

Supplementary Information

The role of chain-end association life time in segmental and chain dynamics of telechelic polymers

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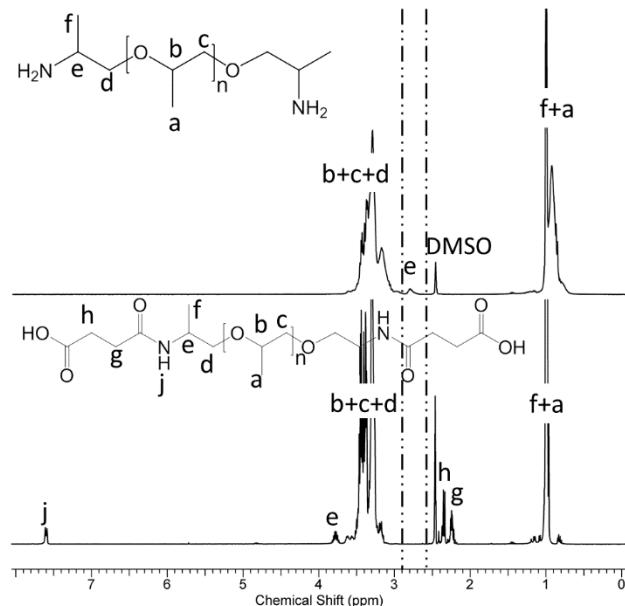


Figure S1. ¹H NMR spectra and chemical structure of (a) PPG-NH₂ and (b) PPG-COOH polymers with *DP* = 33 in DMSO. The dash-dotted lines indicate the region of peak e before the downfield shift corresponding to the end modification.

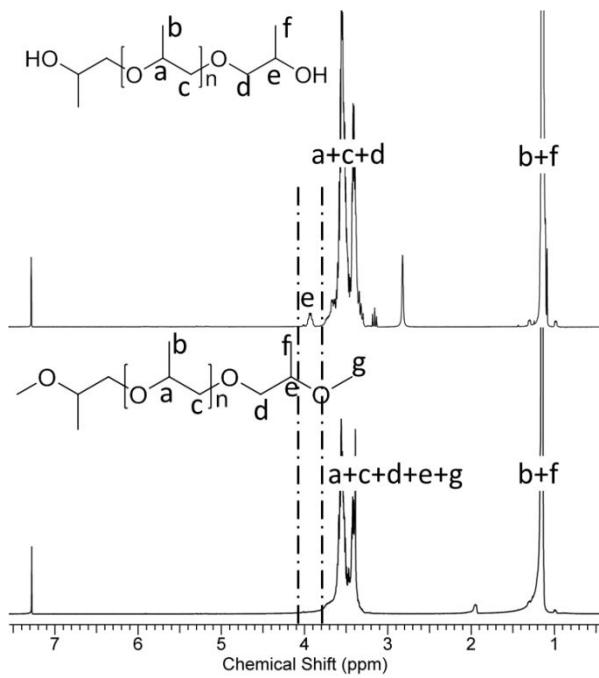


Figure S2. ¹H NMR spectra of (a) PPG-OH and (b) PPG-CH₃ polymers with $DP = 37$ in CDCl₃. The dash-dotted lines indicate the region of peak e before the downfield shift corresponding to the end modification.

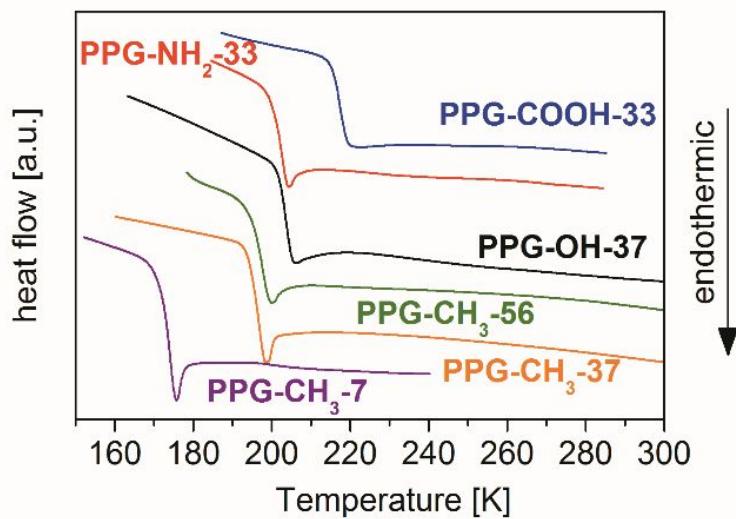


Figure S3. Calorimetric heat flow curves of PPG-COOH, PPG-NH₂, PPG-OH and PPG-CH₃ measured with a constant heating rate $q = 10$ K/min for different DP, as indicated. For clarity, the original curves are shifted vertically.

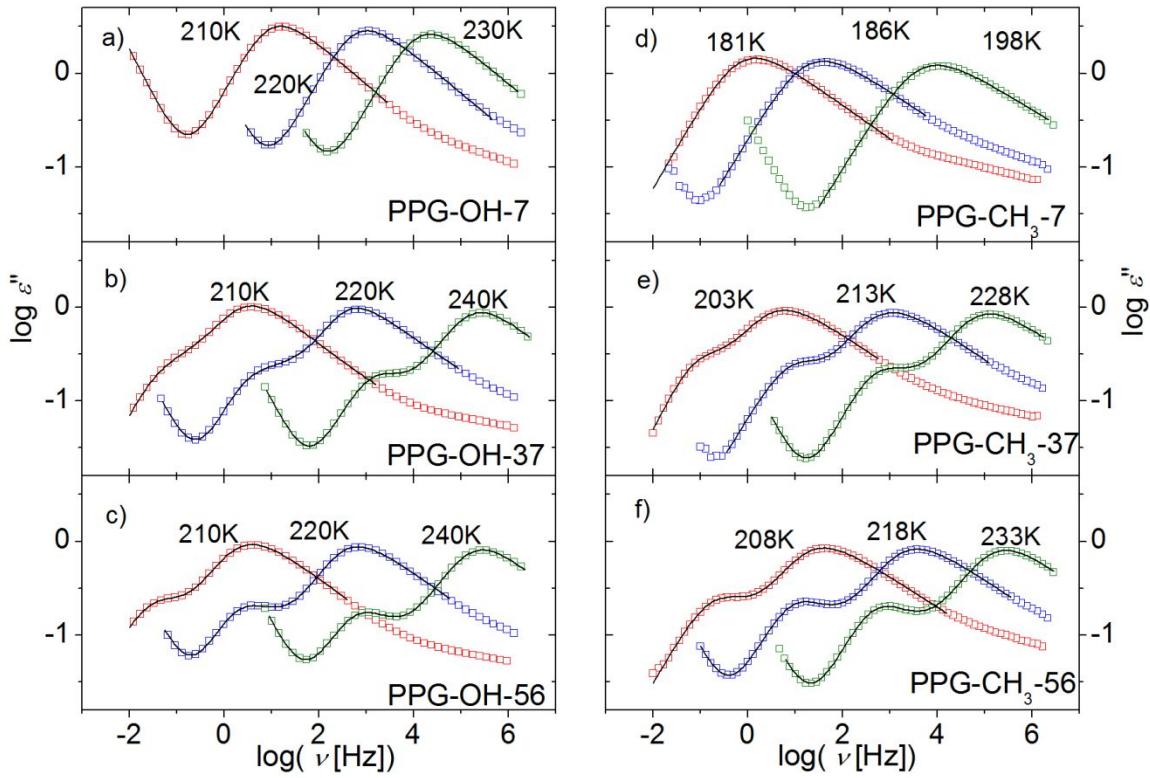


Figure S4. Dielectric loss spectra $\epsilon''(\nu)$ (symbols) at several temperatures as indicated of PPG-OH with DP of 7 (a), 37 (b) and 56 (c) and PPG-CH₃ with DP of 7 (d), 37 (e) and 56 (f). The solid lines are fits to functions consisting of one/two HN functions and a conductivity contribution (eq. 1 of the manuscript).

Table T1. Mean relaxation times of the α -relaxation (τ_α) and normal mode (τ_{NM}) of PPG-CH₃ as determined from fits of eq. 1 to the dielectric loss spectra $\epsilon''(\nu)$ and conversion via eq. 2.

PPG-CH ₃ -7		PPG-CH ₃ -37			PPG-CH ₃ -56		
T[K]	τ_α [s]	T[K]	τ_α [s]	τ_{NM} [s]	T[K]	τ_α [s]	τ_{NM} [s]
175.56	6.36	200.65	1.21e-1	5.65	203.15	7.69e-2	6.77
178.15	7.45e-1	203.15	2.45e-2	1.19	208.15	3.58e-3	5.85 e-1
180.65	1.12e-1	208.15	1.40e-3	1.18e-1	213.15	3.03e-4	6.46 e-2
183.15	1.93e-2	213.15	1.38e-4	1.54e-2	218.15	4.13e-5	1.13 e-2
185.65	4.16e-3	218.15	2.16e-5	2.94e-3	223.15	7.69e-6	2.53e-3
188.15	1.06e-3	223.15	4.57e-6	7.07e-4	228.15	1.79e-6	6.91e-4
190.65	3.49e-4	228.15	1.20e-6	2.01e-4	233.15	5.55e-7	2.16e-4
193.15	1.07e-4	233.15	3.82e-7	6.69e-5	238.15	2.06e-7	7.64e-5
198.15	1.61e-5	238.15	1.55e-7	2.44e-5	243.15	8.89e-8	3.13e-5

203.15	3.17e-6	243.15	6.50e-8	9.79e-6	248.15	4.27e-8	1.42e-5
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Table T2. Mean relaxation times of the α -relaxation (τ_α) and normal mode (τ_{NM}) of PPG-OH as determined from fits of eq. 1 to the dielectric loss spectra $\varepsilon''(\nu)$ and conversion via eq. 2.

T[K]	PPG-OH-7		PPG-OH-37		PPG-OH-56	
	τ_α [s]	τ_α [s]	τ_{NM} [s]	τ_α [s]	τ_{NM} [s]	
210	1.02e-2	3.89e-2	8.96e-1	3.98e-2	3.89	
212	3.65e-3	1.10e-2	3.41e-1	1.16e-2	1.22	
216	6.50e-4	1.39e-3	7.28e-2	1.31e-3	2.24e-1	
220	1.52e-4	2.41e-4	1.29e-2	2.30e-4	4.77e-2	
224	4.17e-5	5.43e-5	5.04e-3	4.75e-5	1.21e-2	
228	1.22e-5	1.36e-5	1.59e-3	1.27e-5	3.49e-3	
232	4.16e-6	4.07e-6	5.46e-4	3.77e-6	1.14e-3	
238	1.08e-6	9.08e-7	1.34e-4	8.30e-7	2.74e-4	
244	3.23e-7	2.63e-7	3.83e-5	2.44e-7	8.06e-5	
250	1.25e-7	8.97e-8	1.25e-5	8.72e-8	2.62e-5	

Table T3. Mean relaxation times of the α -relaxation (τ_α) and normal mode (τ_{NM}) of PPG-NH₂ as determined from fits of eq. 1 to the dielectric loss spectra $\varepsilon''(\nu)$ and conversion via eq. 2.

T[K]	PPG-NH₂-6		PPG-NH₂-33		PPG-NH₂-67	
	τ_α [s]	τ_α [s]	τ_{NM} [s]	τ_α [s]	τ_{NM} [s]	
210	3.61e-4	8.03e-3	1.78e-1	2.09e-2	6.59	
212	1.57e-4	2.79e-3	5.65e-2	5.74e-3	2.25	
214	7.14e-5	1.05e-3	6.43e-2	2.02e-3	8.29e-1	
216	3.19e-5	4.07e-4	1.51e-2	7.46e-4	3.55e-1	
218	1.70e-5	1.81e-4	1.43e-2	3.02e-4	1.64e-1	
222	4.84e-6	3.65e-5	3.52e-3	6.24e-5	3.94e-2	
226	1.53e-6	9.42e-6	1.10e-3	1.48e-5	1.09e-2	
230	6.05e-7	2.81e-6	3.82e-4	4.19e-6	3.58e-3	
234	2.38e-7	1.01e-6	1.44e-4	1.39e-6	1.29e-3	
240	6.82e-8	2.77e-7	3.89e-5	3.68e-7	3.47e-4	

Table T4. Mean relaxation times of the α -relaxation (τ_α) and α^* -relaxation (τ_{α^*}) of PPG-COOH as determined from fits of eq. 1 to the dielectric loss spectra $\varepsilon''(\nu)$ and conversion via eq. 2, and the mean relaxation time of the normal mode (τ_{NM}) for PPG-COOH-67 as determined from fits of a modified form of eq. 5 (see ref. 90 of the manuscript) to the derivative spectra of the permittivity $\partial\varepsilon'(\omega)/\partial\ln\omega$ and conversion via eq. 2.

T[K]	PPG-COOH-6	T[K]	PPG-COOH-33		PPG-COOH-67	
	τ_{α^*} [s]		τ_α [s]	τ_{α^*} [s]	τ_α [s]	τ_{α^*} [s]
258	5.51e-1	224	3.42e-2	1.93	3.96e-4	1.75e-2
262	9.01e-2	226	1.02e-2	6.75e-1	1.64e-4	7.02e-3
268	9.36e-3	228	4.47e-3	2.58e-1	7.29e-5	3.09e-3

275	1.01e-3	230	1.63e-3	1.06e-1	3.41e-5	1.47e-3	7.03e-2
283	1.53e-4	232	6.49e-4	4.68e-2	1.69e-5	7.45e-4	3.94e-2
291	3.27e-5	234	3.49e-4	2.26e-2	8.55e-6	5.29e-4	2.47e-2
299	8.24e-6	236	1.68e-4	1.11e-2	4.49e-6	2.87e-4	1.58e-2
307	2.40e-6	240	3.92e-5	3.06e-3	1.46e-6	8.87e-5	5.58e-3
315	8.92e-7	244	1.05e-5	9.48e-4	5.69e-7	2.87e-5	2.04e-3
325	2.91e-7	250	1.86e-6	2.04e-4	1.59e-7	7.36e-6	6.74e-4