Delft University of Technology

Effect of the Dianhydride/Branched Diamine Ratio on the Architecture and Room Temperature Healing Behavior of Polyetherimides

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

DOI
10.1021/acsami.6b10433

Publication date
2016

Document Version
Accepted author manuscript

Published in
ACS Applied Materials and Interfaces

Citation (APA)
Susa, A., Bose, R., Grande, A., van der Zwaag, S., & Garcia Espallargas, S. (2016). Effect of the Dianhydride/Branched Diamine Ratio on the Architecture and Room Temperature Healing Behavior of Polyetherimides. *ACS Applied Materials and Interfaces*, *8*(49), 34068−34079. Article 10433. https://doi.org/10.1021/acsami.6b10433

Important note
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright
Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy
Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

This work is downloaded from Delft University of Technology.
For technical reasons the number of authors shown on this cover page is limited to a maximum of 10.

SUPPORTING INFORMATION

Doi: 10.1021/acsami.6b10433
ACS Appl. Mater. Interfaces, 2016, 8 (49), pp 34068–34079

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:

Figure S1.	Full IR spectra of the four PEIs as a function of the offset from the theoretical stoichiometric ratio.	**S-2**
Figure S2.	^{1}H NMR spectra of the monomers: ODPA in DMSO and DD1 in $CDCl_3$ and their assignment to the molecular structure.	**S-3**
Figure S3.	^{1}H NMR spectra of the four polymers in $CDCl_3$ and their assignment to the polymer structure.	**S-4, S-5**
Figure S4:	WAXS and temperature controlled SAXS diffractograms.	**S-6**
Figure S5:	TGA curves and DSC curves from the second heating cycle showing glass transitions.	**S-5**
Table S-I.	Results of the swelling tests.	**S-7**
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.	**S-8**
Table S-II:	Tensile properties of the virgin polymers.	**S-9**
Figure S7.	Stress-strain curves showing the **D-0.9** healing behaviour at the higher healing T.	**S-9**
Table S-III.	Effect of branching on the generic polymer properties.	**S-10**
Figure S8.	**a)** TTS mastercurve of ND-1.0 and **b)** van Gurp-Palmen plots of the referent non-branched PEI ND-1.0 in comparison to its branched counterpart D-1.0	**S-10**
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).	**S-10**
Figure S9.	Temperature dependant rheological behaviour of the neat DD1.	**S-11**

ATR/FTIR spectra

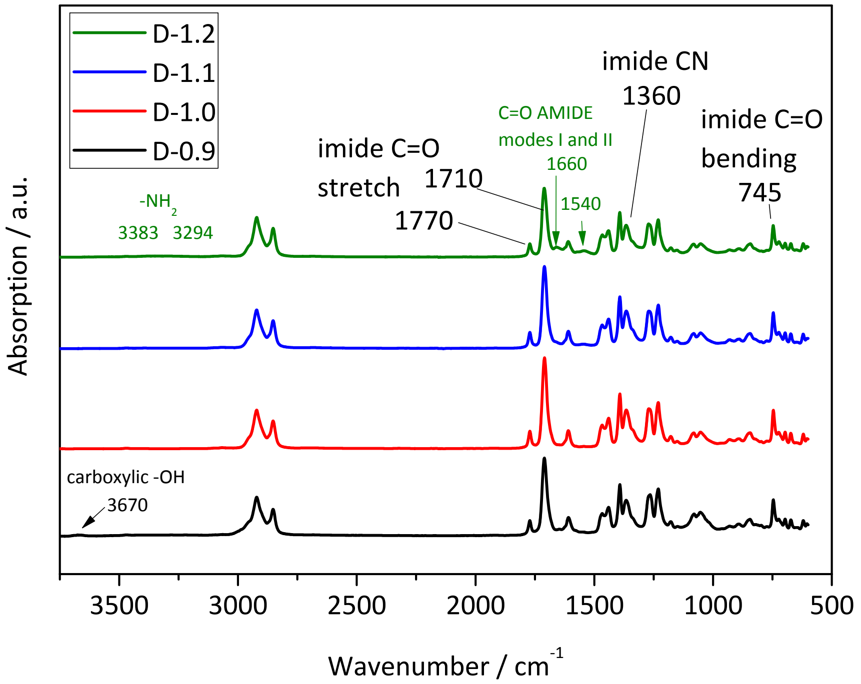


Figure S1. Full IR spectra of the four PEIs as a function of the offset from the theoretical stoichiometric ratio.

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):

$$Predicted\ mass\ of\ the\ product/g = m(ODPA)+m(DD1)\text{-}m(H_{2}0)$$

^{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.

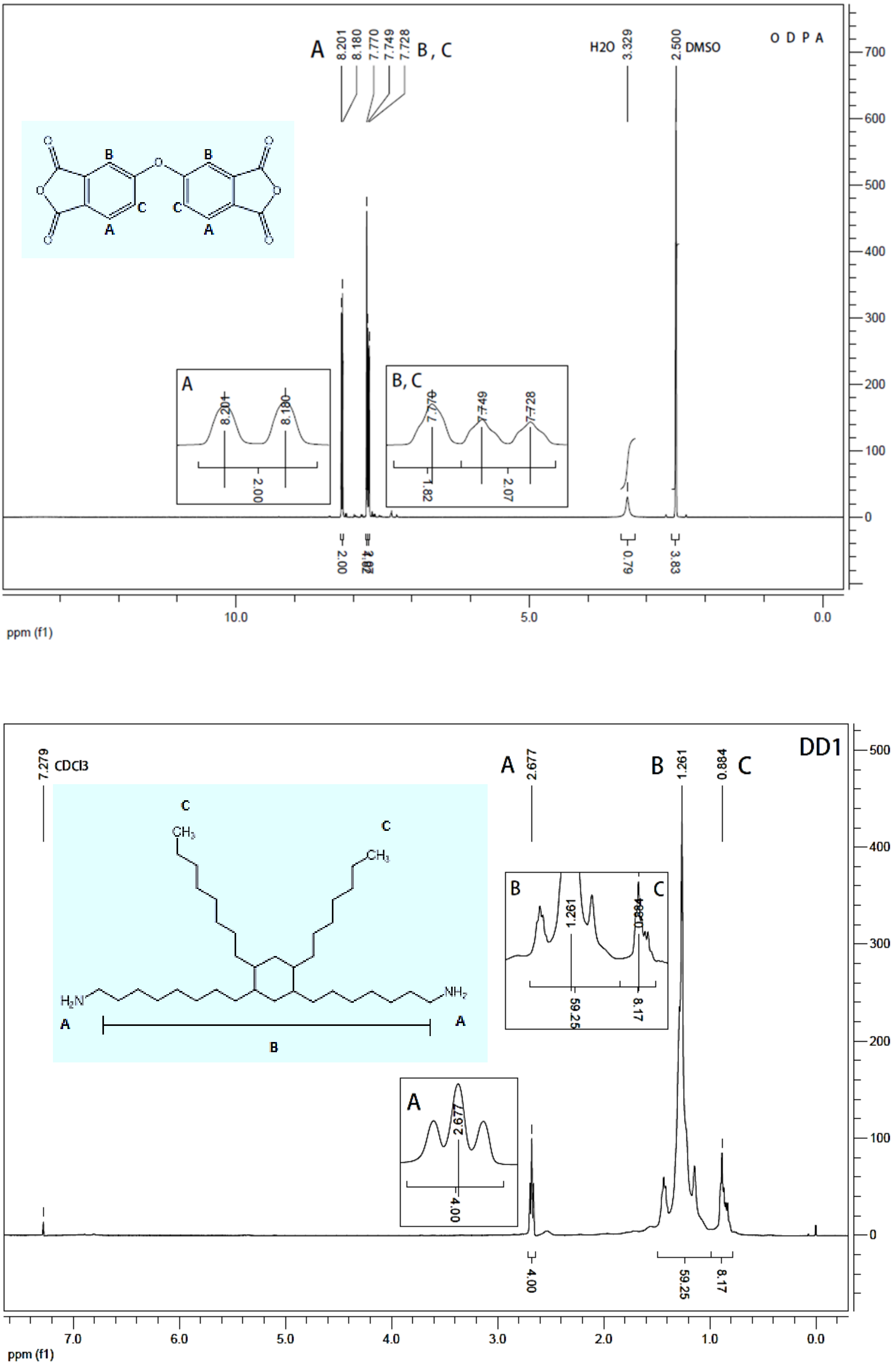
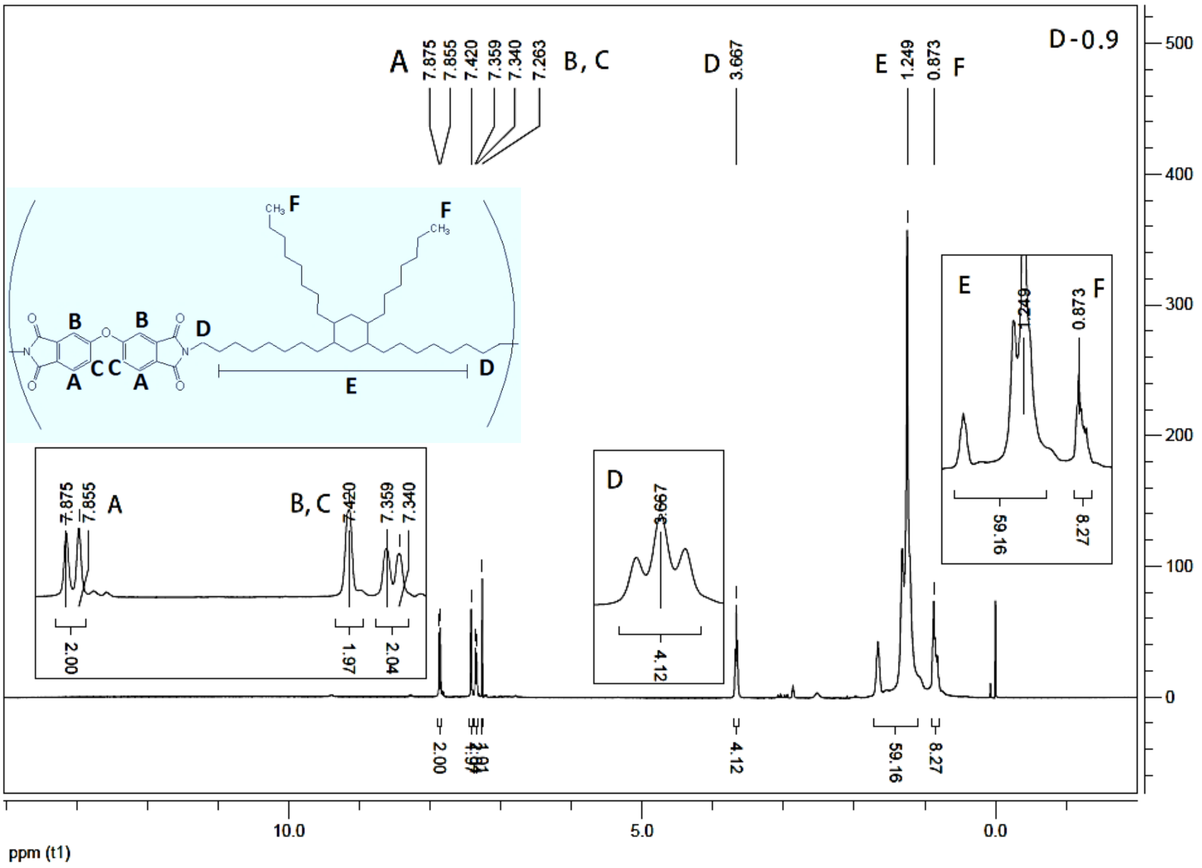
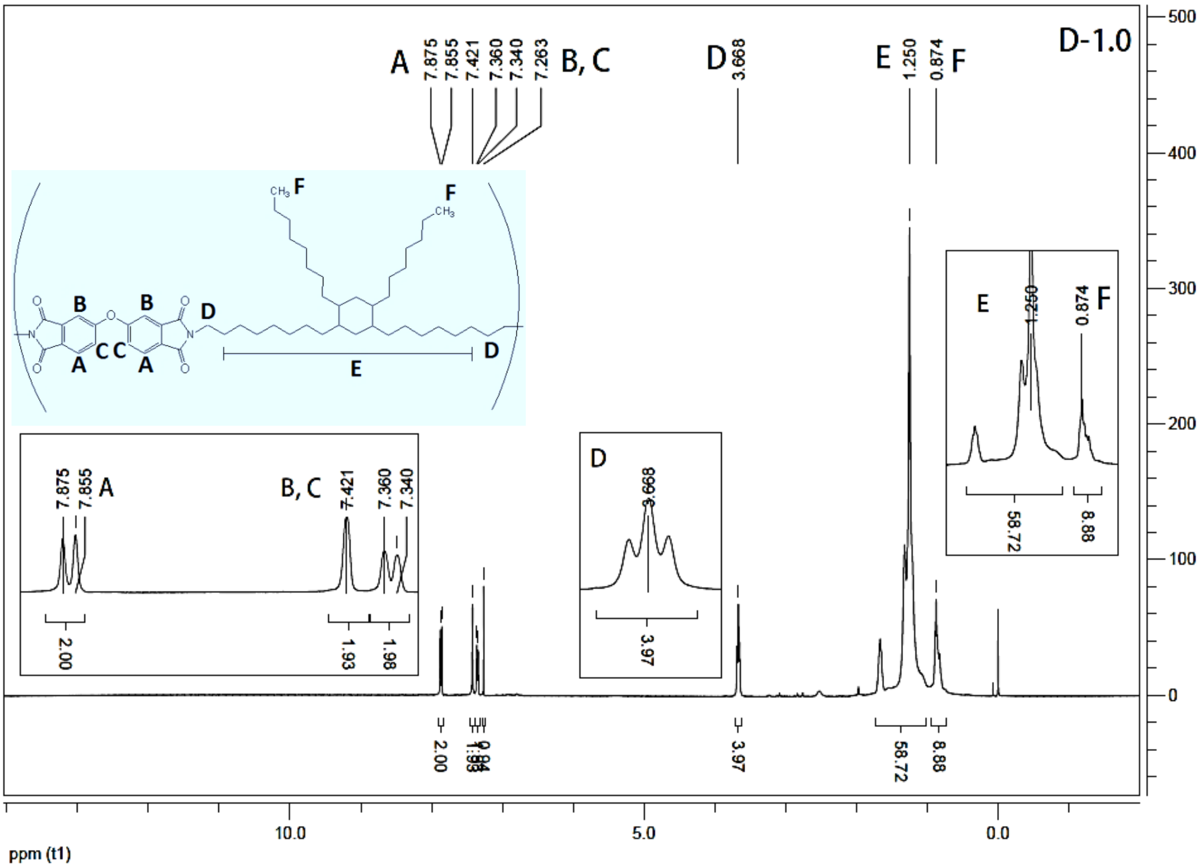


Figure S2. ^{1}H NMR spectra of the monomers: ODPA in DMSO and DD1 in $CDCl_3$ and their assignment to the molecular structure.


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
A
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
A
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)

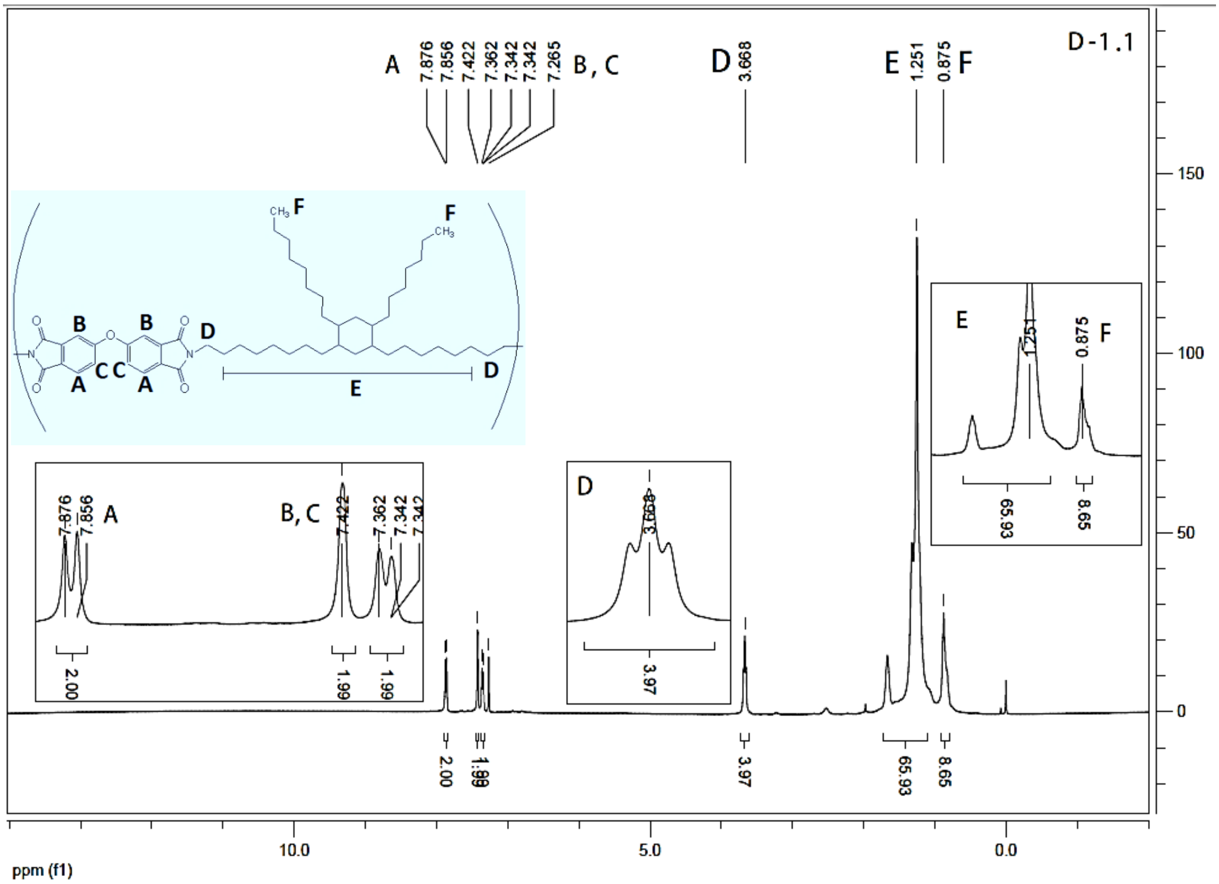


Figure S3. ^{1}H NMR spectra of the three polymers in $CDCl_3$ and their assignments to the polymer structure.

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.

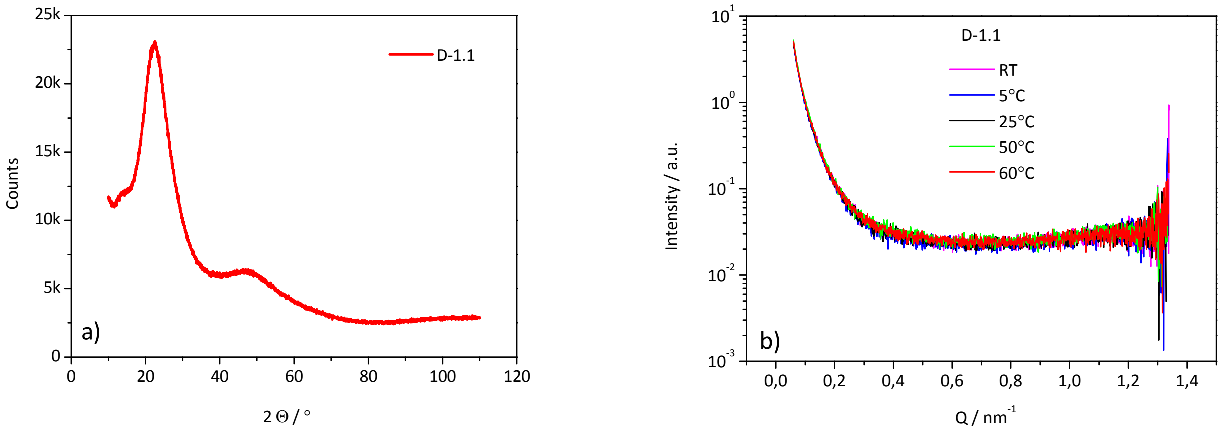


Figure S4. a) WAXS and **b)** temperature controlled SAXS diffractogram of the D-1.1 polymer with representative patterns of all polymers in this work.

Thermal analysis

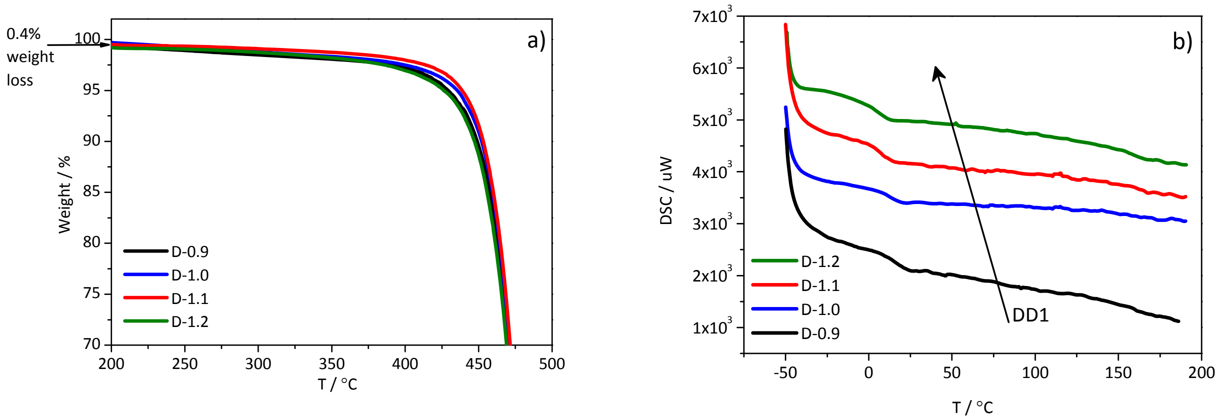


Figure S5. a) TGA curves showing weight loss of SH-PEIs in the high temperature range; **b)** DSC curves from the second heating cycle showing glass transitions.

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

---

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

Rheological parameters

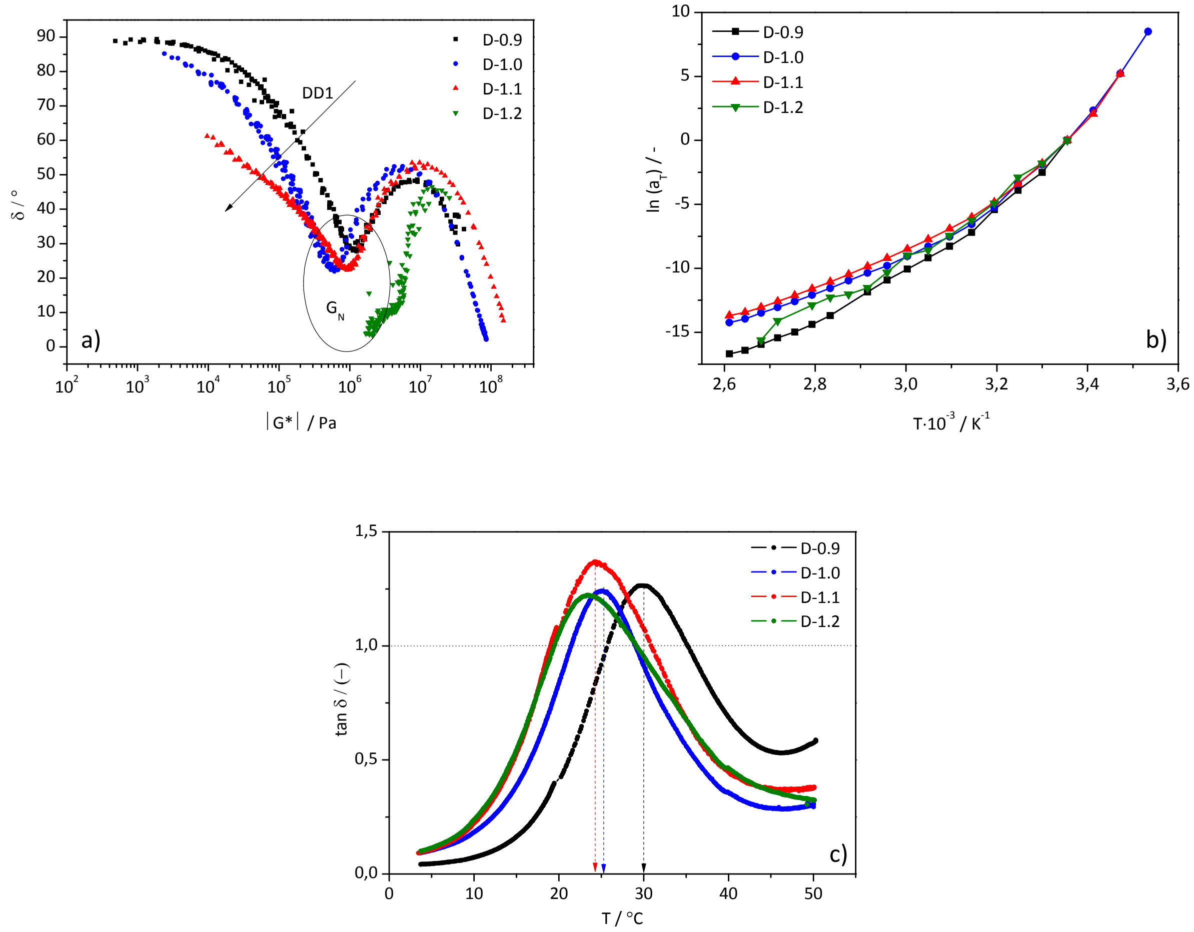


Figure S6: a) van Gurp-Palmen plot; **b)** horizontal shift factors (a_T) from the TTS mastercurves, T_{ref}=25°C; **c)** loss tangent (tanδ) as a function of temperature (T) from the temperature sweep experiments. Dotted lines are guidance for a reader's eye showing the elastic/viscous dominance region determined by tanδ=1. Arrows point the values of T (tanδ_{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

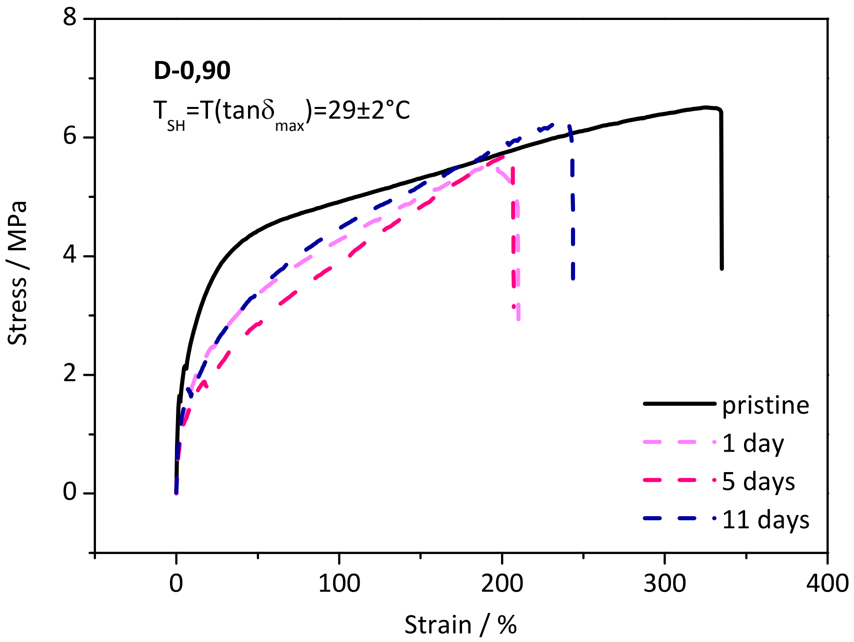


Figure S7. Stress-strain curves showing the **D-0.9** healing behaviour at the higher healing T, that corresponds to T of the maximum of tanδ determined from the rheological T-sweep test, as function of the healing time. Full lines represent pristine (—) and dashed lines represent healed (---) samples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

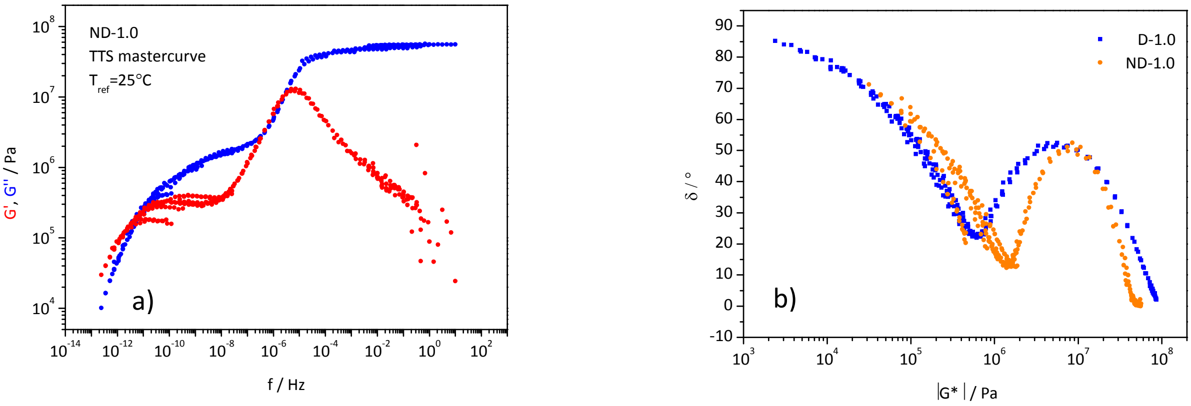


Figure S8. a) TTS mastercurve of ND-1.0 and **b)** van Gurp-Palmen plots of the referent non-branched PEI (orange) ND-1.0 in comparison to its branched counterpart D-1.0 (blue). T_{ref}=25°C

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.

---

[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

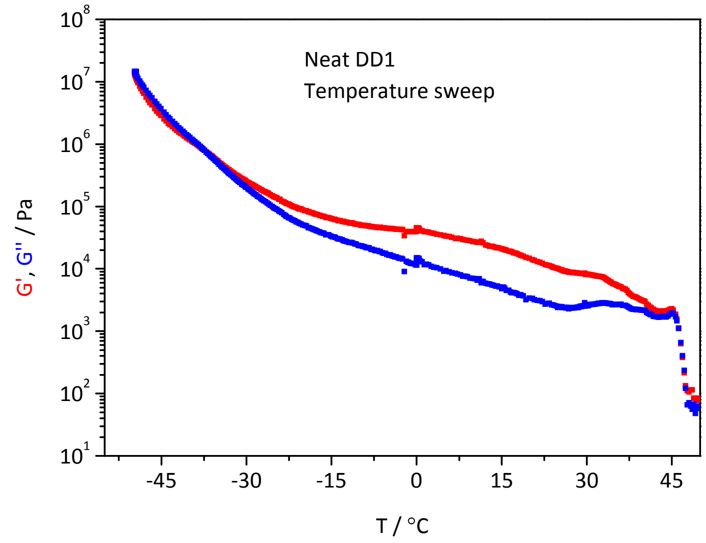


Figure S9. Temperature dependant rheological behaviour of the neat DD1.