Supporting Information

A family of polypropylene glycol-grafted polyethyleneimines reversibly absorb and release carbon dioxide to blow polyurethanes

Yuanzhu Long,‡ Fuhua Sun,‡ Chao Liu, Xingyi Xie*

College of Polymer Science and Engineering, Sichuan University, Chengdu, Sichuan 610065, China.

‡ Both authors equally contributed to the paper.

* Corresponding author: Tel: +86-28-85405129; Fax: +86-28-85405402; E-mail addresses: xiexingyi@263.net or xiexingyi@mail.scu.edu.cn (X. Xie)

1. Characterisation of PPG-PEIs and PPG-PEI-CO$_2$s

The ^{1}H nuclear magnetic resonance (NMR) spectrum of each PPG-PEI in 0.5 ml of $CDCl_3$ was recorded using a Varian 400 MHz NMR spectrometer (Varian Inc., USA). The N–CH_2 signals at 2.3–2.9 ppm from both bPEI backbones and PPG side chains (H_δ, Fig. 1, main text) overlapped with active proton signals of N–H from the backbones and O–H from the side chains. These active proton signals were removed by adding about 100 µl of CD_3OD in the sample solution. Thus the peak area of pure N–CH_2 signals ($A_{N–CH2}$) relative to that of H_j signal (A_j) at 1.53 ppm from PPG chains (Fig. 1, main text) was used to calculate the grafting rate (y), i.e., the percentage of N atoms to which PPG chains were attached.

The molecular weights before and after PPG grafting were measured by gel permeation chromatography (GPC) on a Waters 1515-2414 instrument (Waters Associates, USA). Molecular weights are relative to monodisperse poly(methyl methacrylate) standards. The mobile phase was 1 wt% LiBr in *N*, *N*-dimethylformamide. The sample concentration was about 3 mg/ml, and the flow rate was 1.00 ml/min at 40°C.

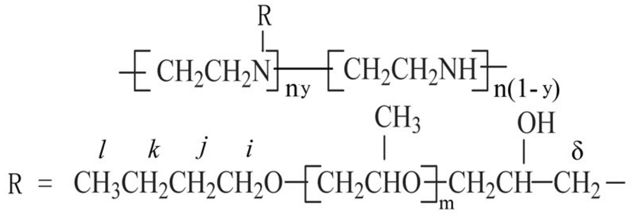
The change in chemical structure before and after CO_2 adduction was characterised by Fourier transform infrared (FTIR) spectroscopy, using a Nicolet 560 IR spectrometer (Nicolet Instrument Corp., USA). Spectra from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} were recorded in a transmission mode. The CO_2 content of each PPG-PEI-CO_2 was measured by thermogravimetry (TG) analysis on a TG 209F1 apparatus (Netzsch instruments, Germany) operated from 30 to 300 °C at 10 °C/min under a nitrogen flow of 100 ml/min. The same operation parameters were used to measure the enthalpy change (ΔH) due to the CO_2 release by differential scanning calorimetry (DSC) on a PE DSC-2C instrument (Perkin–Elmer, USA).

2. Characterisation of PU foams

Foams were cut into cuboids of about 30 mm × 30 mm × 20 mm in size, whose precise weights (±0.1 mg) and dimensions (±0.1 mm) were measured to give the densities (averaged with five samples i.e. n=5). To measure the mechanical properties, the same sized samples (n=5) were compressed at the foam rise direction on an Instron 5507 Universal Testing Machine (Instron Corp., USA) at a strain rate of 15% per min (i.e. 3 mm/min) according to ASTM D1621. Selective samples were also tested perpendicularly to the foam rise direction, revealing their anisotropic mechanical property. Meanwhile, their anisotropic cell morphology was examined under a JSM-9600 scanning electron microscope (Jeol, Japan).

The thermal conductivity was measured on a Hot Disk TPS 2500-OT thermal analyser (Hot Disk AB, Sweden) based on the transient plane source (TPS) method (n=5). In detail, a disk-shaped TPS sensor with a diameter of 3.189 mm was sandwiched by two sample pieces with diameters above 30 mm and thicknesses above 5 mm. The sensor generated a pulse heat source of 0.005 W for 20 s, and simultaneously measured the temperature change due to the loss of heat through the test sample, which was used to calculate the thermal conductivity assuming that the test sample was infinite in size. The dimensional stability was measured on cubic samples (about 27 cm^3, n=5) after annealing at 100 °C and −20 °C for 96 h, respectively, according to ISO 2796. The water uptake was determined by the weight change before and after immersion into distilled water at 23±2 °C for 96 h (ISO 2896), using cubic samples with a volume of about 125 cm^3. The water vapour permeability (n=5) was determined by standard method (GB/T 2411) as well. A cylinder sample with a diameter of 60 mm and a height of 30 mm was inserted into a slightly larger impermeable cup with 50 g of $CaCl_2$ in it as a water vapour absorbent. The gap between the sample and cup was sealed by paraffin. The sample in the cup was put in a dessicator (internal diameter of 284 mm) containing 1000 ml of saturated KCl solution at 23 °C. This condition corresponds to a relative humidity of 85% and a vapour pressure of 2.39 kPa in the desiccator. The steady vapour mass across the test sample per day was used to calculate the water vapour permeability.

3. Calculation grafting rate and PPG content in 1:x-PPG-PEIs



$$-\!\!\left[CH_2CH_2\overset{R}{\overset{|}{N}}\right]_{ny}\!\!-\!\!\left[CH_2CH_2NH\right]_{n(1-y)}$$

$$R = \overset{l}{C}H_3\overset{k}{C}H_2\overset{j}{C}H_2\overset{i}{C}H_2O\!-\!\left[CH_2\overset{CH_3}{\overset{|}{C}}HO\right]_m\!\!CH_2\overset{OH}{\overset{|}{C}}H\!-\!\overset{\delta}{C}H_2-$$

Fig. S1. Representative structure of PPG-PEI, ignoring the branching structure.

The proton signals at 2–3 ppm of PPG-PEIs are from $-CH_2-$ in the PEI backbone and from H_δ in the PPG side chain. Signals from active protons (–OH, and N–H , Fig. 1, main text). After addition of CD_3OD, the mixture signal of all active protons was shifted downfield (indicated by #, Fig. 1C, main text). Let the grafting rate to be y (Fig. S1), the peak area at 2–3 ppm ($S_{N\text{-}CH2}$, including the contribution from H_δ) relative to the H_j area (S_j) can be calculated as

$$S_{N\text{-}CH2} : S_j = [4ny+4n(1-y)+2ny] : 2ny = (2+y) : y.$$

From Fig. 1C (main text), S_j is normalised to 2; thus $S_{N\text{-}CH2} : 2 = (2+y) : y$, and one obtain

$$y = 2/(0.5\ S_{N\text{-}CH2}-1).$$

For sample **1:11-PPG-PEI**, $S_{N\text{-}CH2}$ = 45.30 (Fig. 1C, main text), thus $\boldsymbol{y = 0.0924 = 9.24\%}$. For other samples, y can be calculated the same way.

Since the molar mass of PPG chain is 396 and the molar mass of PEI repeating unit is 43, the average molecular weight of the repeating unit of PPG-PEI should be $(396+43)y+43(1-y)$, based on the chemical structure shown in Fig. S1. Therefore the weight content of PPG in PPG-PEI should be:

$$396y/[(396+43)y+43(1-y)] = 396y/(396y+43).$$

For sample **1:11-PPG-PEI**, y=9.24%, thus **PPG% = 0.460 = 46.0%**. For other samples, PPG% can be calculated the same way.

4. Calculation the theoretical CO_2 content, real PPG content and normalised ΔH in 1:x- PPG-PEI-CO_2s

Without water, two amine groups capture one CO_2 molecule, forming a carbamate anion and an alkylammonium. In other words, two repeating PEI units (–CH_2CH_2NH–, molar mass 43 Da) can react with one CO_2 molecule (molar mass 44 Da). In this case, t**heoretical CO_2 content of PEI-CO_2** should be:

$$44/(2\times43+44) = 0.338 = 33.8\%.$$

For PPG-PEIs (the grafting rate is y and the molecular weight of PPG chain is 396), the average molecular weight of the repeating unit is $(396+43)y+43(1-y)$, or $396y+43$. Again two repeating units react with one CO_2 molecule, thus giving a **theoretical CO_2 content** of PPG-PEI-CO_2 as

$$44/[2(396y+43)+44]=22/(396y+65).$$

For 1:x-PPG-PEI-CO_2, y=9.24%; thus theoretical CO_2% should be 21.7%. The theoretical CO_2 content of other 1:x-PPG-PEI-CO_2 can be calculated similarly.

The real CO_2 content was measured by TG. Since CO_2 has been incorporated in 1:x-PPG-PEI-CO_2, its PPG content should be lowered relative to that of 1:x-PPG-PEI. The **real PPG content in 1:x-PPG-PEI-CO_2** can be calculated as:

$$\text{PPG\% in 1:x-PPG-PEI-CO}_2 = (1-\text{measured CO}_2\ \%)\times(\text{PPG\% in 1:x-PPG-PEI}).$$

For 1:11-PPG-PEI-CO_2, measured CO_2 % was 19.4% and PPG% in 1:11-PPG-PEI was 46.0% (Table 2, main text); thus the real PPG content should be

$$(1-19.4\%)\times46.0\% = 37.1\%.$$

Since PPG content cannot absorb CO_2, the normalised ΔH is calculated by excluding the mass of PPG side chains in each 1:x-PPG-PEI-CO_2 and just based on the mass of the PEI-CO_2 backbones. Thus, the **normalised ΔH** is calculated as

$$\text{Normalised } \Delta H = (\text{Measured } \Delta H)/(1-\text{PPG\% in 1:x-PPG-PEI-CO}_2).$$

For 1:11-PPG-PEI-CO_2, the measured ΔH was 185 (J/g) (Table 2, main text) and real PPG% was 37.1%; thus its normalised ΔH was 184/(1-37.1%) = 294 (J/g).

The real PPG content and normalised ΔH of other 1:x-PPG-PEI-CO_2 can be calculated similarly.