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## Effect of the dianhydride/branched diamine ratio on the architecture and room temperature healing behaviour of polyetherimides

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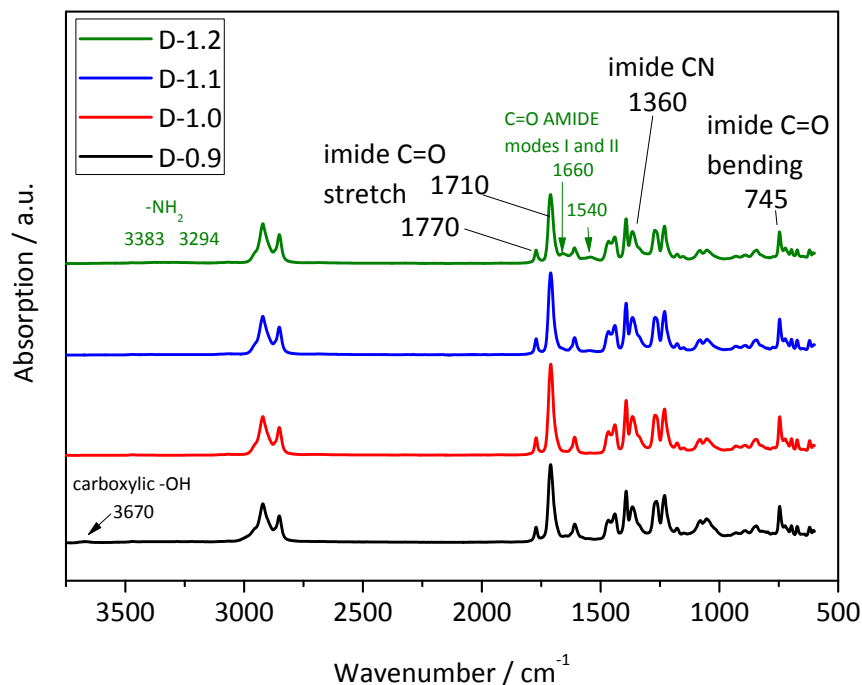
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## ATR/FTIR spectra



**Figure S1.** Full IR spectra of the four PEIs as a function of the offset from the theoretical stoichiometric ratio.

## Yield

Percent yield of the polymer was calculated according to equation:

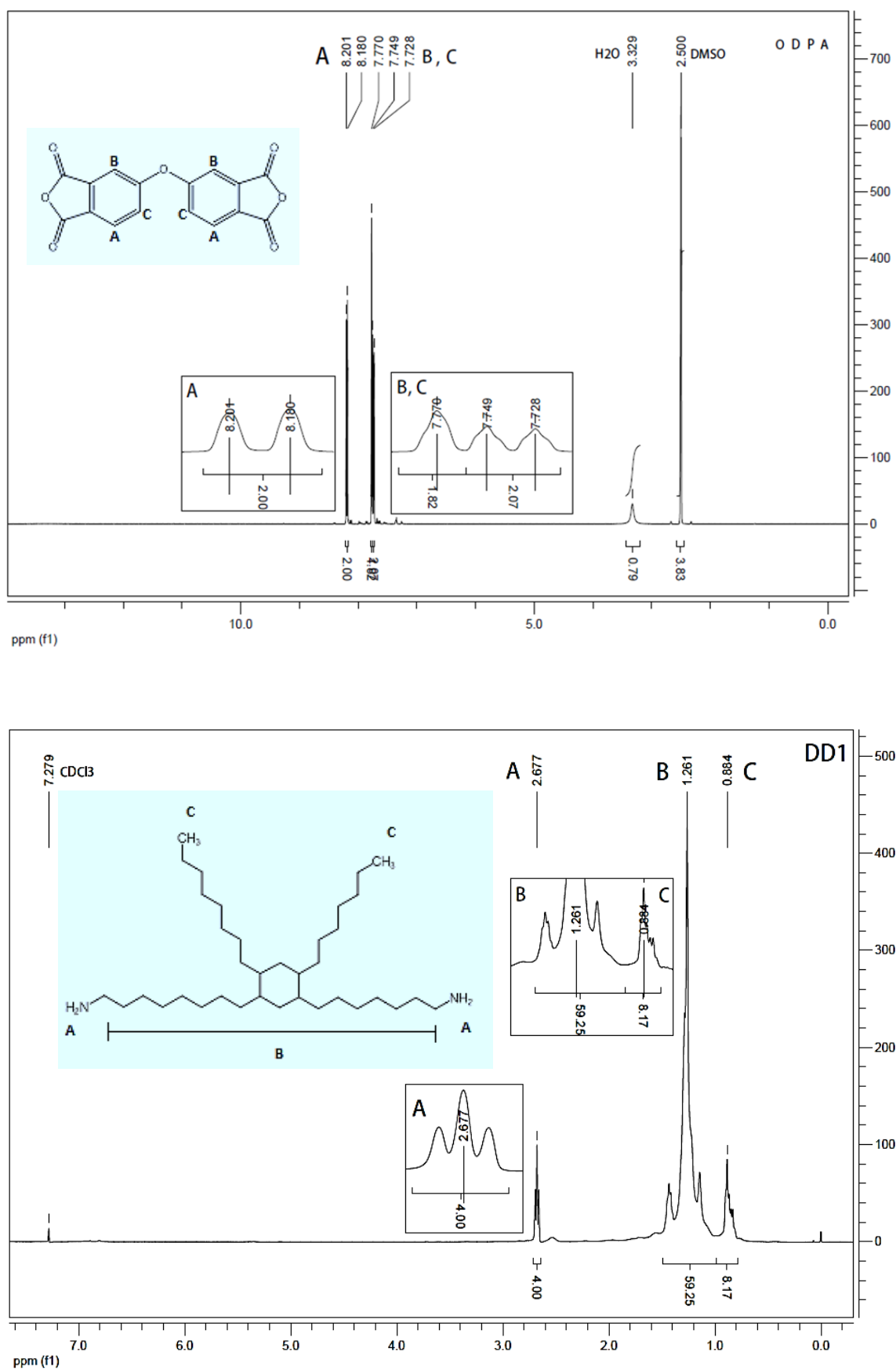
$$\text{Percent yield (\%)} = 100 \left( \frac{\text{Actual mass of the product}}{\text{Predicted mass of the product}} \right)$$

where predicted mass of the product was calculated according to the stoichiometric balance, assuming that 1 mol of ODPA and 1 mol of DD1 give 1 mol of PEI and 2 mol of water (4.25 wt% of water):

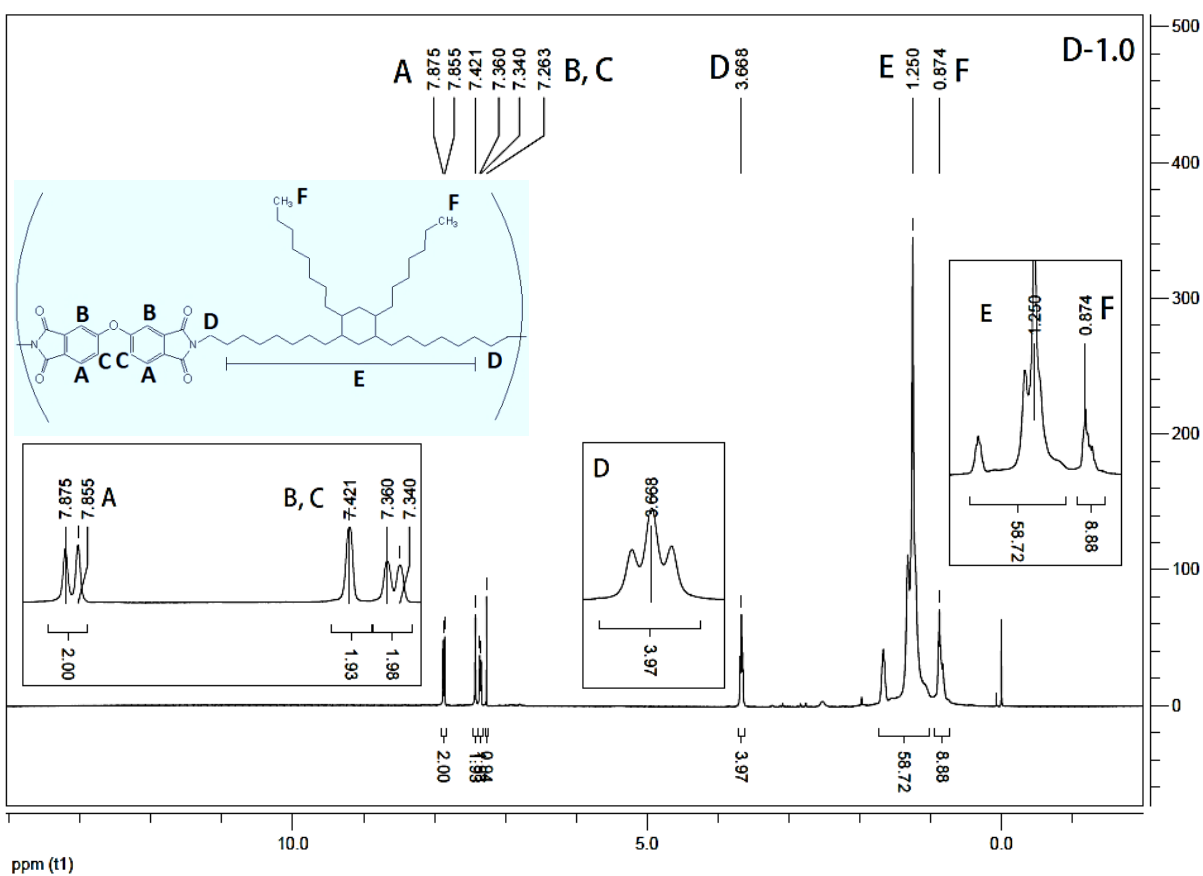
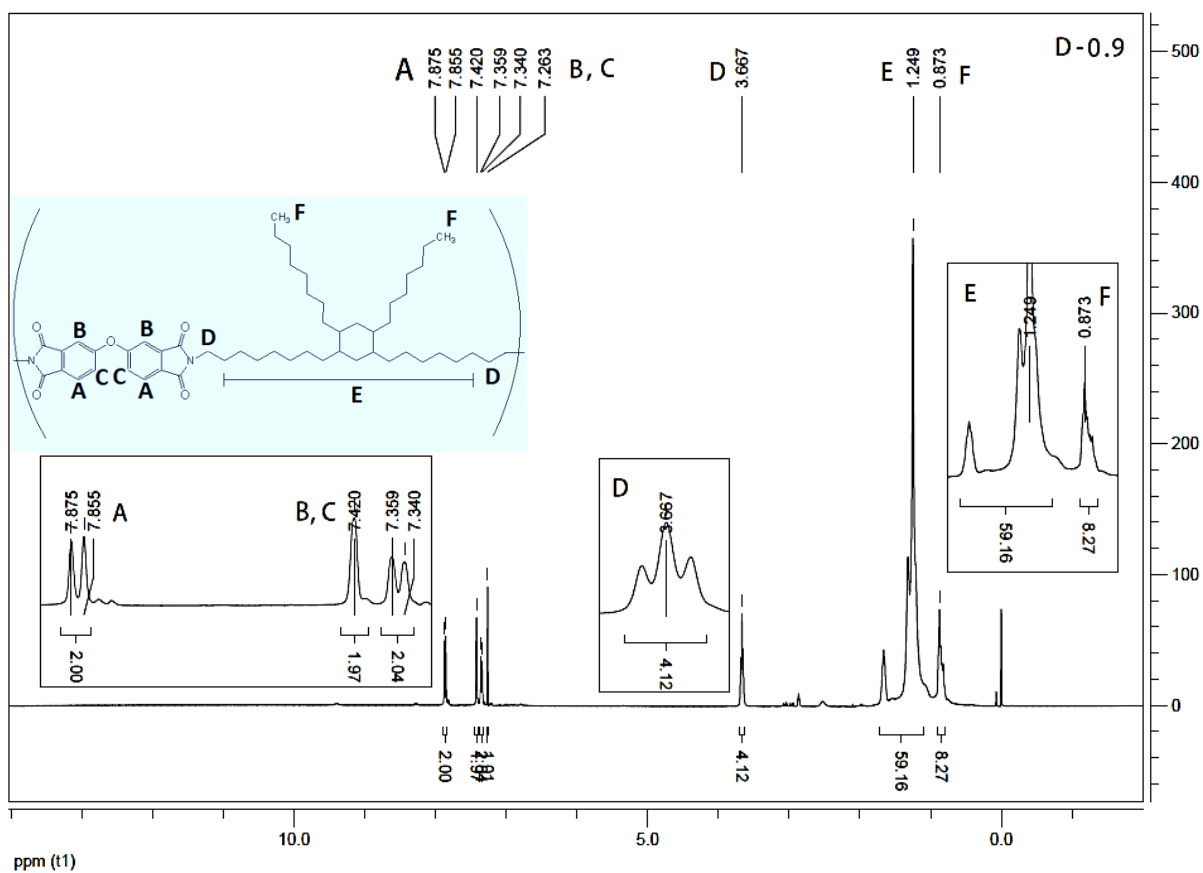
$$\text{Predicted mass of the product/g} = m(\text{ODPA}) + m(\text{DD1}) - m(\text{H}_2\text{O})$$

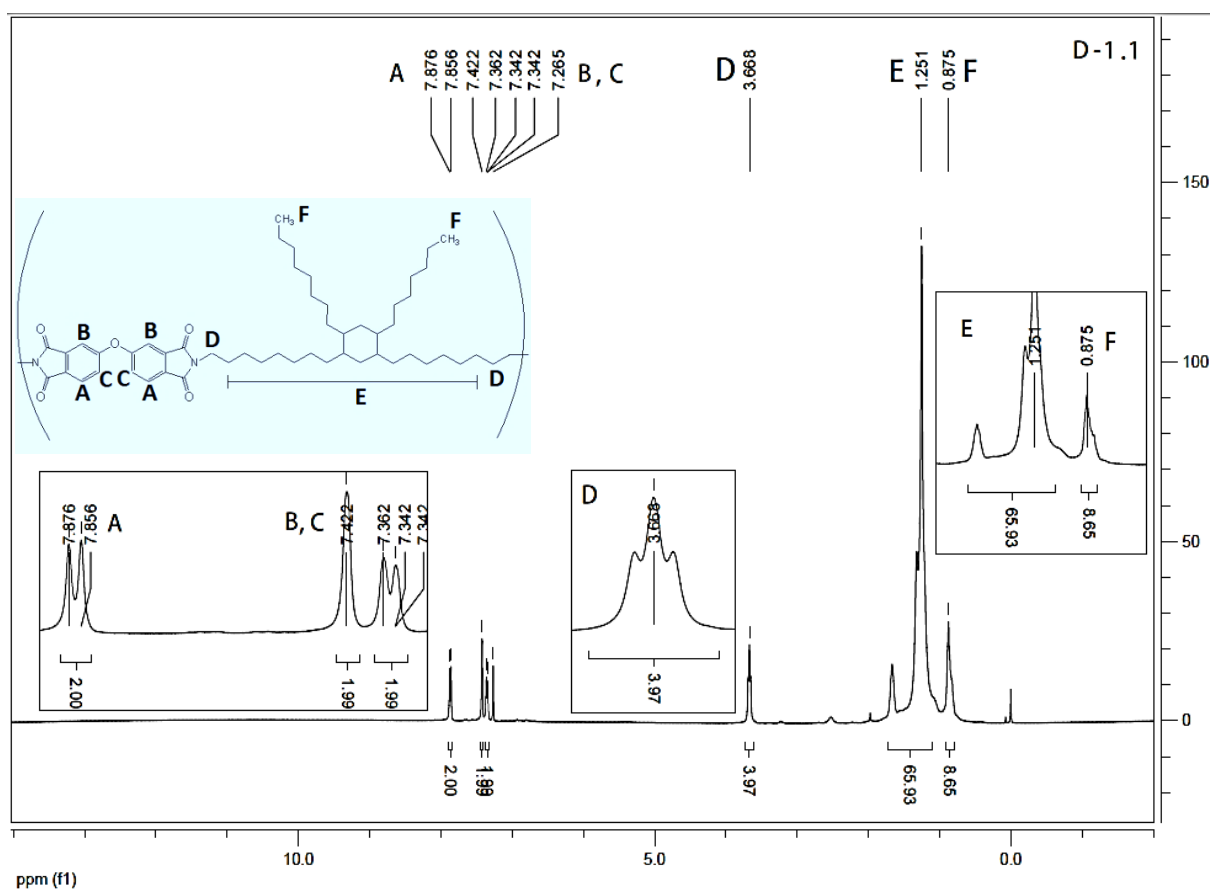
<sup>1</sup>H NMR

Solution state <sup>1</sup>H NMR spectra were collected using the Agilent-400 MR DD2 at 25°C at 400 MHz. The solutions of polymers and DD1 were prepared in CDCl<sub>3</sub>, and ODPA was measured in deuterated DMSO. Spectra were referenced to the solvent residual peak for DMSO and to TMS for CDCl<sub>3</sub>, respectively. Spectra were not normalized. PAA's were not tested due to the insolubility in the available NMR solvents. Furthermore, D-1.2 was insoluble as well, but due to the partial crosslinked nature.



**Figure S2.** <sup>1</sup>H NMR spectra of the monomers: ODPA in DMSO and DD1 in CDCl<sub>3</sub> and their assignment to the molecular structure.

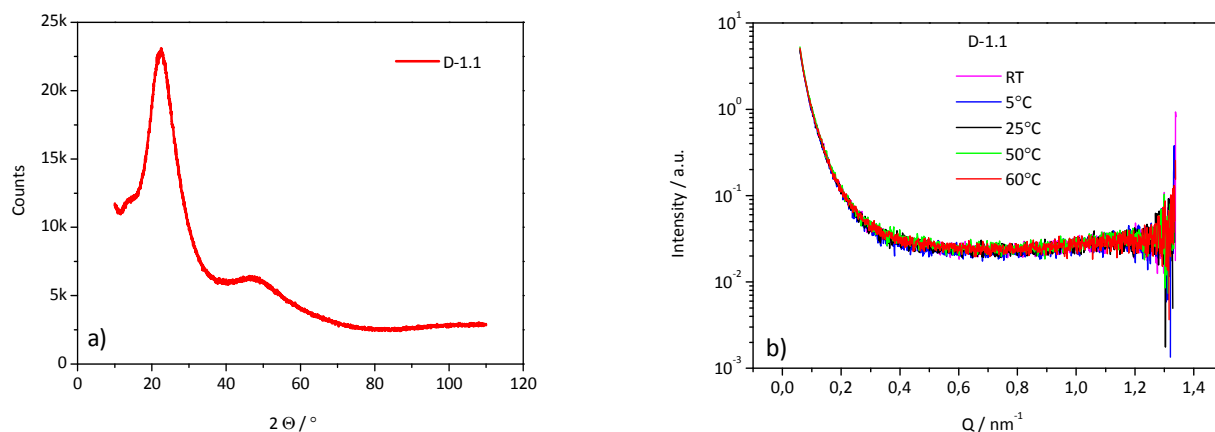




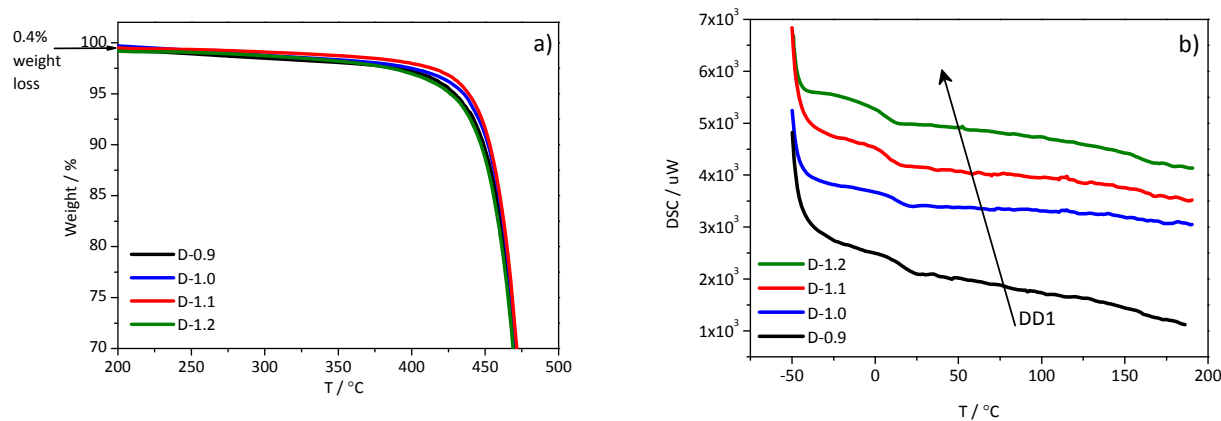
**Figure S3.**  $^1\text{H}$  NMR spectra of the three polymers in  $\text{CDCl}_3$  and their assignments to the polymer structure.

*X-ray diffraction measurements*

Wide Angle X-ray diffraction (WAXS) data were collected on a Bruker D8 Advance diffractometer with Co K $\alpha$  radiation at the room temperature. Temperature controlled Small Angle X-ray Scattering (SAXS) was conducted using an AXS D8 Discover instrument from Bruker AG. SAXS scans were collected at five different temperatures: preliminary scan at room temperature followed by heating to 60°C. In a cooling ramp at the 0.5°C/min rate, the scans were further collected at 50, 25 and 5°C.



**Figure S4.** a) WAXS and b) temperature controlled SAXS diffractogram of the D-1.1 polymer with representative patterns of all polymers in this work.

*Thermal analysis*

**Figure S5.** a) TGA curves showing weight loss of SH-PEIs in the high temperature range; b) DSC curves from the second heating cycle showing glass transitions.

## Swelling tests

The crosslinking density was determined by solvent-swelling measurements for 72h and calculated according to the Flory–Rehner equation (eq. S1).

$$\ln(1 - \Phi_r) + \Phi_r + \chi\Phi_r^2 = -\frac{\rho_r}{M_c} V_s \left( \Phi_r^{1/3} - \frac{2\Phi_r}{f} \right) \quad \text{eq-S1}$$

where:

$\Phi_r$ = volume fraction of swollen polymer

$\chi$ = polymer-solvent interaction parameter. In this work a value of 0.3 (cis-polybutadiene raw elastomer-toluene<sup>1</sup>) was taken as reference due to the lack of existing values for this new class of polymers.

$\rho_r$ = polymer density

$M_c$ = molecular weight of polymer between two crosslinks

$V_s$ = molar volume of solvent (106.8 mL/mol for toluene<sup>1</sup>)

$f$ = functional cross-links (3)

The volume fraction ( $\Phi_r$ ) of swollen polymer was calculated according to:

$$\Phi_r = \frac{w_i/\rho_r}{w_i/\rho_r + (w_s - w_d)/\rho_s} \quad \text{eq-S2}$$

where:

$w_i$ = initial weight of the sample

$w_s$ = swollen weight of the sample after 72h of immersion

$w_d$ = weight of the sample dried at 60°C in vacuum for 72h

$\rho_s$ = solvent density (0.87 g/cm<sup>3</sup> for toluene)

The crosslink density ( $\nu$ ) is then calculated as:

$$\nu = \frac{1}{2M_c} \quad \text{eq-S3}$$

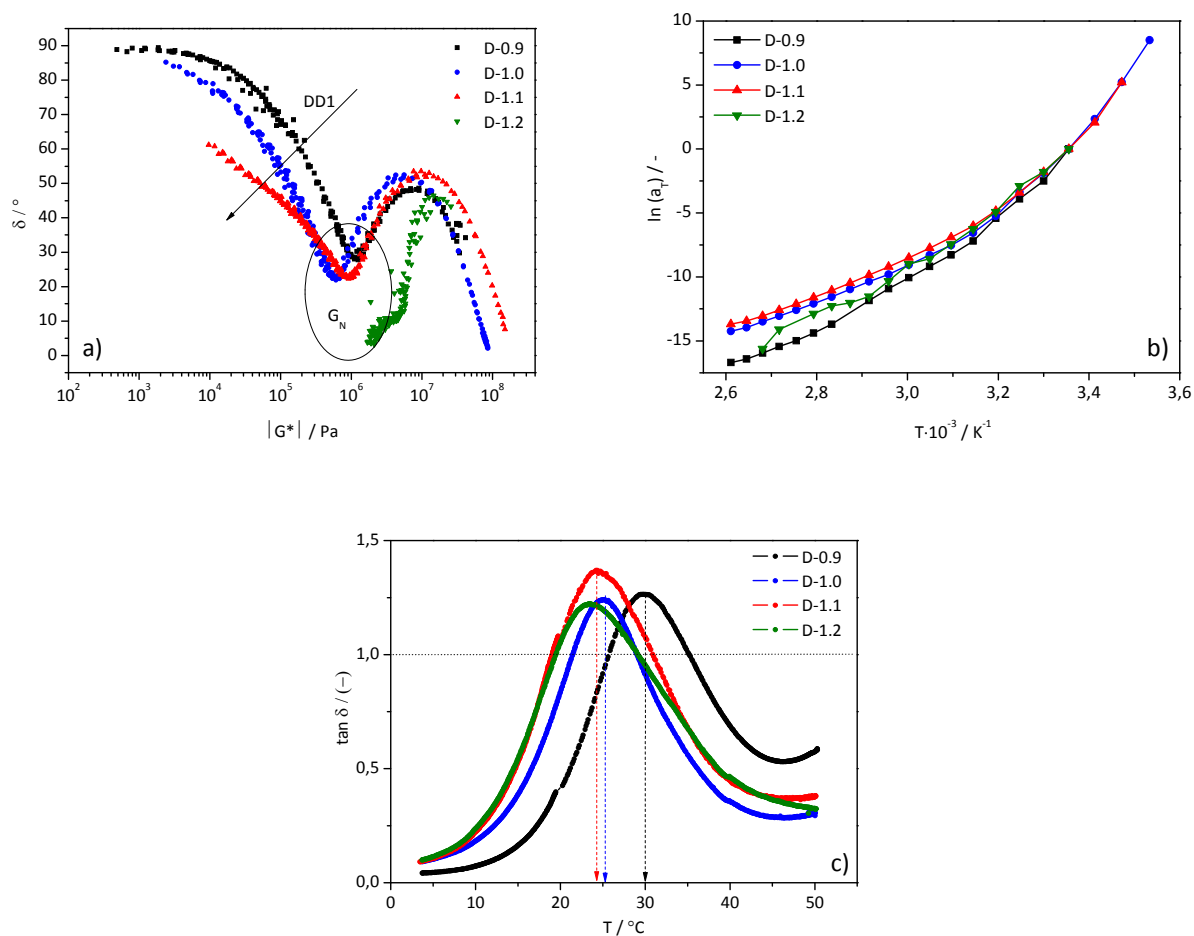
**Table S-I.** Results of the swelling tests.

Polymer	Q, Swelling ratio after 72h (%)	Soluble fraction (%)	$M_c$ (g/mol)	$\nu$ , Crosslinking density (mol/cm <sup>3</sup> )
D-0.9	/	100	/	/
D-1.0	/	100	/	/
D-1.1	2680 ± 186	60 ± 8	2609 ± 62	1.92 ± 0.05
D-1.2	441 ± 8	13 ± 0,3	929 ± 14	5.39 ± 0.08

<sup>1</sup> Hansen, C.M., *Hansen solubility parameters: a user's handbook*, CRC Press LLC: USA, 2000.



## Rheological parameters

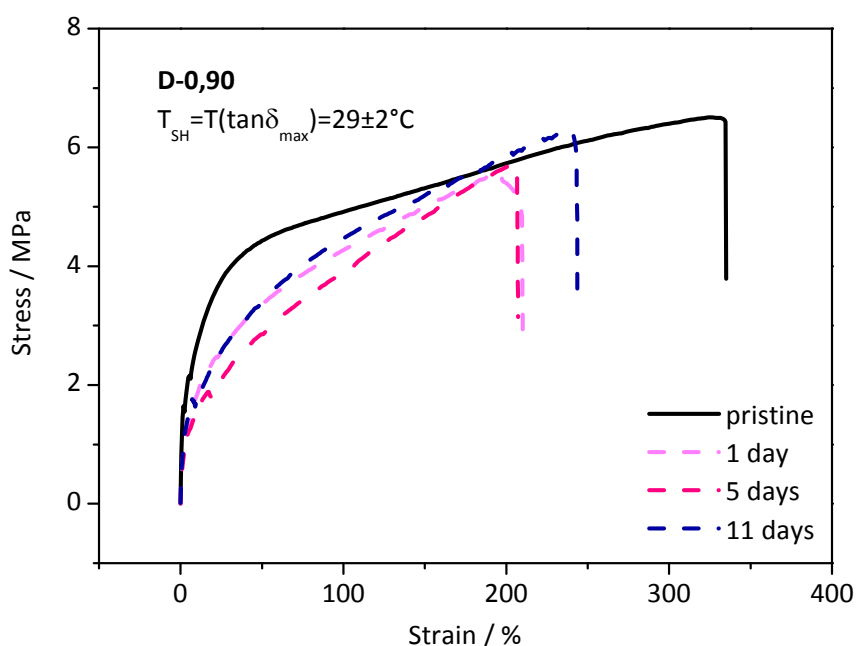


**Figure S6:** **a)** van Gurp-Palmen plot; **b)** horizontal shift factors ( $a_T$ ) from the TTS mastercurves,  $T_{\text{ref}}=25^\circ\text{C}$ ; **c)** loss tangent ( $\tan\delta$ ) as a function of temperature ( $T$ ) from the temperature sweep experiments. Dotted lines are guidance for a reader's eye showing the elastic/viscous dominance region determined by  $\tan\delta=1$ . Arrows point the values of  $T$  ( $\tan\delta_{\text{max}}$ ) for the non-crosslinked polymers that heal at  $25^\circ\text{C}$  (red and blue) and does not heal at  $25^\circ\text{C}$  (black).

## Tensile test

**Table S-II:** Tensile properties of the virgin polymers.

Polymer	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	E (MPa)
D-0.9	5.9±0.2	330±20	110
D-1.0	5.7±0.1	440±20	54
D-1.1	4.4±0.2	560±10	33
D-1.2	2.0±0.4	360±50	6.5

Healing tests in tension at elevated  $T$ 

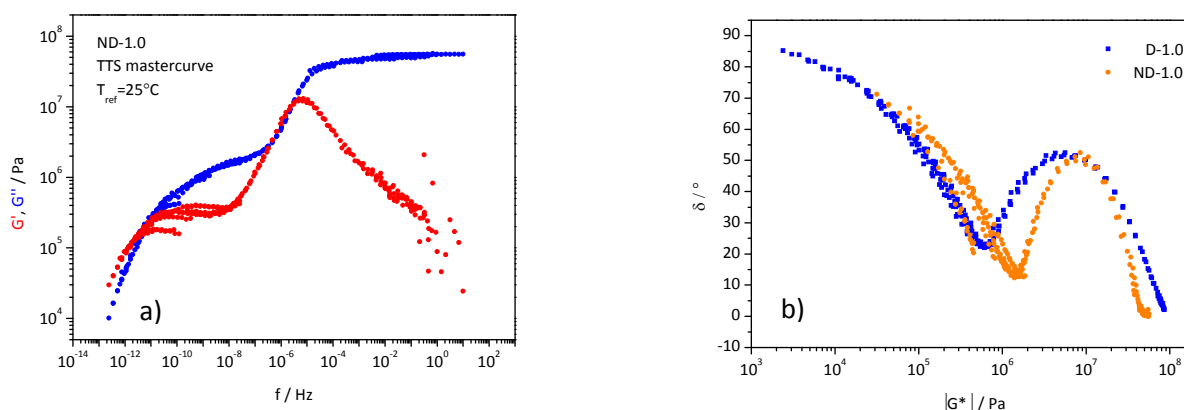
**Figure S7.** Stress-strain curves showing the **D-0.9** healing behaviour at the higher healing  $T$ , that corresponds to  $T$  of the maximum of  $\tan\delta$  determined from the rheological  $T$ -sweep test, as function of the healing time. Full lines represent pristine (—) and dashed lines represent healed (---) samples after given healing time.

Reference: non-branched PEI

**Table S-III.** Effect of branching on the generic polymer properties. Where ND-1.0 contains a linear non-branched C12 aliphatic diamine and D-1.0 a branched C18 aliphatic diamine (DD1) in (theoretical) stoichiometric ratio.

polymer	Mw (g/mol)	Mn (g/mol)	PDI	DSC-T <sub>g</sub> (°C)	TGA-T (2% weight loss) (°C)	Density (g/cm <sup>3</sup> )
ND-1.0	*	*	*	69	435	1.20
D-1.0	32k	16k	2,0	13	380	1.05

\* GPC data not available since ND-1.0 is not soluble in the GPC solvents available.



**Figure S8.** a) TTS mastercurve of ND-1.0 and b) van Gorp-Palmen plots of the referent non-branched PEI (orange) ND-1.0 in comparison to its branched counterpart D-1.0 (blue). T<sub>ref</sub>=25°C

**Table S-IV.** Characteristic parameters obtained from rheology for the non-branched PEI (ND-1.0) as compared to its branched counterpart (D-1.0).

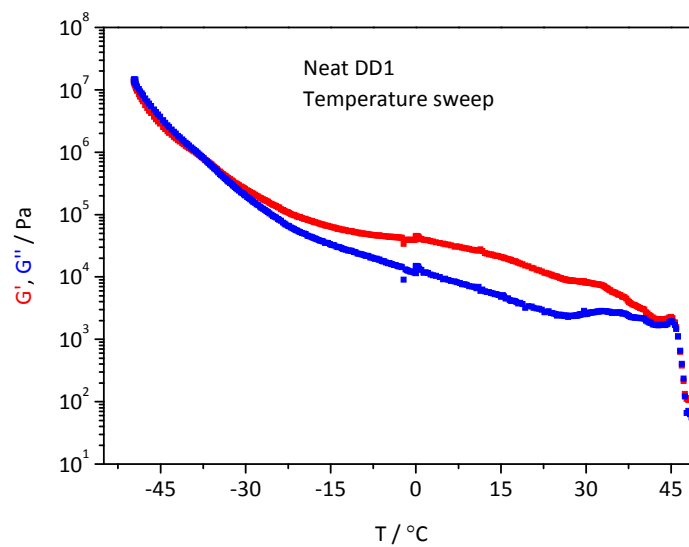
Polymer	f <sub>s</sub> (Hz)	f <sub>d</sub> (Hz)	f <sub>g</sub> (Hz)	τ <sub>s</sub> (s)	τ <sub>d</sub> (s)	τ <sub>g</sub> (s)	G' slope at f < f <sub>s</sub>	G'' slope at f < f <sub>s</sub>	G <sub>N</sub> * (Pa)	M <sub>e</sub> ** (g/mol)
ND-1.0	7.5 · 10 <sup>-12</sup>	3.8 · 10 <sup>-7</sup>	2.8 · 10 <sup>-6</sup>	13.3 · 10 <sup>11</sup>	2.6 · 10 <sup>6</sup>	3.6 · 10 <sup>5</sup>	1.06	0.49	1.39 · 10 <sup>6</sup>	2140
D-1.0	2.0 · 10 <sup>-5</sup>	0.035	1.5	5.0 · 10 <sup>4</sup>	28.0	0.7	1.25	0.83	6.09 · 10 <sup>5</sup>	4270

\* G<sub>N</sub> calculated from the Van Gorp-Palmen plot, δ(|G\*|)\*.<sup>2,3</sup>

\*\* M<sub>e</sub> were calculated using experimentally determined densities (Table S-III) according to M<sub>e</sub> = ρRT / G<sub>N</sub> (Doi and Edwards) equation.

<sup>2</sup> Ahmadi, M.; Hawke, L. G. D.; Goldansaz, H.; van Ruymbeke, E. *Macromolecules* **2015**, *48*, 7300.

<sup>3</sup> Trinkle, S.; Friedrich, C. *Rheol. Acta* **2001**, *40*, 322.

*Neat branched dimer diamine (DD1); T-sweep*

**Figure S9.** Temperature dependant rheological behaviour of the neat DD1.