Supporting Information

Association and Relaxation of Supra-Macromolecular Polymers

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Size Exclusion Chromatography (SEC)

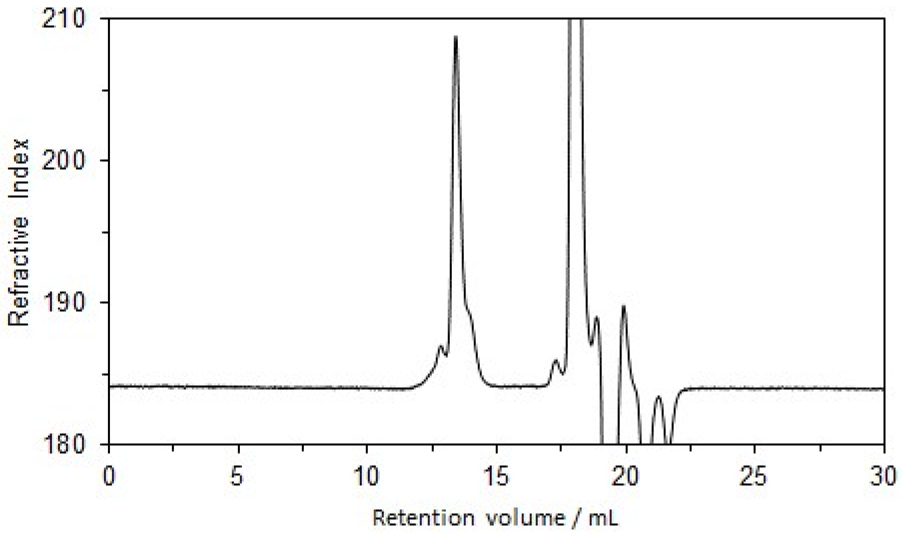

Figure S1: SEC of UPy1

Fig. S1 shows a representative SEC sample, for UPy1. The sample was measured using a Viscotek TDA 302 instrument. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}, and the M_w calibrated with PBd standards. M_w was determined to be 27,800 Da, and M_n was 21,000 Da. SEC data for all samples is reported in Table 1 in the main text.

Differential scanning calorimetry (DSC)

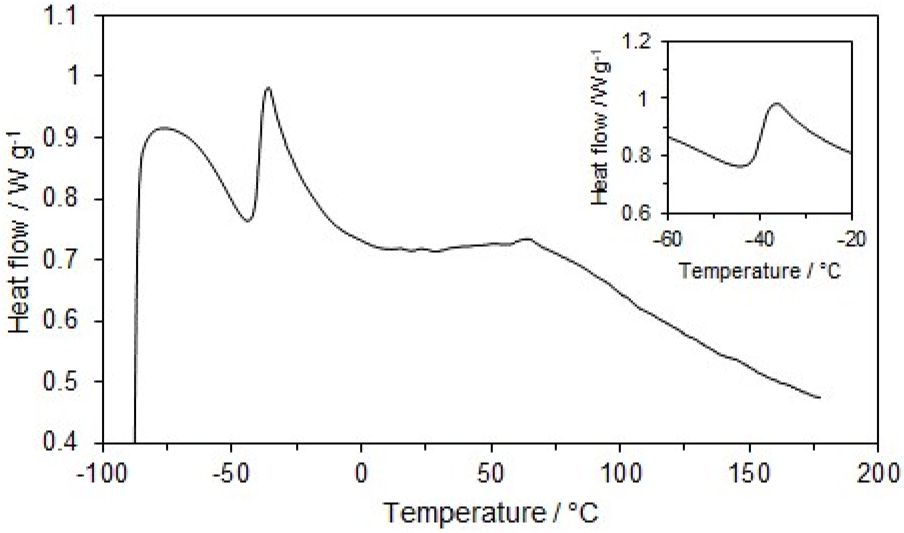

Figure S2: DSC heating curve of UPy1. Inset highlights the glass transition.

Fig. S2 shows a representative DSC curve, of UPy1, determined using a TA instruments Q1000. Samples were subjected to a heating and cooling cycle at a rate of 10 °C min^{-1} from -90 – 180 °C. The glass transition (T_g) was taken as the inflection point of the heat flow curve, analysed using the TA Universal Analysis software. The T_g was determined to be -39.6 °C.

Creep Recovery Spectra

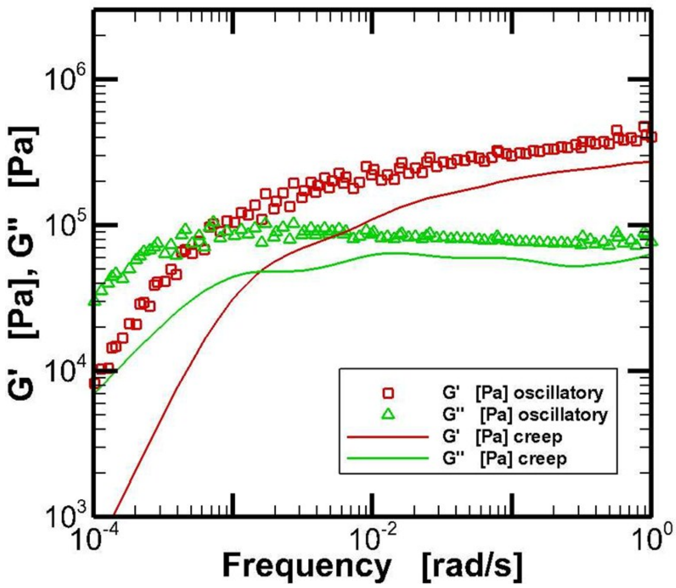

Figure S3: Creep recovery spectra (lines) of UPy1 at 25 °C, and comparison with TTS shifted oscillatory data (see main text)

Fig. S3 shows a comparison between the creep recovery spectra of UPy1 at 25 °C and the corresponding oscillatory data, TTS shifted as described in the main text. The creep recovery data was collected by first applying a constant stress of 2000 Pa for 10 minutes to the sample using an 8 mm parallel plate, equipped with a peltier plate. The stress was then removed and the strain recovery monitored for ~ 10,000 s. A discrete retardation spectra[1] was then fitted to the recovery data, using the TA Rheology Advantage Data Analysis software:

$$J_r(t) = \sum_{k-1}^{N} J_k\left(1 - exp\left(\frac{-t}{\lambda_k}\right)\right)$$

where λ_k is the retardation time and J_k the retardation strength. The fitted parameters are shown in Table S1:

Table S1: Retardation spectrum paprameters fitted to creep relaxation data

λ_k	J_k	η_0	J_0
s	Pa^{-1}	Pa s	Pa^{-1}
721.9	2.86×10^{-6}	1.19×10^{8}	4.45×10^{-11}
97.2	2.68×10^{-6}		
8.2	1.46×10^{-6}		
1.75	1.08×10^{-7}		
0.23	2.18×10^{-6}		
8.04×10^{-3}	1.32×10^{-6}		

The corresponding viscoelastic data can then be determined from the creep recovery.[1] Firstly the storage and loss compliance (*J′* and *J″* respectively) are calculated from the retardation spectrum as a function of frequency (ω):

$$J^{'}(\omega) = J_0 + \sum_{k-1}^{N} J_k \frac{1}{1 + \omega^2 \lambda_k^2}$$

$$J^{''}(\omega) = \frac{1}{\omega \eta_0} \sum_{k-1}^{N} J_k \frac{\omega \lambda_k}{1 + \omega^2 \lambda_k^2}$$

From this the storage and loss moduli (*G′* and *G″* respectively) are calculated:

$$G^{'}(\omega) = \frac{J'(\omega)}{\{J'(\omega)\}^2 + \{J''(\omega)\}^2}$$

$$G^{''}(\omega) = \frac{J''(\omega)}{\{J'(\omega)\}^2 + \{J''(\omega)\}^2}$$

The corresponding data is shown in Fig. S3, and is compared with the time temperature superposition (TTS) oscillatory data. A good match between the TTS and creep recovery data is seen, given the differences in technique. This shows that despite the fanning in the TTS data it remains a good representation of the viscoelastic properties of UPy1.

Multimode Modelling

Table S2: Multi-mode modelling fit parameters for extensional data of UPy1 at 25 °C

		Maxwell fit		Pom-Pom	Stretch Rolie-Poly	
Mode	Type	τ_{di} (s)	G_i (Pa)	τ_d/τ_s	τ_s (s)	*q* arms
1	Pom-pom	10000	6294	12	-	15
2	Pom-pom	3511	33763	15	-	10
3	Stretch Rolie-Poly	1233	111611	-	0.6	-
4	Stretch Rolie-Poly	433	60893	-	0.5	-
5	Stretch Rolie-Poly	152	47484	-	0.4	-
6	Non-stretch Rolie-Poly	53.4	50531		-	-
7	Non-stretch Rolie-Poly	18.7	47484		-	-
8	Non-stretch Rolie-Poly	6.6	46031		-	-
9	Non-stretch Rolie-Poly	2.3	44622		-	-
10	Non-stretch Rolie-Poly	0.81	48810		-	-
11	Non-stretch Rolie-Poly	0.28	55470		-	-
12	Non-stretch Rolie-Poly	0.10	103302		-	-

References

1 J. D. Ferry, *Viscoelastic properties of polymers*, Wiley, 1980.