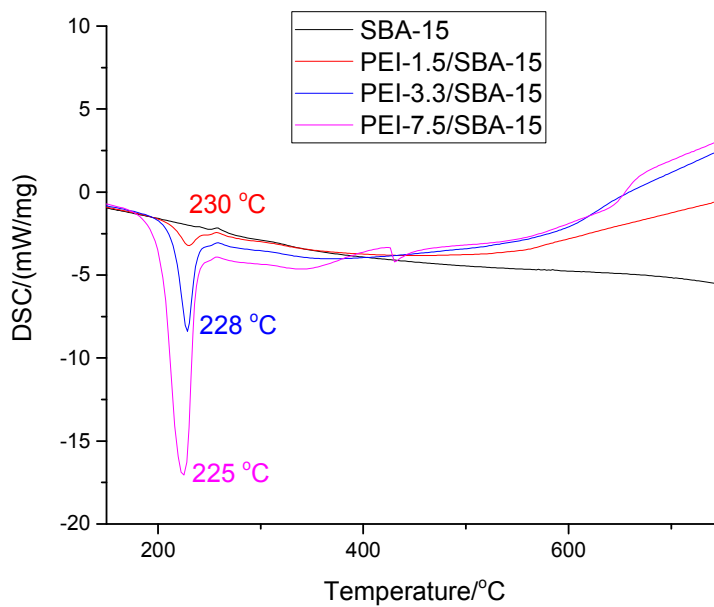**Figure S3:** Powder XRD pattern confirming the ordered structure of the bare SBA-15.

Figure S4: Differential scanning calorimetry curves of the thermogravimetric data collected. Labels correspond to the minima of the appropriate samples showing increased PEI leads to a lower minimum in the DSC curve.
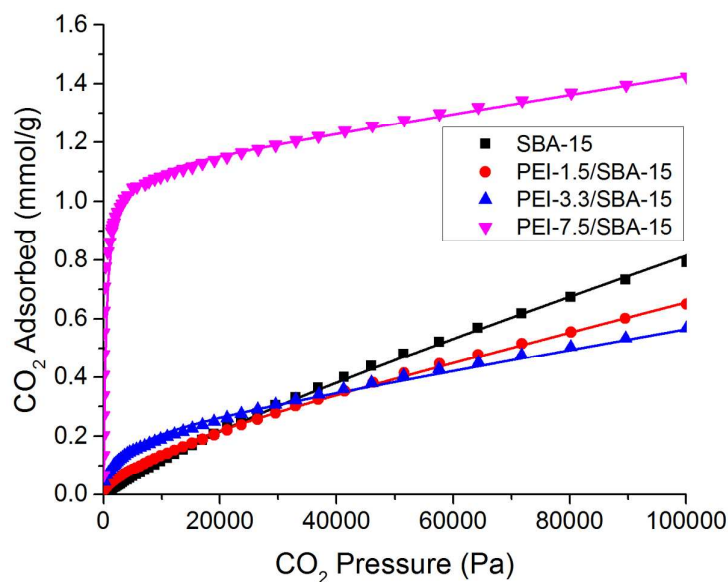
Figure S5: Dual-mode sorption fits and parameters fit to CO_2 adsorption isotherms on PEI/SBA-15. Adsorption was fit by a combination of Langmuir and Henry adsorption (coefficients reported in Table S1):

$$Q = S_{max} \frac{k_L P_{CO_2}}{1 + k_L P_{CO_2}} + k_H P_{CO_2}$$

The Langmuir adsorption coefficient (k_L) and total number of sites available for chemisorption (S_{max}) both increased as PEI loading was increased, indicating that higher loadings of PEI provided additional sites for chemisorption. However, the Henry's law constant (k_H) decreased with increased PEI loading, suggesting that physisorption was correlated with available pore volume and surface area (see Table S2).

Table S1: Langmuir and Henry coefficients for dual-mode fits shown in Figure S4.

	S_{max} (mmol g^{-1})	k_L (Pa^{-1})	k_H (mmol g^{-1} Pa^{-1})
SBA-15	0.18	0.42 × 10^{-4}	6.7 × 10^{-6}
PEI-1.5/SBA-15	0.17	1.3 × 10^{-4}	5.0 × 10^{-6}
PEI-3.3/SBA-15	0.22	3.5 × 10^{-4}	3.5 × 10^{-6}
PEI-7.5/SBA-15	1.1	22 × 10^{-4}	3.2 × 10^{-6}

Table S2: Henry coefficients normalized for surface area and pore volume.

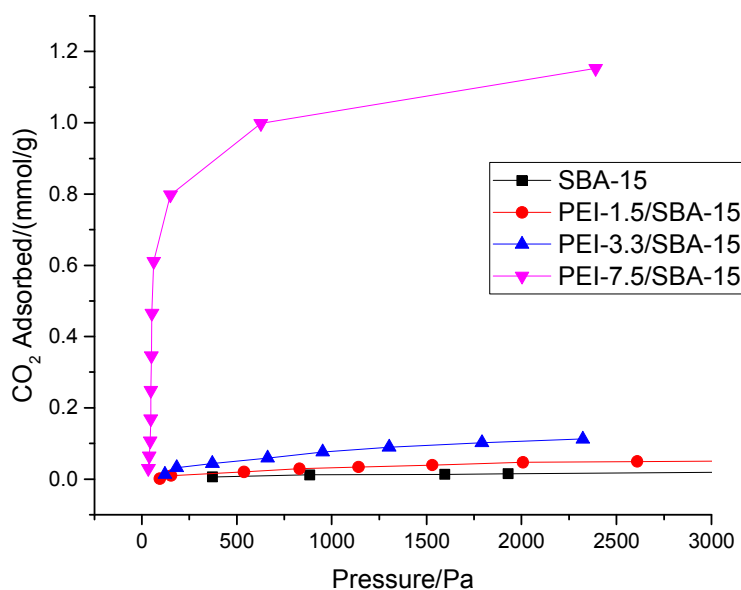|	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	k_H (mmol $g^{-1}\,Pa^{-1}$)	k_H/SA (mmol $Pa^{-1}\,m^{-2}$)	k_H/PV (mmol $Pa^{-1}\,cm^{-3}$)
SBA-15	789	0.93	6.7×10^{-6}	8.5×10^{-9}	7.2×10^{-6}
PEI-1.5/SBA-15	512	0.77	5.0×10^{-6}	9.8×10^{-9}	6.5×10^{-6}
PEI-3.3/SBA-15	361	0.65	3.5×10^{-6}	9.7×10^{-9}	5.4×10^{-6}
PEI-7.5/SBA-15	236	0.51	3.2×10^{-6}	14×10^{-9}	6.3×10^{-6}

Figure S6: CO_2 adsorbed as a function CO_2 pressure for the tandem volumetric uptake - microcalorimetry experiments.