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Susa, Arijana; Bose, Ranjita; Grande, Antonio; van der Zwaag, Sybrand; Garcia Espallargas, Santiago

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SUPPORTING INFORMATION

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

A. Susa, R. K. Bose, A. M. Grande, S. van der Zwaag, S. J. Garcia*

Novel Aerospace Materials group, Faculty of Aerospace Engineering,

Delft University of Technology, Kluyverweg 1, 2629 HS, Delft, The Netherlands

e-mail: s.j.garciaespallargas@tudelft.nl

List of figures and tables:

ATR/FTIR spectra

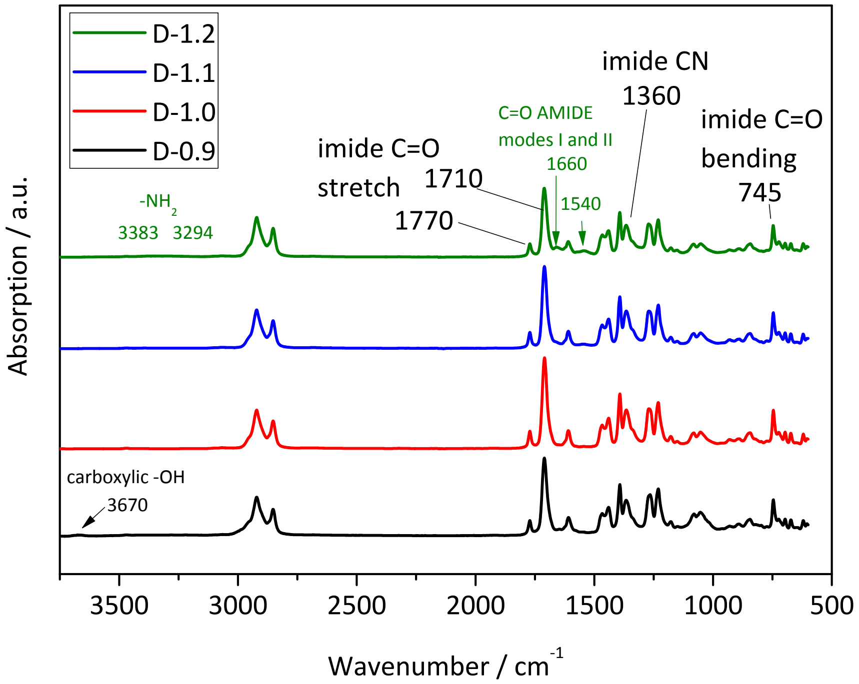


Figure S1. Full IR spectra of the four PEIs as a function of the offset from the theoretical stoichiometric ratio.

Yield

Percent yield of the polymer was calculated according to equation:

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

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):

$$Predicted\ mass\ of\ the\ product/g = m(ODPA)+m(DD1)-m(H_20)$$

^{1}H NMR

Solution state ^{1}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 $CDCl_3$, and ODPA was measured in deuterated DMSO. Spectra were referenced to the solvent residual peak for DMSO and to TMS for $CDCl_3$, 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.

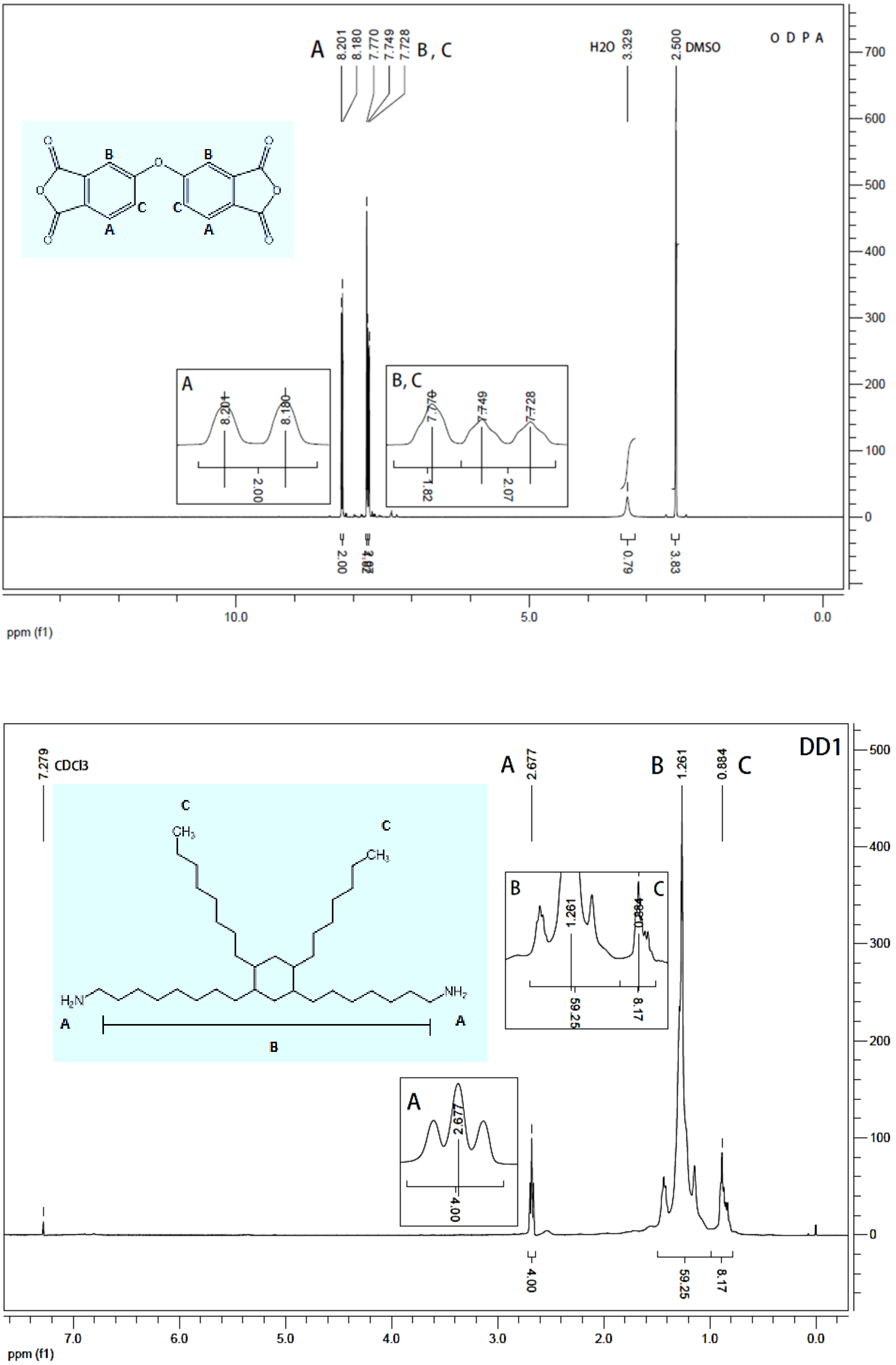
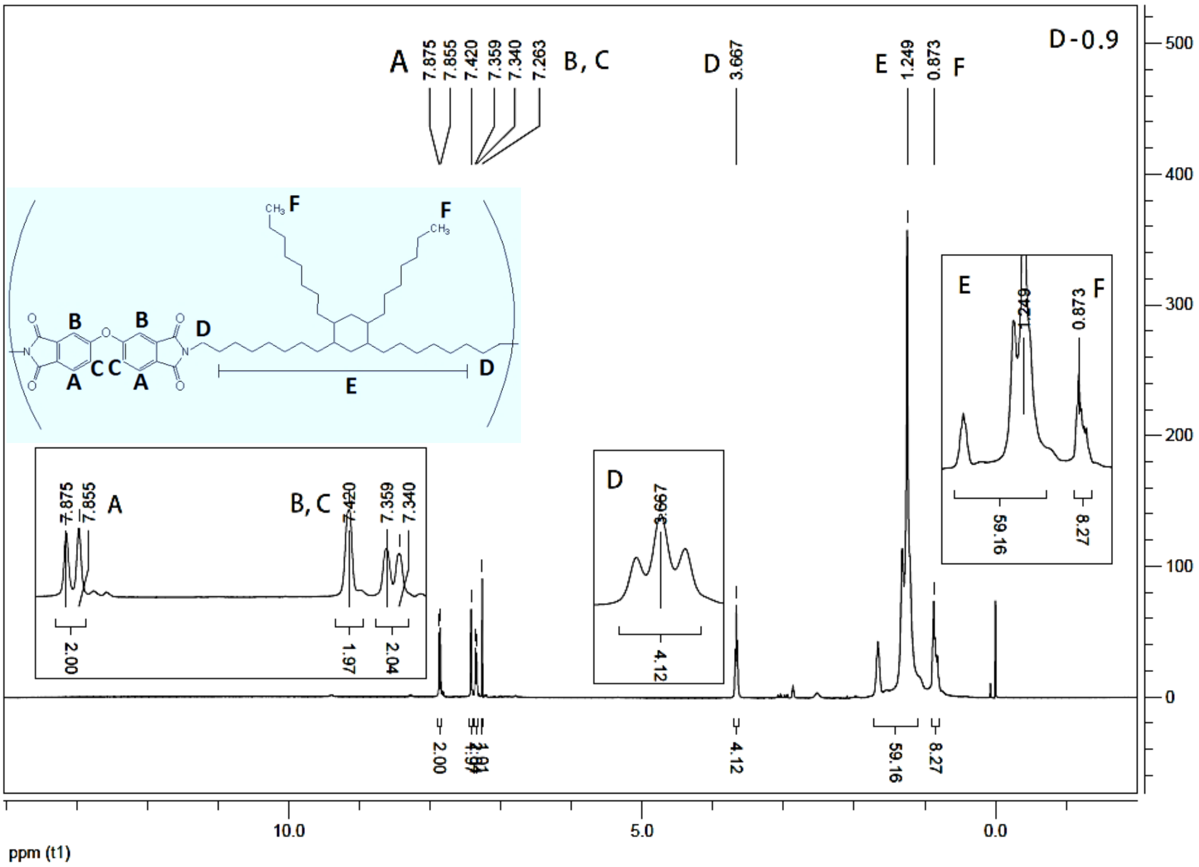
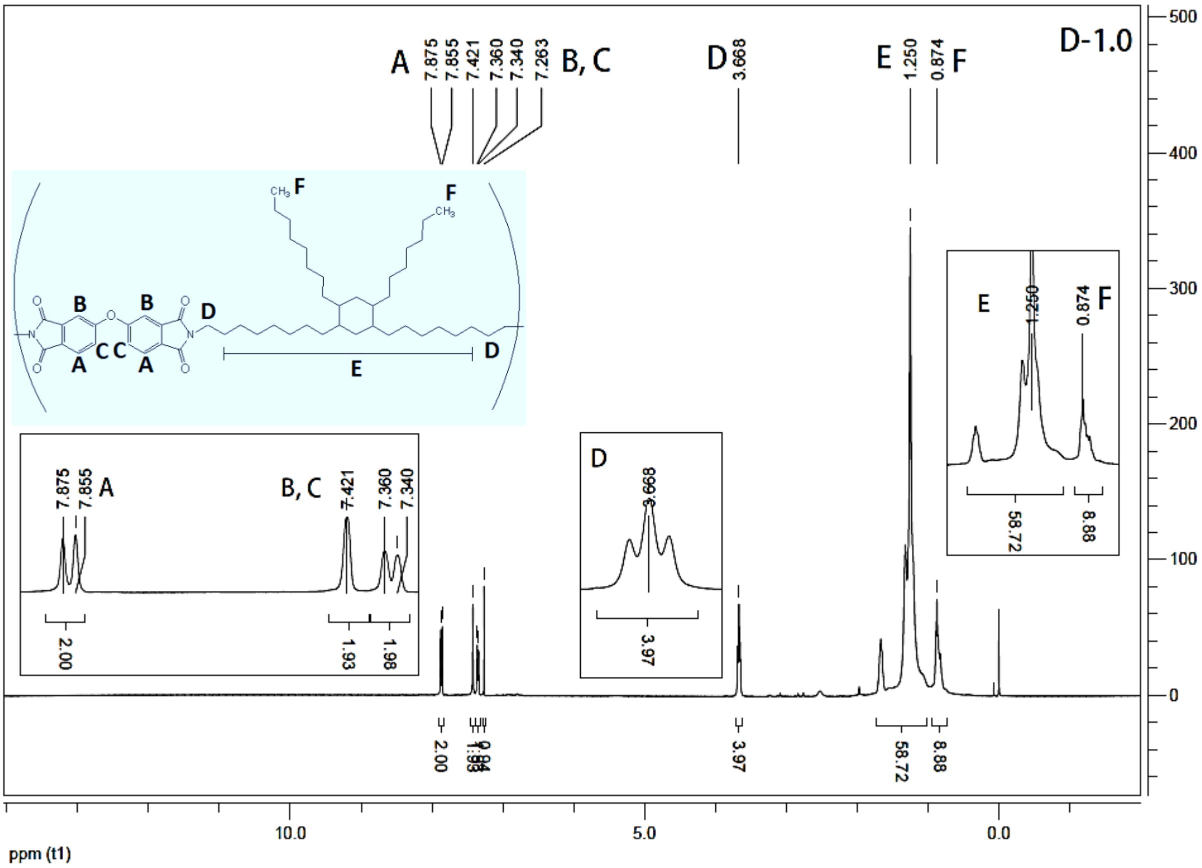


Figure S2. ^1H NMR spectra of the monomers: ODPA in DMSO and DD1 in $CDCl_3$ and their assignment to the molecular structure.


D-0.9
A
7.875
7.855
7.420
7.359
7.340
7.263
B, C
D
3.667
E
1.249
0.873
F
CH3
B
C
D
E
2.00
1.97
2.04
4.12
59.16
8.27
500
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)


D-1.0
A
7.875
7.855
7.421
7.360
7.340
7.263
B, C
D
3.668
E
1.250
0.874
F
CH3
B
C
D
E
2.00
1.93
1.98
3.97
58.72
8.88
500
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)

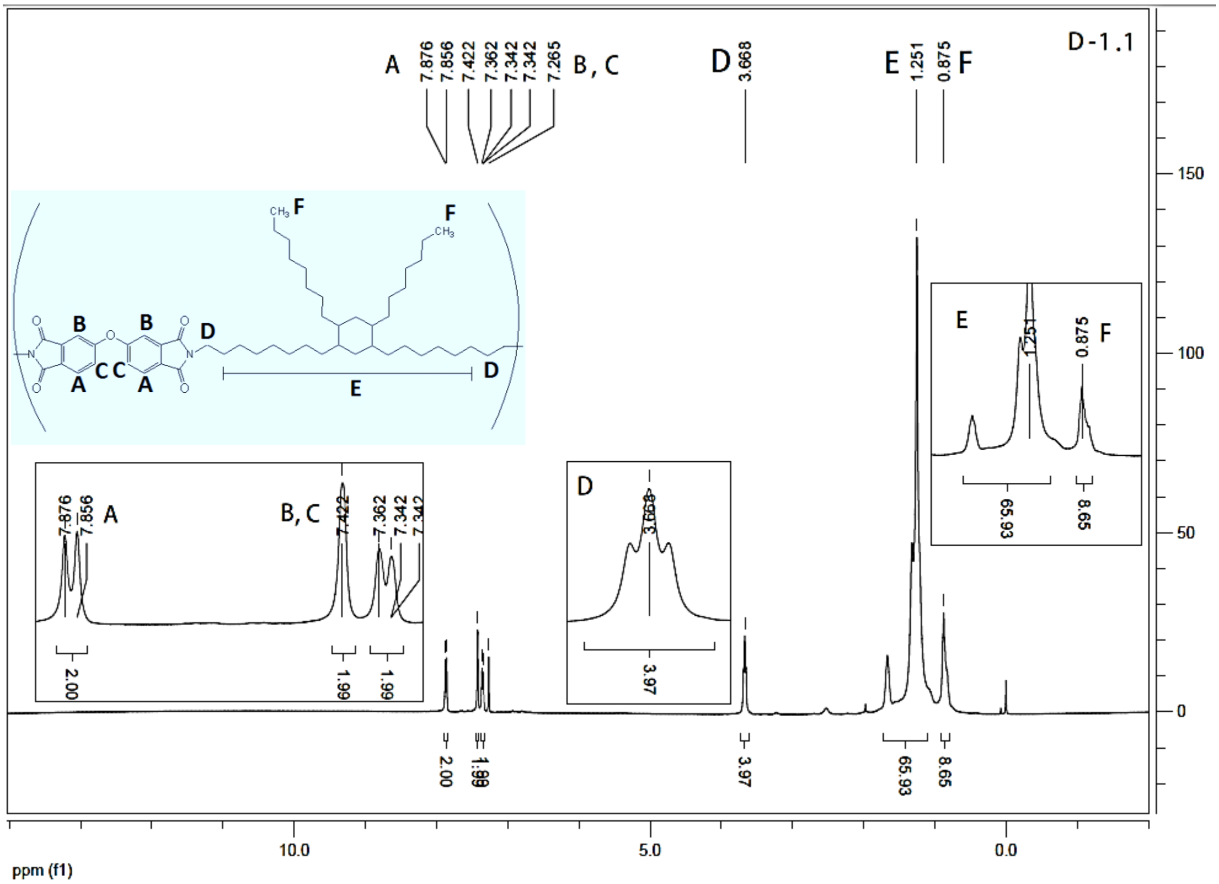


Figure S3. ^{1}H NMR spectra of the three polymers in $CDCl_3$ and their assignments to the polymer structure.

X-ray diffraction measurements

Wide Angle X-ray diffraction (WAXS) data were collected on a Bruker D8 Advance diffractometer with Co Kα 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.

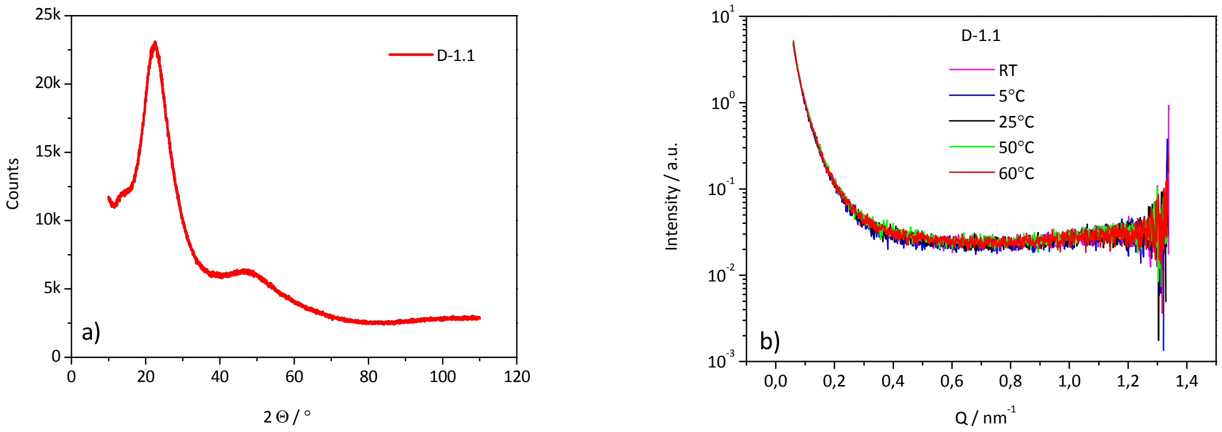


Figure S4. a) WAXS and **b)** temperature controlled SAXS diffractogram of the D-1.1 polymer with representative patterns of all polymers in this work.

Thermal analysis

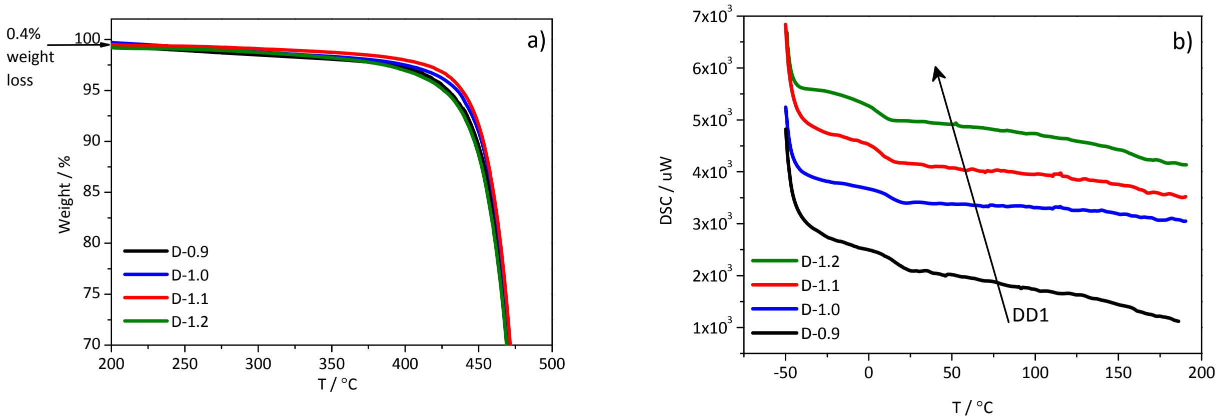


Figure S5. a) TGA curves showing weight loss of SH-PEIs in the high temperature range; **b)** DSC curves from the second heating cycle showing glass transitions.

Swelling tests

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

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

where:

Φ_r= volume fraction of swollen polymer
χ= polymer-solvent interaction parameter. In this work a value of 0.3 (cis-polybutadiene raw elastomer-toluene[1]) was taken as reference due to the lack of existing values for this new class of polymers.
ρ_r= polymer density
M_c= molecular weight of polymer between two crosslinks
V_s= molar volume of solvent (106.8 mL/mol for toluene[1])
f= functional cross-links (3)

The volume fraction (Φ_r) of swollen polymer was calculated according to:

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

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
ρ_s= solvent density (0.87 g/cm^3 for toluene)

The crosslink density ($\boldsymbol{v}$) is then calculated as:

$$\boldsymbol{v}=\frac{1}{2M_c} \qquad \text{eq-S3}$$

Table S-I. Results of the swelling tests.

Polymer	Q, Swelling ratio after 72h (%)	Soluble fraction (%)	M_c (g/mol)	v, Crosslinking density (mol/cm^3)
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

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[1] Hansen, C.M., *Hansen solubility parameters: a user's handbook*, CRC Press LLC: USA, 2000.

Rheological parameters

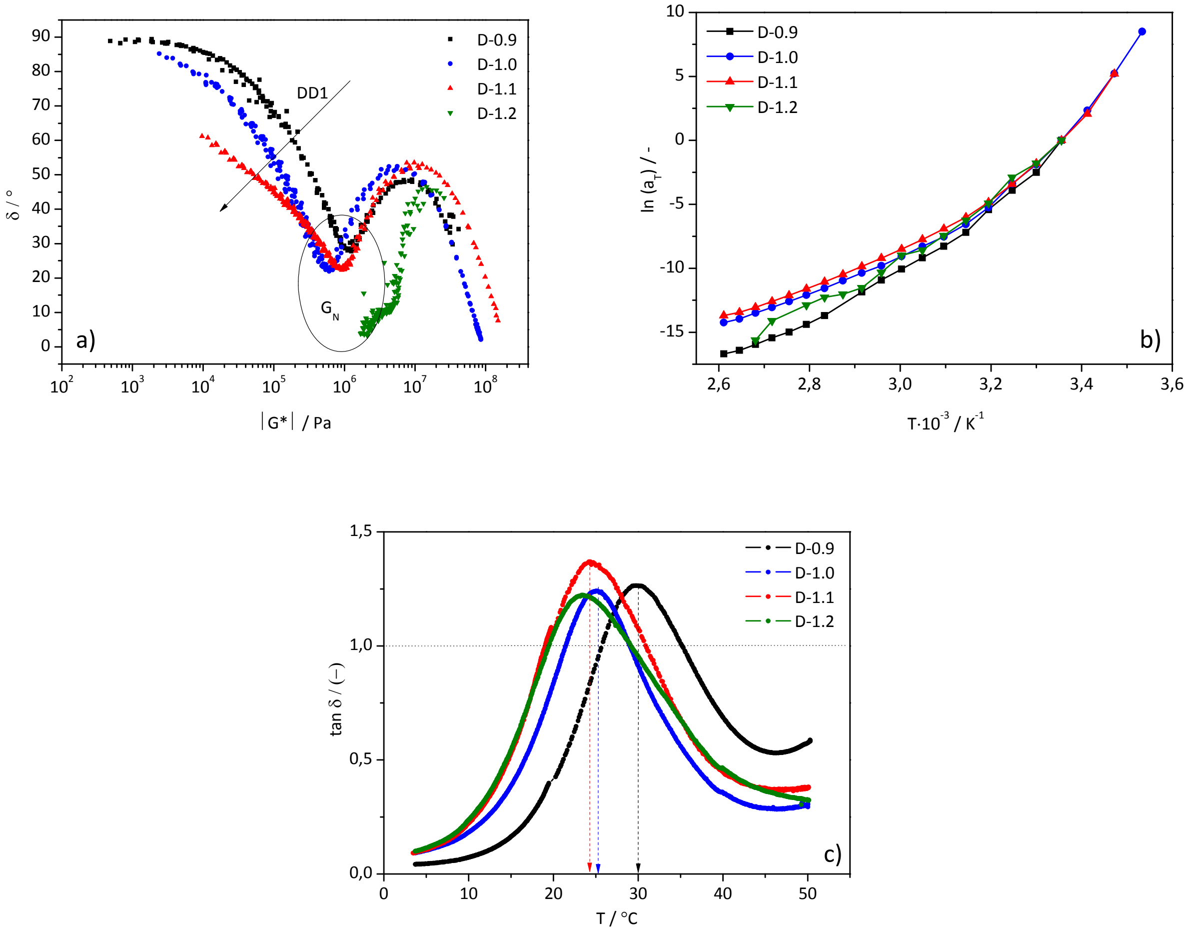

Figure S6: a) van Gurp-Palmen plot; **b)** horizontal shift factors (a_T) from the TTS mastercurves, T_{ref}=25°C; **c)** loss tangent (tanδ) as a function of temperature (T) from the temperature sweep experiments. Dotted lines are guidance for a reader's eye showing the elastic/viscous dominance region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

Tensile test

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

Polymer	σ_b (MPa)	ε_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

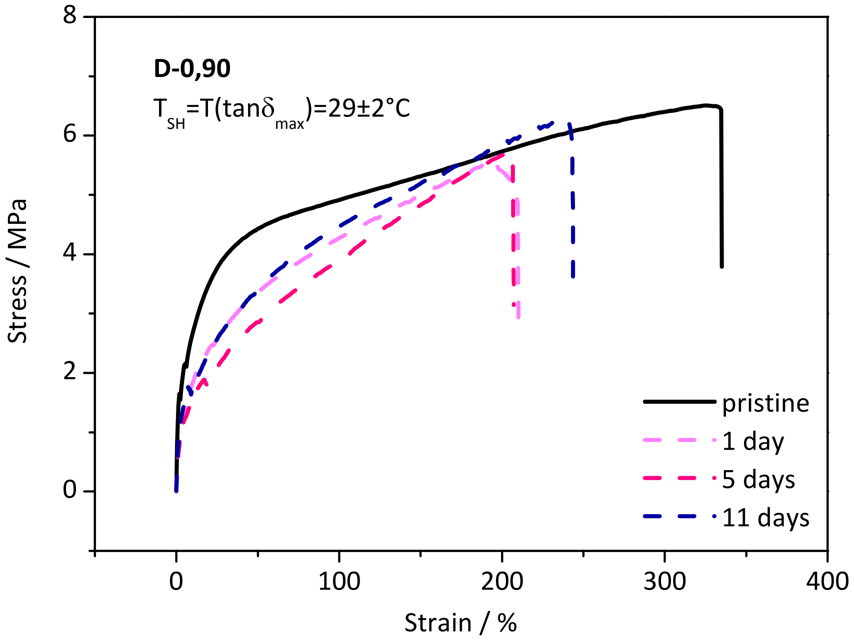

Figure S7. Stress-strain curves showing the **D-0.9** healing behaviour at the higher healing T, that corresponds to T of the maximum of tanδ determined from the rheological T-sweep test, as function of the healing time. Full lines represent pristine (—) and dashed lines represent healed (---) samples 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_g (^{o}C)	TGA-T (2% weight loss) (°C)	Density (g/cm^3)
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.

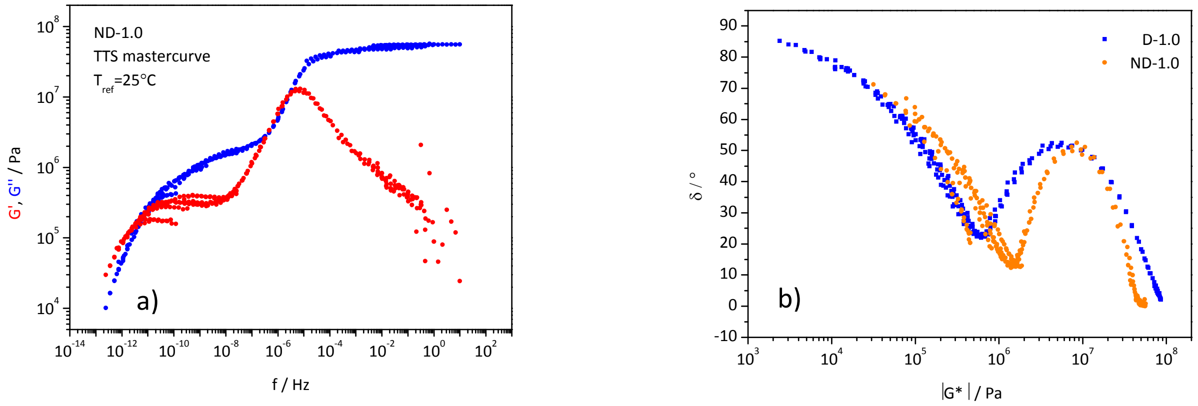

Figure S8. a) TTS mastercurve of ND-1.0 and **b)** van Gurp-Palmen plots of the referent non-branched PEI (orange) ND-1.0 in comparison to its branched counterpart D-1.0 (blue). T_{ref}=25°C

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_s (Hz)	f_d (Hz)	f_g (Hz)	τ_s (s)	τ_d (s)	τ_g (s)	G' slope at f<f_s	G'' slope at f<f_s	G_N* (Pa)	M_e** (g/mol)
ND-1.0	$7.5\cdot 10^{-12}$	$3.8\cdot 10^{-7}$	$2.8\cdot 10^{-6}$	$13.3\cdot 10^{11}$	$2.6\cdot 10^{6}$	$3.6\cdot 10^{5}$	1.06	0.49	$1.39\cdot 10^{6}$	2140
D-1.0	$2.0\cdot 10^{-5}$	0.035	1.5	$5.0\cdot 10^{4}$	28.0	0.7	1.25	0.83	$6.09\cdot 10^{5}$	4270

* G_N calculated from the Van Gurp-Palmen plot, δ(|G|*).[2, 3]

** M_e were calculated using experimentally determined densities (Table S-III) according to $M_e = \rho RT / G_N$ (Doi and Edwards) equation.

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[2] Ahmadi, M.; Hawke, L. G. D.; Goldansaz, H.; van Ruymbeke, E. *Macromolecules* **2015**, *48,* 7300.

[3] Trinkle, S.; Friedrich, C. *Rheol. Acta* **2001**, *40*, 322.

Neat branched dimer diamine (DD1); T-sweep

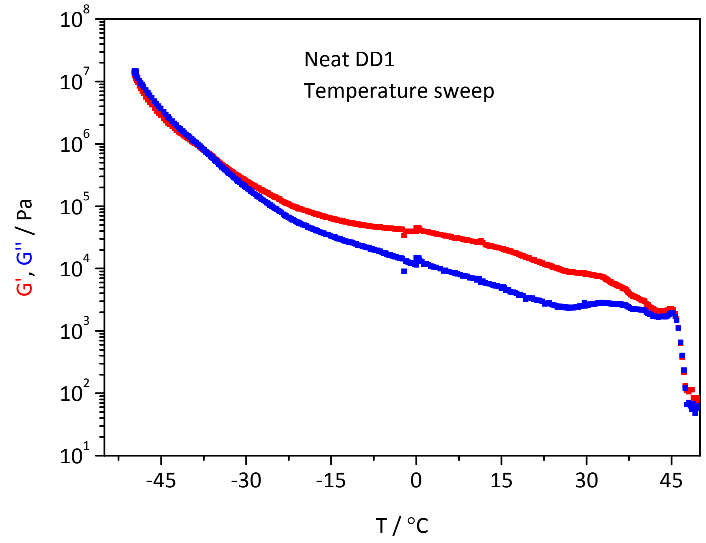

Figure S9. Temperature dependant rheological behaviour of the neat DD1.