SUPPORTING INFORMATION

Polyurea Networks from Moisture-cure, Reaction-Setting, Aliphatic Polyisocyanates with Tunable Mechanical and Thermal Properties

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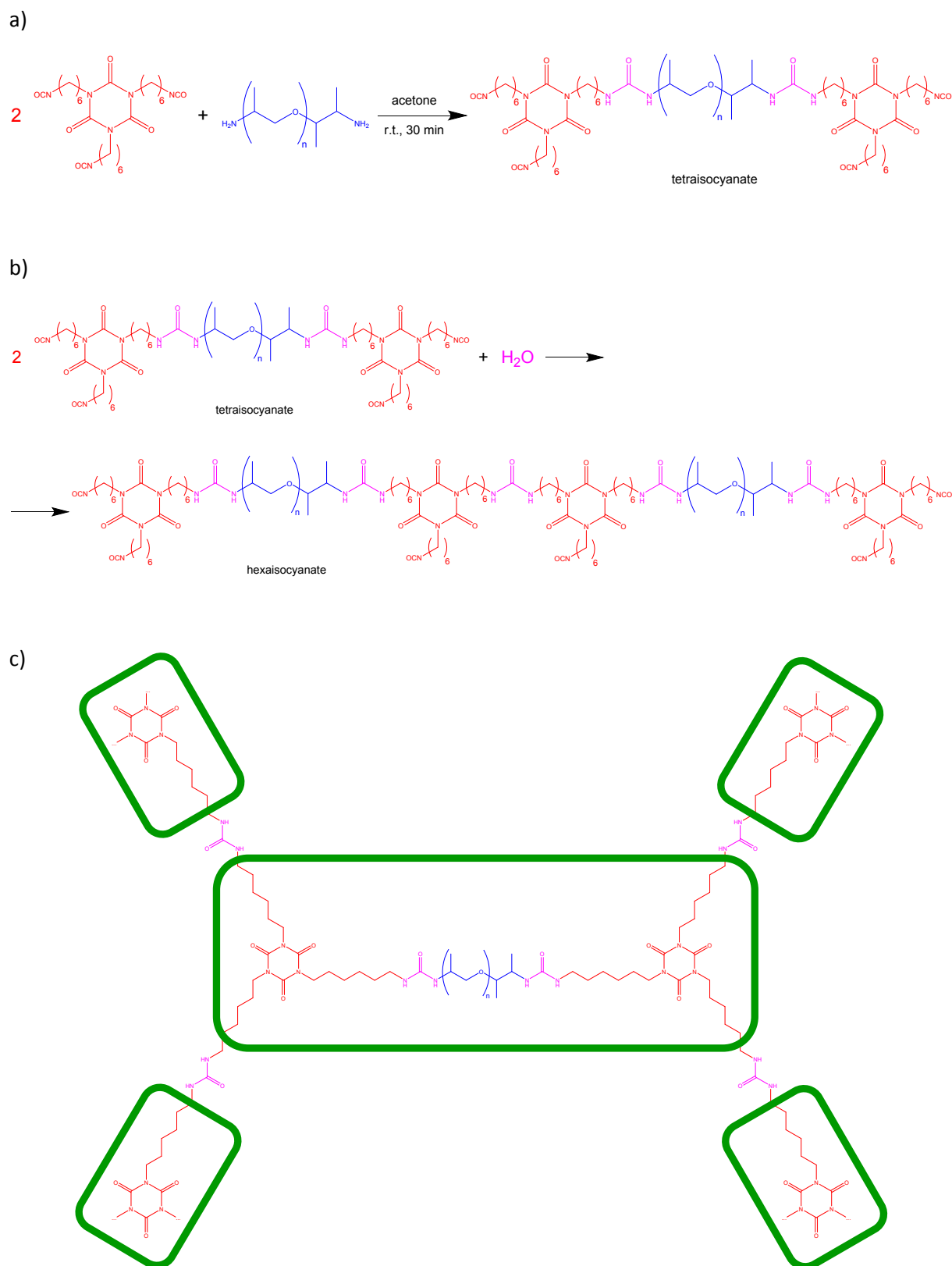
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SUMMARY

a)

tetraisocyanate

b)

tetraisocyanate + H_2O ⟶

hexaisocyanate

c)

Scheme S1. a) Synthesis of the tetrafunctionalized aliphatic isocyanates. b) Formation of the hexafunctionalized aliphatic isocyanates when reacted with a residual water molecule present in the solvent. c) Connectivity between the reactive polymers (green box) when cured by moisture. Note: the soft polypropylene oxide backbone is in blue, the hard triisocyanate is in red and the urea motifs connecting both the soft and hard segment are in purple.
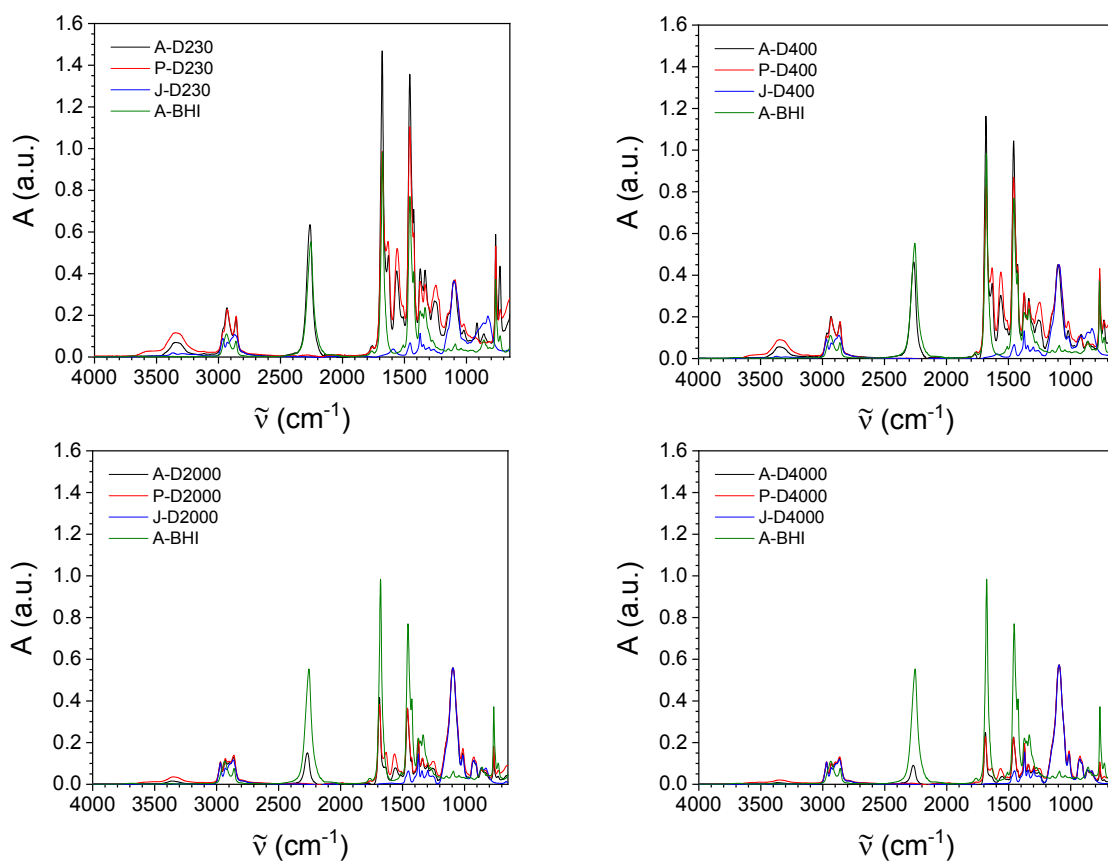
Figure S1. FTIR spectra for the four aliphatic polyisocyanates (A-D230, A-D400, A-D2000 and A-D4000, black), the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000, red), the four diaminoterminated polypropylene oxide polymers (J-D230, J-D400, J-D2000 and J-D4000, blue) and the reference aliphatic triisocyanate (A-BHI, green). The curing process shows the disappearance of the free isocyanate reactive group at 2262 cm^{-1}, with an increase in the intensity of the peaks corresponding to the formation of new urea groups (1629 and 1563 cm^{-1}) and hydrogen bonding (3335 cm^{-1}).
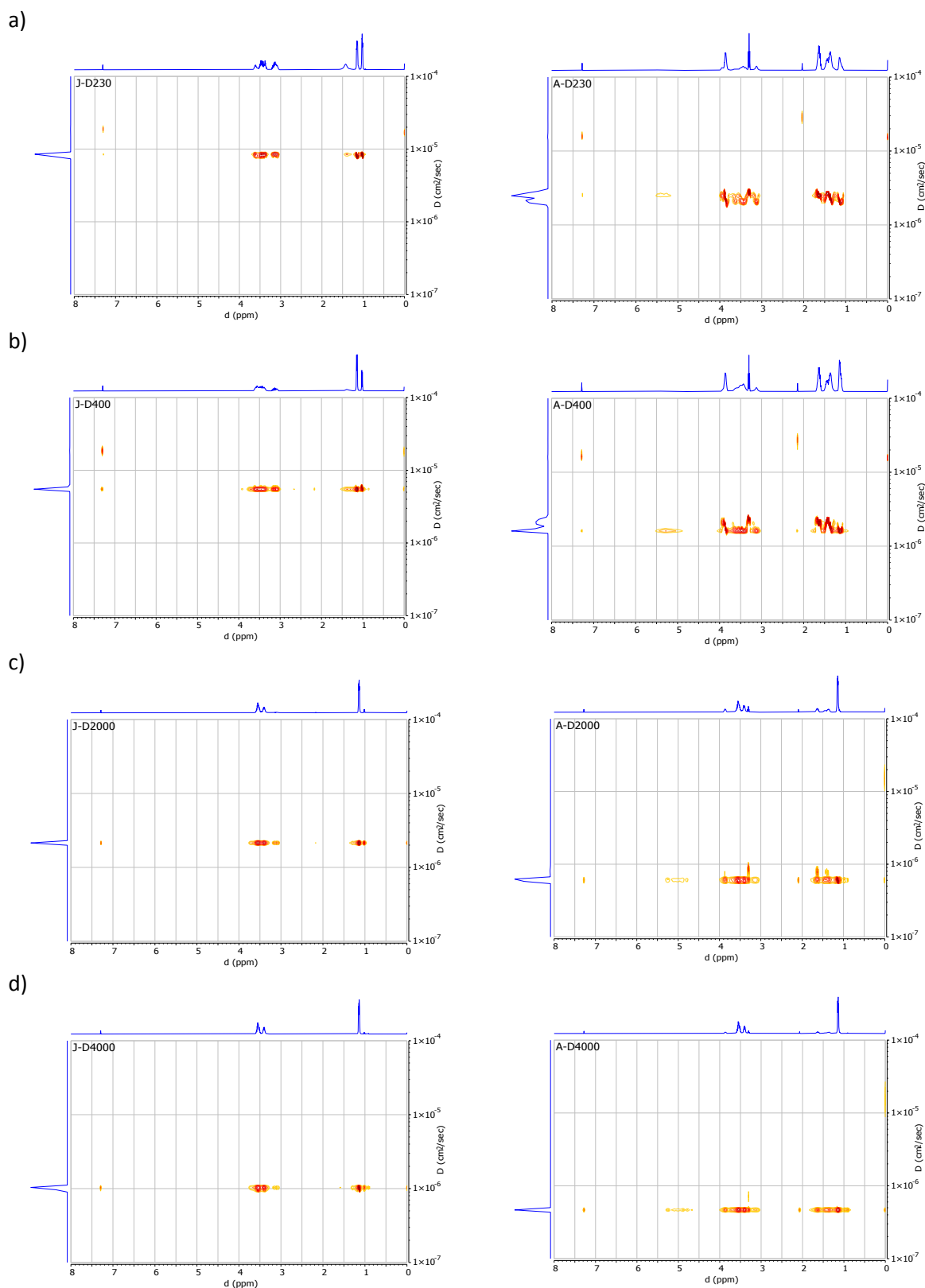
Figure S2. 2D DOSY ^{1}H NMR spectra for the four diaminoterminated polypropylene oxide polymers (left: a) J-D230, b) J-D400, c) J-D2000 and d) J-D4000) and the four aliphatic polyisocyanates (right: a) A-D230, b) A-D400, c) A-D2000 and d) A-D4000). In the top x-axis projection, the 1D ^{1}H NMR spectra of the compound are shown; in the left y-axis projection, the intensity corresponding to the signals at the same level is represented, and in the right y-axis, the diffusion coefficient values.
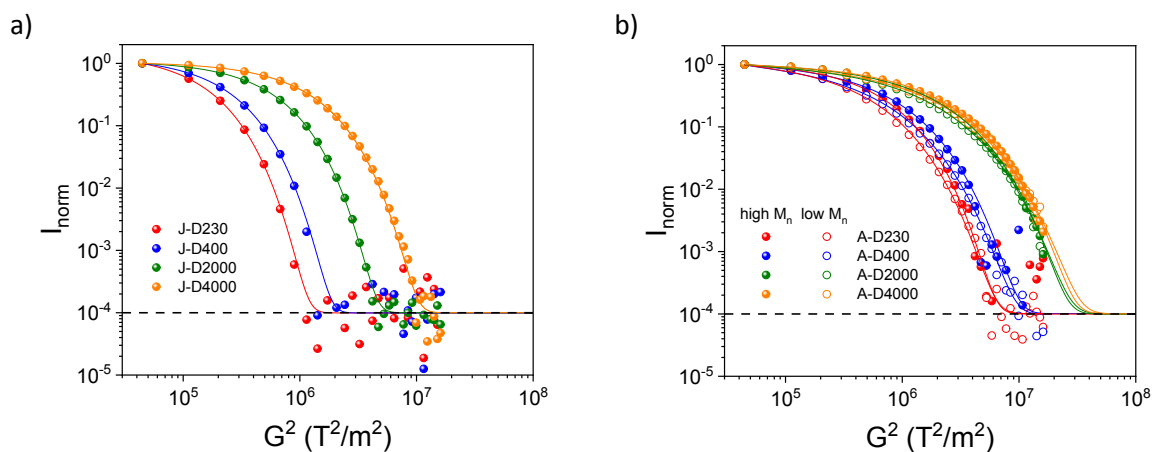
Figure S3. Regression analysis for the calculation of the diffusion coefficient, D, for a) the four diaminoterminated polypropylene oxide polymers (J-D230, J-D400, J-D2000 and J-D4000) and b) the four aliphatic polyisocyanates (A-D230, A-D400, A-D2000 and A-D4000) by fitting the data to a modified Stejskal-Tanner function, I_{norm} vs. G^2. The filled and empty symbols in b) correspond to the high and low molar mass components, respectively, detected in the 2D DOSY ^1H NMR spectra.

$$f = 1 - \exp(-0.463 \cdot M_n^{0.34})$$
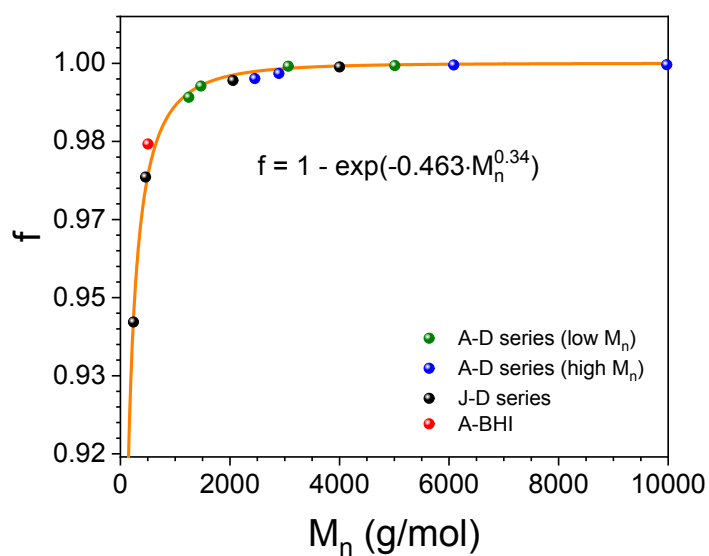
Figure S4. Stokes-Einstein scaling factor, f, calculated for the evaluation of the 2D DOSY ^1H NMR experiments.
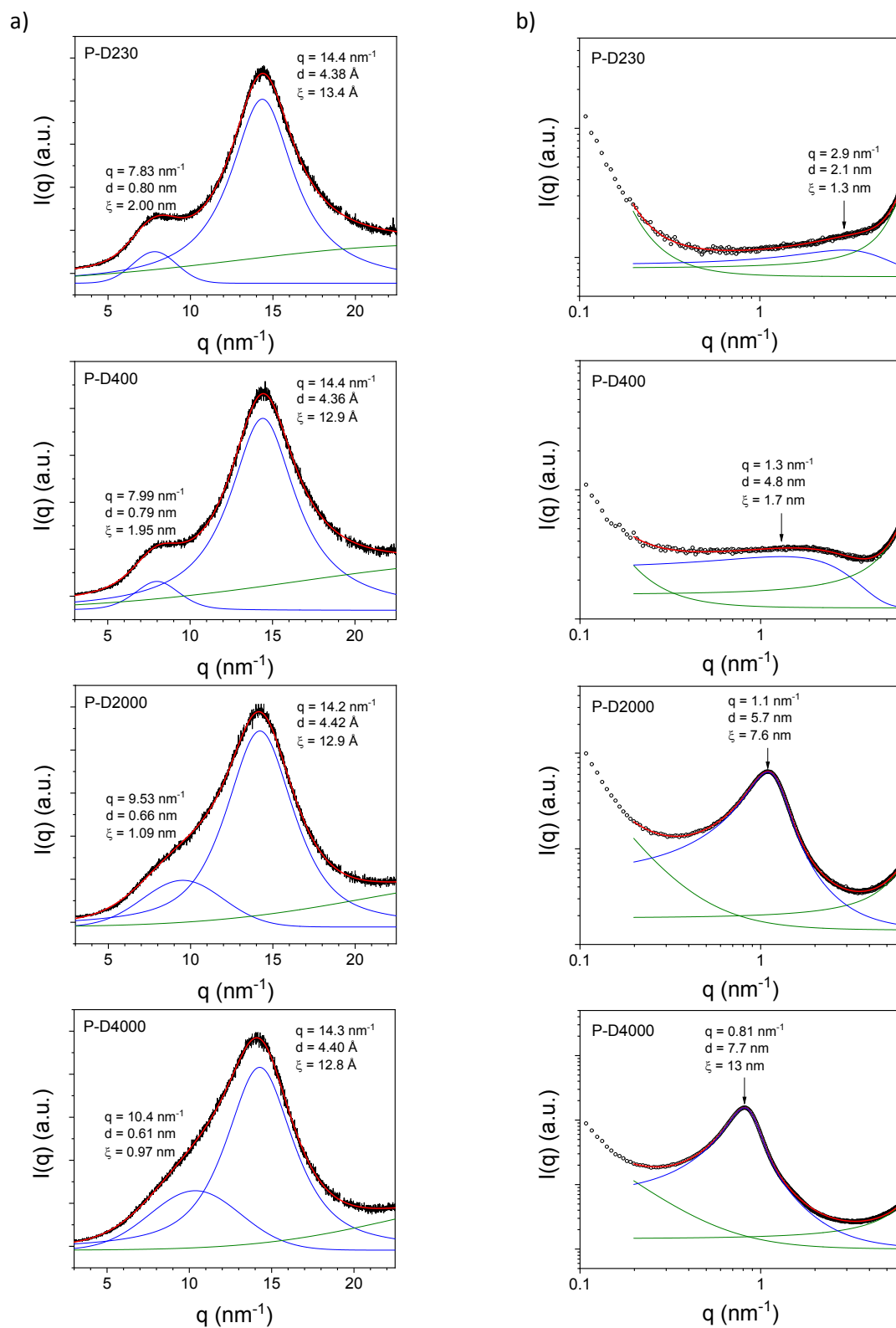
Figure S5. a) WAXS and b) SAXS intensity profiles for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000).

Figure S6. DSC thermograms for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI). Only the first and the second heating run are shown.
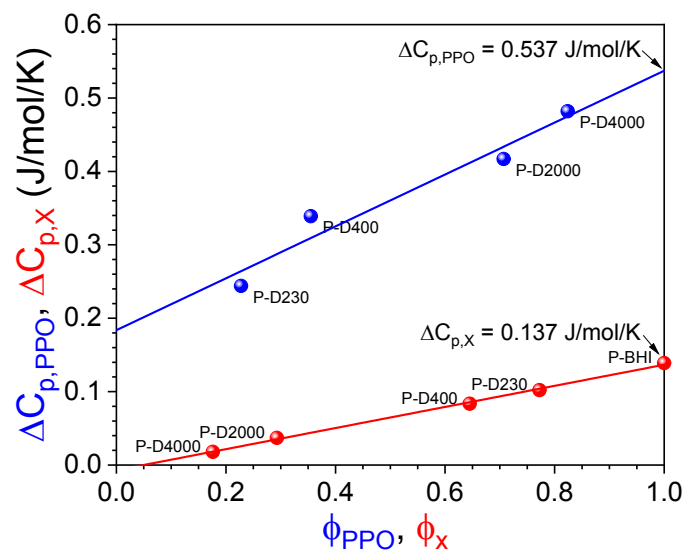
Figure S7. Evaluation of the theoretical heat capacity for the soft (blue) and hard (red) domain from heat capacity values obtained by DSC measurements and by extrapolating to volume fraction values of 1.
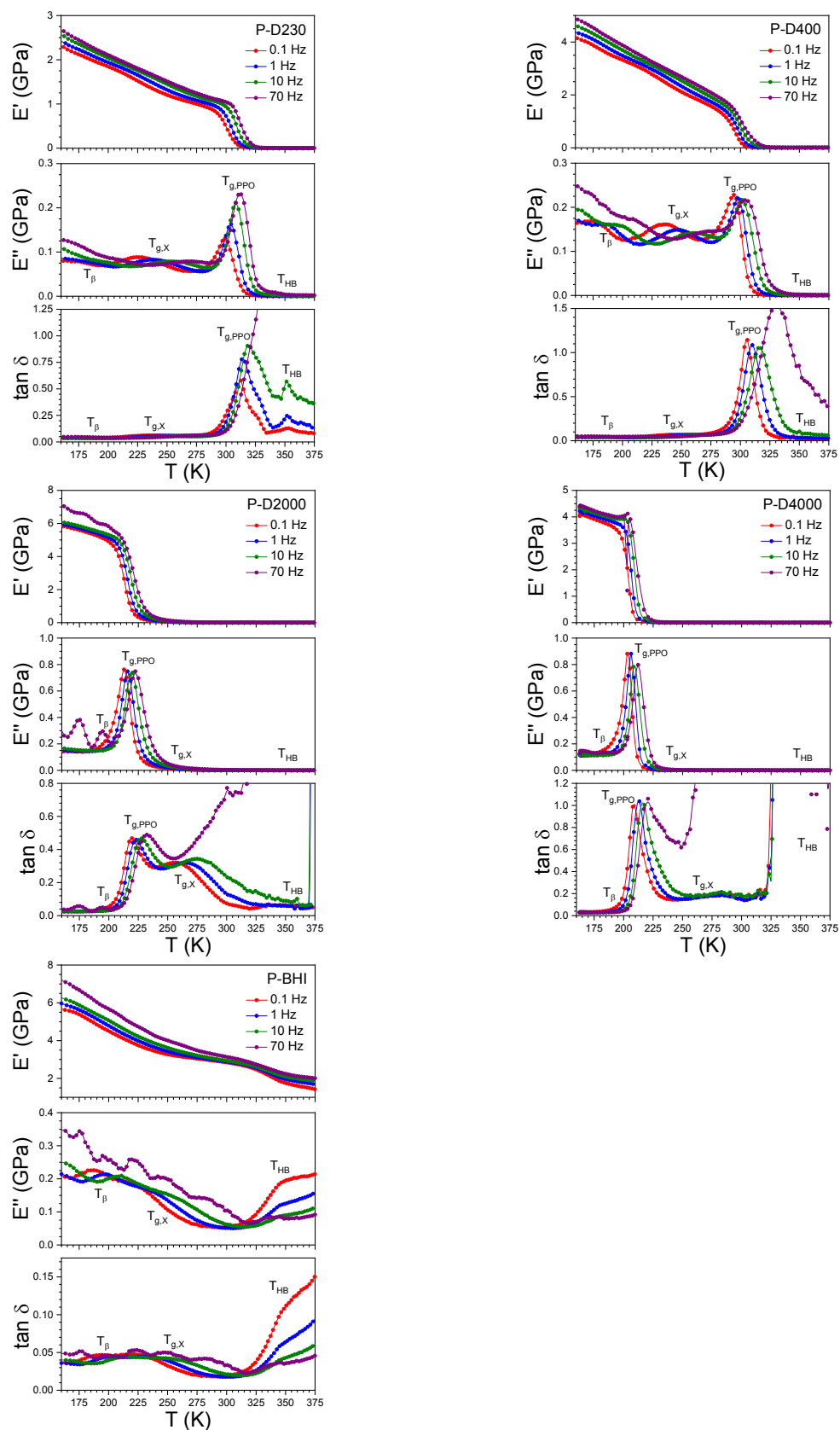
Figure S8. DMA temperature-sweep experiments showing the storage, E', and loss, E", modulus, as well as the loss factor, tan δ, as a function temperature and at the frequency values of 0.1, 1, 10 and 70 Hz for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI).
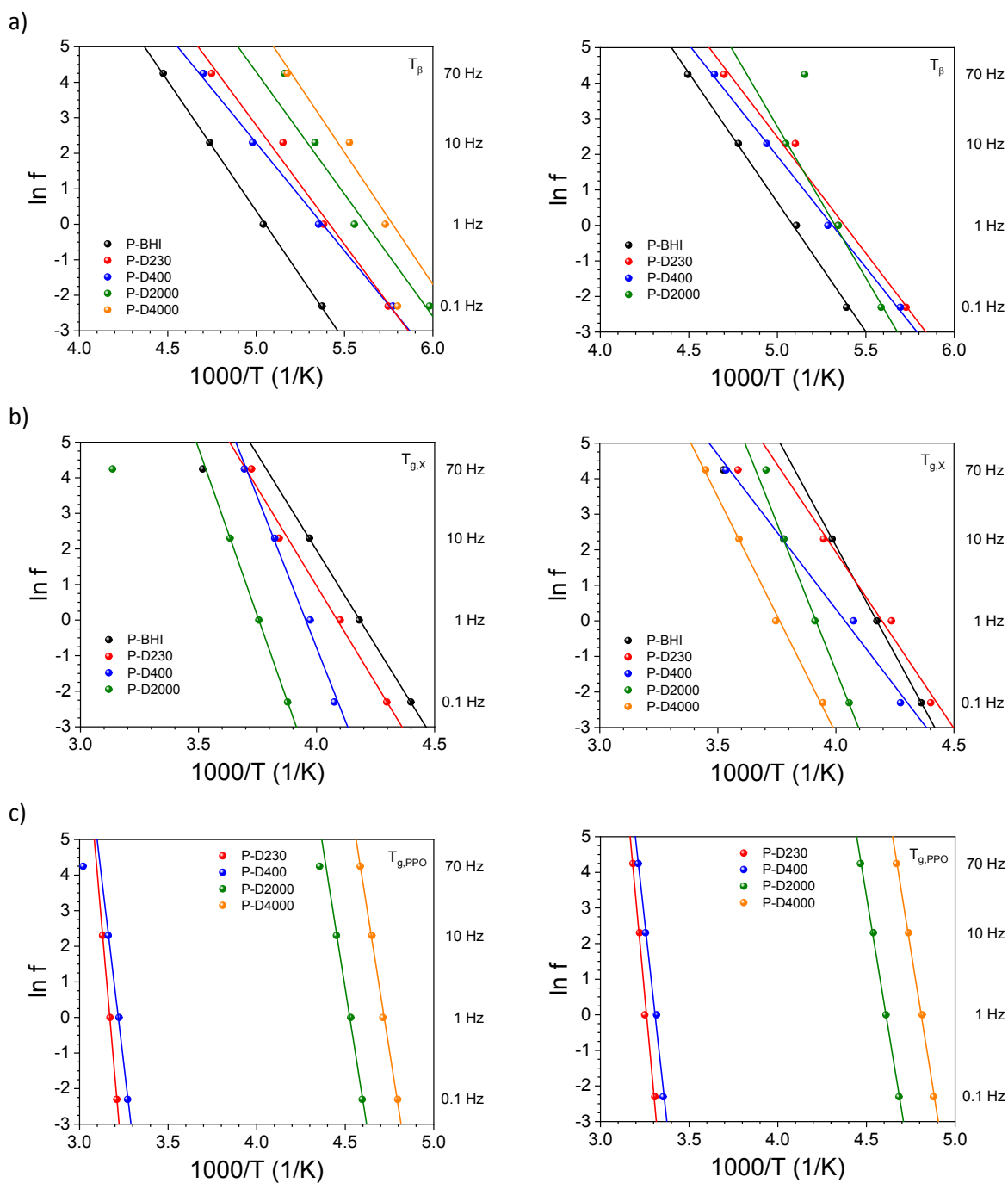
Figure S9. Arrhenius plots for the calculation of the activation energy, E_a, related to the relaxation process a) T_b, b) $T_{g,X}$ and c) $T_{g,PPO}$ from the loss factor profile (tan δ, left) and the loss modulus profile (E", r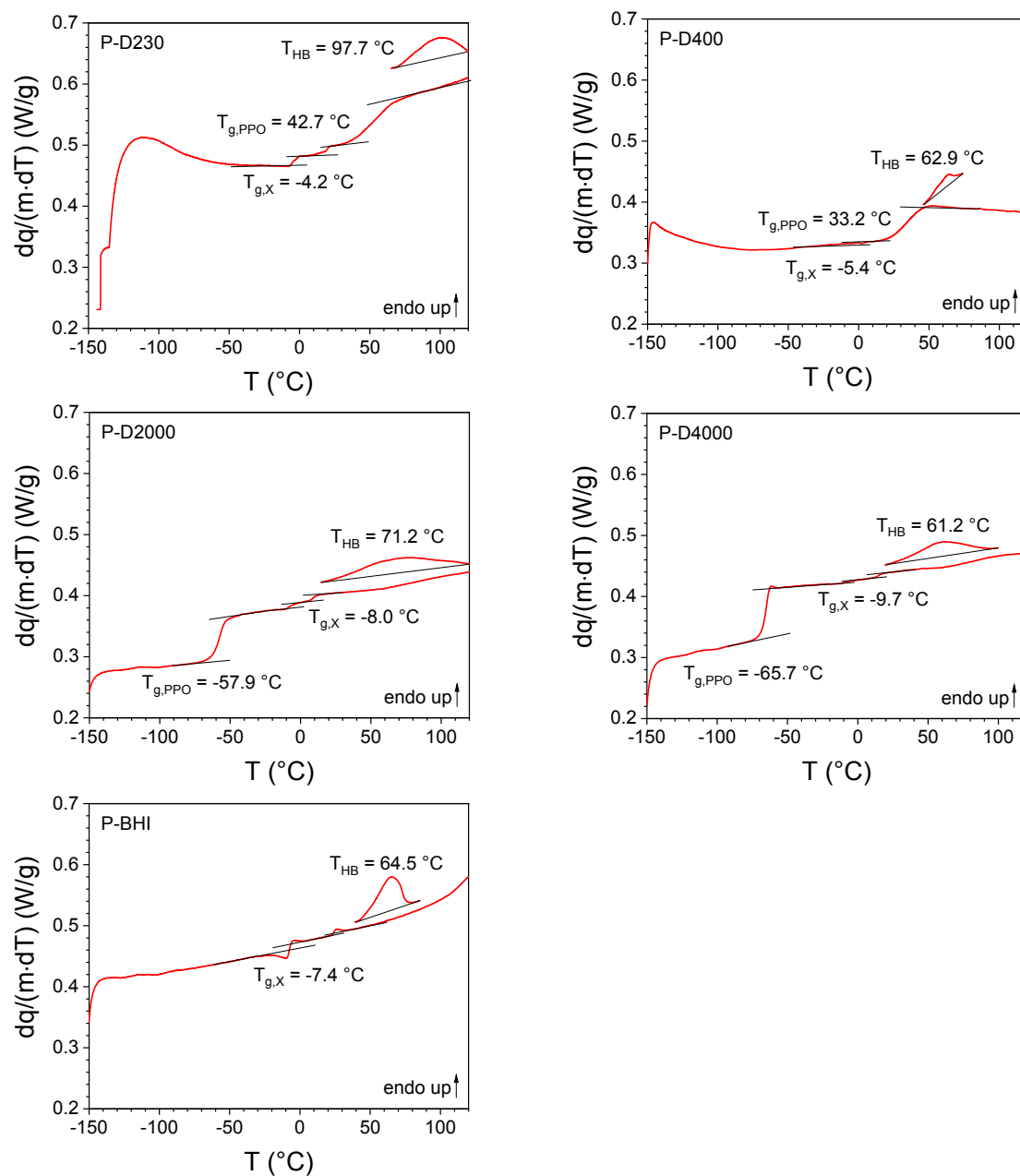ight) for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI).
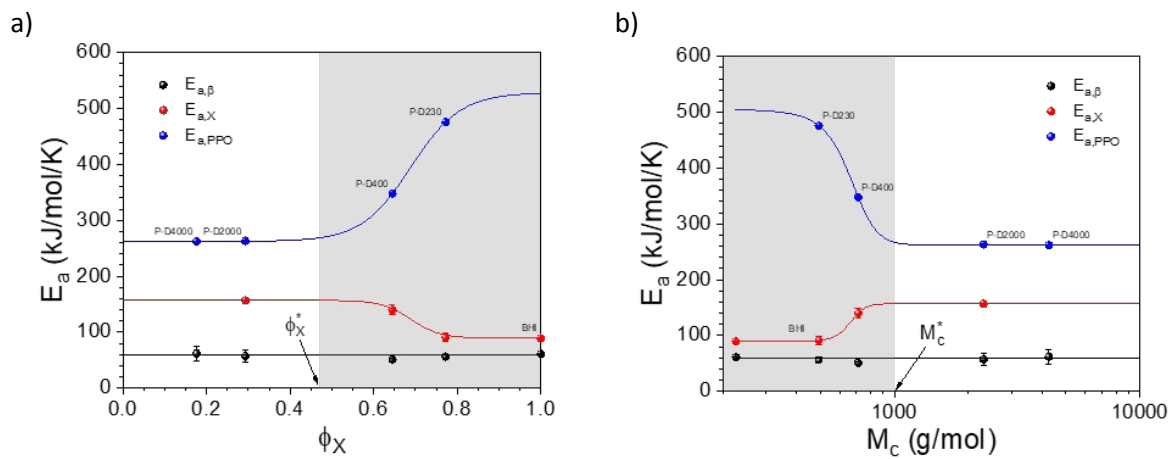
Figure S10. The activation energy of the two α- and one β-relaxation process as a function of a) the hard domain volume fraction, ϕ_X, and b) the segmental molecular weight, M_c.
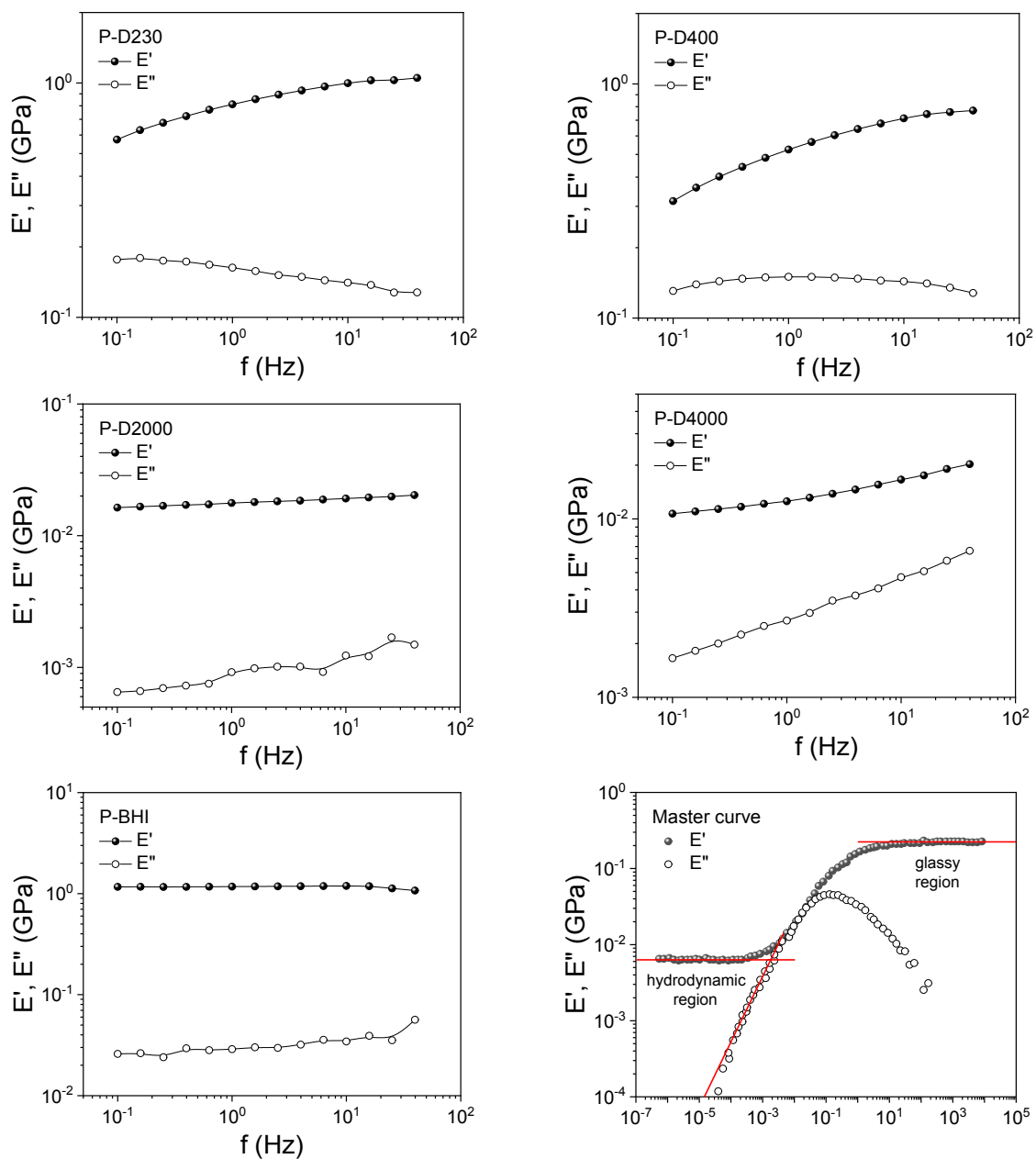
Figure S11. DMA frequency-sweep experiments showing the storage, E', and loss, E", modulus at T = 0 °C for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI). The bottom right figure shows the master curve by applying the time-temperature superposition method for a polyurea network showing the frequency behavior from the hydrodynamic region (low-frequency values) to the glassy region (high-frequency values). Data taken from A. Sánchez-Ferrer *et al.*, *R. Soc. Chem. Adv.* **2015**, *5*, 6758-6770.
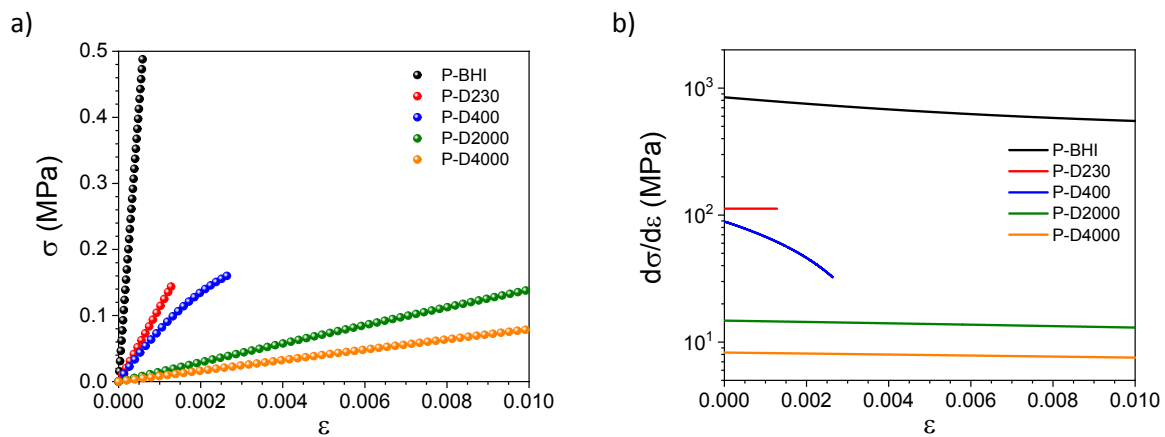
Figure S12. a) TSS experiments at T = 20 °C and $\dot{\varepsilon}$ = 1.66 10^{-4} s^{-1} for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI). b) Derivative curves for the evaluation of the elastic modulus, E', at the zero strain value.

Table S1. Molar mass (M_n), diffusion coefficient (D), hydrodynamic radius (R_h), the radius of gyration (R_g), and Stokes-Einstein scaling factor (f), for the four diaminoterminated polypropylene oxide polymers (J-D230, J-D400, J-D2000 and J-D4000), the four aliphatic polyisocyanates (A-D230, A-D400, A-D2000 and A-D4000), and the reference triisocyanate (A-BHI).

sample	M_n (g/mol)	%	D (cm²/s)	R_h (nm)	R_g (nm)	f
A-BHI	505	100	4.80E-06	0.85	1.10	0.9828
J-D230	240	100	8.56E-06	0.50	0.65	0.9448
J-D400	460	100	5.65E-06	0.73	0.95	0.9757
J-D2000	2056	100	2.35E-06	1.72	2.24	0.9964
J-D4000	4000	100	1.16E-06	3.46	4.50	0.9992
A-D230 [a]	1249	66.95	3.21E-06	1.27	1.65	0.9928
	2454	33.05	2.23E-06	1.81	2.35	0.9967
A-D400 [a]	1469	43.98	2.67E-06	1.52	1.97	0.9952
	2894	56.02	1.85E-06	2.18	2.83	0.9978
A-D2000 [a]	3065	2.31	1.05E-06	3.85	5.00	0.9994
	6086	97.69	8.31E-07	4.85	6.30	0.9996
A-D4000 [a]	5009	0.04	9.38E-07	4.30	5.59	0.9995
	9974	99.96	7.56E-07	5.33	6.93	0.9997

[a] The low molar mass value corresponds to the targeted adhesive molecule, and the high molar mass value to the dimer.

Table S2. DMA peak maxima of the relaxation processes (T_β, $T_{g,x}$ and $T_{g,PPO}$) from the loss factor profile, tan δ, at the frequency values of 0.1, 1, 10 and 70 Hz for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI).

	T_β (°C)				$T_{g,x}$ (°C)				$T_{g,PPO}$ (°C)			
sample	0.1 Hz	1 Hz	10 Hz	70 Hz	0.1 Hz	1 Hz	10 Hz	70 Hz	0.1 Hz	1 Hz	10 Hz	70 Hz
P-BHI	-87.1	-74.8	-62.1	-49.7	-45.9	-34.0	-21.3	11.2				
P-D230	-99.2	-87.4	-79.1	-62.6	-40.5	-29.3	-12.9	-4.6	38.4	42.2	46.4	62.1
P-D400	-100.0	-86.4	-72.4	-60.5	-27.8	-21.5	-11.6	-2.4	32.6	37.2	43.2	58.0
P-D2000	-106.0	-93.2	-85.7	-79.4	-15.3	-6.8	2.1	45.8	-55.6	-52.5	-48.5	-43.6
P-D4000	-100.8	-98.7	-92.3	-80.0	-	-	-	-	-64.7	-61.0	-58.2	-55.1

Table S3. DMA peak maxima of the relaxation processes (T_β, $T_{g,x}$ and $T_{g,PPO}$) from the loss modulus profile, E", at the frequency values of 0.1, 1, 10 and 70 Hz for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI).

	T_β (°C)				$T_{g,x}$ (°C)				$T_{g,PPO}$ (°C)			
sample	0.1 Hz	1 Hz	10 Hz	70 Hz	0.1 Hz	1 Hz	10 Hz	70 Hz	0.1 Hz	1 Hz	10 Hz	70 Hz
P-BHI	-87.7	-77.4	-64.0	-50.7	-43.9	-33.6	-22.2	10.7				
P-D230	-98.6	-86.0	-77.2	-60.4	-46.0	-37.1	-19.9	5.8	29.3	34.6	37.4	41.0
P-D400	-97.6	-84.0	-70.8	-57.9	-39.2	-27.8	-8.5	9.8	25.1	28.4	34.2	38.1
P-D2000	-94.2	-86.1	-75.1	-79.2	-26.6	-17.5	-8.5	-3.2	-59.7	-56.3	-52.9	-49.3
P-D4000	-	-	-	-	-19.7	-6.1	5.5	16.9	-68.2	-65.5	-62.1	-59.0

Table S4. DMA peak maxima of the removal of hydrogen bonds (T_{HB}) from the loss factor profile, tan δ, and from the loss modulus profile, E", at the frequency values of 0.1, 1, 10 and 70 Hz for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI).

sample	T_{HB} (°C) from tan δ				T_{HB} (°C) from E"			
	0.1 Hz	1 Hz	10 Hz	70 Hz	0.1 Hz	1 Hz	10 Hz	70 Hz
P-BHI	79	80	78	70	68	72	72	62
P-D230	79	79	79	81	73	71	69	70
P-D400	72	82	83	83	72	82	84	77
P-D2000	71	71	77	67	39	44	46	50
P-D4000	65	64	66	53	46	40	38	44

Table S5. Storage (E') and loss (E") modulus, as well as loss factor (tan δ) from the DMA frequency-sweep experiments for the four aliphatic polyurea networks (P-D230, P-D400, P-D2000 and P-D4000) and the reference polyurea network (P-BHI).

sample	E' (GPa)		E" (GPa)		tan δ	
	0.1 Hz	1 Hz	0.1 Hz	1 Hz	0.1 Hz	1 Hz
P-BHI	1.166	1.172	0.0259	0.0288	0.022	0.025
P-D230	0.574	0.812	0.176	0.163	0.307	0.201
P-D400	0.316	0.525	0.131	0.151	0.415	0.288
P-D2000	0.0163	0.0177	$6.50 \ 10^{-4}$	$9.21 \ 10^{-4}$	0.040	0.052
P-D4000	0.0107	0.0125	0.00166	0.00269	0.155	0.215

Modified Stejskal-Tanner function
$$I = I_0 e^{-\left[D\left(\Delta - \delta/3\right)(\gamma\delta G)^2\right]^{\beta}}$$
(Eq. S1)

Stokes-Einstein equation
$$D = \frac{k_B T}{6f\pi\eta R_h}$$
(Eq. S2)

Scaling factor function
$$f = \frac{1}{1 + 0.695\left(\frac{R_{solvent}}{R_h}\right)^{2.234}}$$
(Eq. S3)

Fox-Flory empirical function
$$T_g = T_g^{\infty} + \frac{k}{M_c}$$
(Eq. S4)