

**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.

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: <u>s.j.garciaespallargas@tudelft.nl</u>

# *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.			
Figure S2.	<sup>1</sup> H NMR spectra of the monomers: ODPA in DMSO and DD1 in CDCl <sub>3</sub> and their	S-3		
	assignment to the molecular structure.			
Figure S3.	<sup>1</sup> H NMR spectra of the four polymers in CDCl₃ and their assignment to the	S-4,		
	polymer structure.	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	S-5		
	transitions.			
Table S-I.	Results of the swelling tests.	S-7		
Figure S6:	<b>a)</b> van Gurp-Palmen plot; <b>b)</b> horizontal shift factors ( $a_T$ ) from the TTS	S-8		
	mastercurves, $T_{ref}$ =25°C; <b>c)</b> loss tangent (tan $\delta$ ) as a function of temperature.			
Table S-II:	Tensile properties of the virgin polymers.	S-9		
Figure S7.	Stress-strain curves showing the <b>D-0.9</b> healing behaviour at the higher healing	S-9		
	т.			
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	S-10		
	non-branched PEI ND-1.0 in comparison to its branched counterpart D-1.0			
Table S-IV.	Characteristic parameters obtained from rheology for the non-branched PEI	S-10		
	(ND-1.0) as compared to its branched counterpart (D-1.0).			
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/
$$g = m(ODPA)+m(DD1)-m(H_20)$$

### <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.

# SUPPORTING INFORMATION





**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.

# SUPPORTING INFORMATION







**Figure S3.** <sup>1</sup>H NMR spectra of the three polymers in CDCl<sub>3</sub> and their assignments to the polymer structure.

# SUPPORTING INFORMATION

#### 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).

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

 $M_{\rm c}$ = molecular weight of polymer between two crosslinks

 $V_{\rm s}$ = 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:

$$\Phi_r = \frac{\frac{w_i/\rho_r}{w_i/\rho_r + (w_s - w_d)/\rho_s}}{(w_s - w_d)/\rho_s}$$
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 (v) is then calculated as:

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

Table S-I. Results of the swelling tests.

Polymer	Q, Swelling ratio after 72h (%)	Soluble fraction (%)	M <sub>c</sub> (g/mol)	v, Crosslinking density (mol/cm³)	
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<sub>ref</sub>=25°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 $\delta_{max}$ ) for the non-crosslinked polymers that heal at 25°C (red and blue) and does not heal at 25°C (black).

#### Tensile test

Polymer	σ <sub>b</sub> (MPa)	ε <sub>b</sub> (%)	E (MPa)		
D-0.9	<b>D-0.9</b> 5.9±0.2		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		

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

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/cm³)
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<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</f<sub>	G" slope at f <f<sub>s</f<sub>	G <sub>∾</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∙ 10⁴	28.0	0.7	1.25	0.83	6.09· 10 <sup>5</sup>	4270

\*  $G_N$  calculated from the Van Gurp-Palmen plot,  $\delta(|G|^*)$ .<sup>2,3</sup>

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