Polymer Conformation Determination by NMR Spectroscopy: Comparative Diffusion Ordered ^{1}H-NMR Spectroscopy of Poly(2-Ethyl-2-Oxazoline)s and Poly(Ethylene Glycol) in D_2O

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Electronic Supplementary Information

Supplementary Tables

Table S1: Molecular weight characterisation of the PEG used in this study. ND = not determined (insufficient signal in the MALS for resolution from baseline).

Nominal	SEC-RI (vs PMMA)				SEC-MALS				Corrected SEC-RI			
kDa	M_n	M_w	Đ	M_p	M_n	M_w	Đ	M_p	M_n	M_w	Đ	M_p
2	2.4	3.2	1.30	2.1	ND	ND	ND	ND	**1.4**	**1.8**	**1.30**	**1.2**
5	7.5	10.1	1.35	7.0	ND	ND	ND	ND	**4.2**	**5.7**	**1.35**	**4.0**
10	16.3	19.3	1.19	14.5	ND	ND	ND	ND	**9.2**	**10.9**	**1.19**	**8.2**
20	32.5	34.9	1.07	33.4	**21.4**	**22.5**	**1.05**	**19.2**	18.4	19.7	1.07	18.9
40	77.9	104.8	1.34	68.9	**48.2**	**58.0**	**1.20**	**38.3**	44.0	59.2	1.34	38.9

Table S2: Comparison of peak characteristics determined by (a) SEC-MALS and (b) from the positive projection (Fig 4, right) being processed via a log-log relationship derived from the M_p of the P(EtOx).

	SEC-MALS[a]				DOSY[b]			
Nominal MW	M_n	M_w	M_p	Đ	M_n	M_w	M_p	Đ
10 kDa	10.5	11	10.7	1.05	9.5	9.6	9.3	1.01
20 kDa	18	18.8	18.7	1.04	18	18.5	17.6	1.03
30 kDa	29.1	30.3	30	1.04	34.6	34.7	34.4	1
40 kDa	41.4	43.4	43	1.05	45.9	48.2	45.5	1.05
50 kDa	54.3	57.6	57.9	1.06	ND	ND	ND	ND
60 kDa	56.2	62.5	66	1.11	68.8	77.9	66.4	1.13
100 kDa	95.2	107.6	108.7	1.13	123.8	125.1	124	1.01
200 kDa	183.2	216.5	215.9	1.18	216.2	249.9	208.5	1.16
300 kDa	287.4	330.5	366.1	1.15	318.4	332.4	319.5	1.04

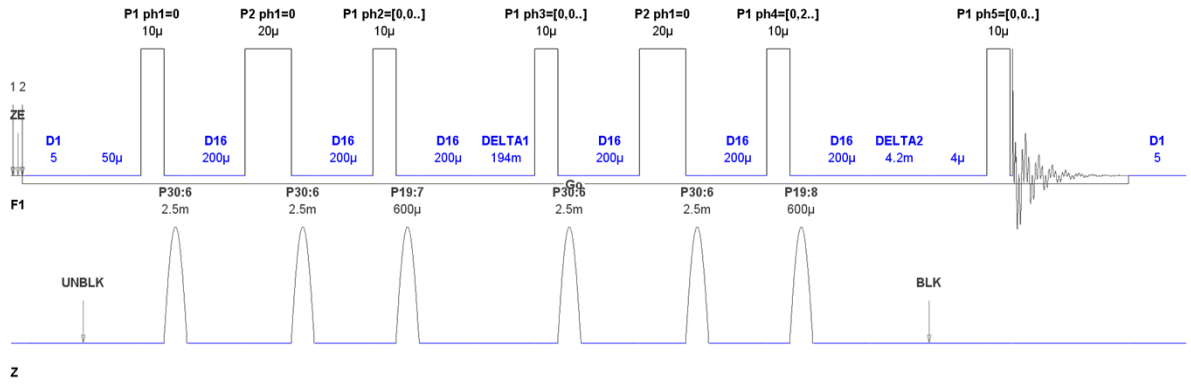
Table S3: The constants and exponents for diffusion coefficient (eq. 1a), intrinsic viscosity (eq. 1b) and hydrodynamic radius (eq. 1c) of P(EtOx) at different temperatures.

	Diffusion (eq. 1a)		IV (eq. 1b)		R_H (eq. 1c)	
Temp (K)	c	-b	K_η	α	K_H	*v*
278	9.25E-09	0.598	1.03E-08	0.792	1.18E-02	0.597
283	9.36E-09	0.594	1.21E-08	0.807	1.24E-02	0.603
288	1.19E-08	0.599	1.57E-08	0.782	1.36E-02	0.594
293	1.20E-08	0.581	2.28E-08	0.733	1.54E-02	0.578
298	1.38E-08	0.557	1.97E-08	0.734	1.46E-02	0.578
303	1.57E-08	0.560	2.26E-08	0.677	1.53E-02	0.559

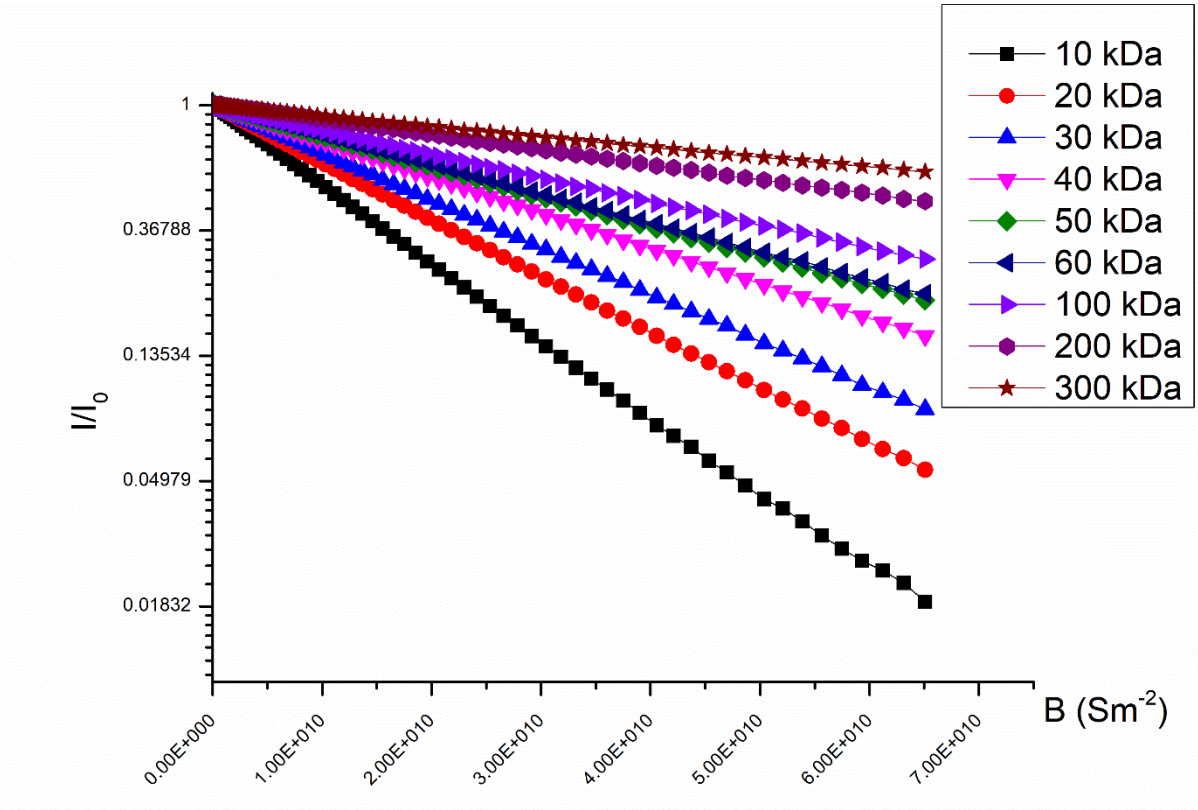
Table S4: The constants and exponents for diffusion coefficient (eq. 1a), intrinsic viscosity (eq. 1b) and hydrodynamic radius (eq. 1c) of PEG at different temperatures. The highest M_W (59.2 kDa) was excluded as off-trend at 283 K, apparently due to helix formation.

	Diffusion (eq. 1a)		IV (eq. 1b)		RH (eq. 1c)	
Temp (K)	c	-b	K	α	K_H	*v*
283	4.95E-09	0.537	1.10E-07	0.5992	2.59E-02	0.5331
288	5.01E-09	0.513	1.65E-07	0.5437	2.97E-02	0.5146
293	6.10E-09	0.516	1.71E-07	0.5388	3.01E-02	0.5113
298	5.69E-09	0.489	3.03E-07	0.4633	3.63E-02	0.4978
303	6.57E-09	0.488	3.42E-07	0.4513	3.79E-02	0.4818

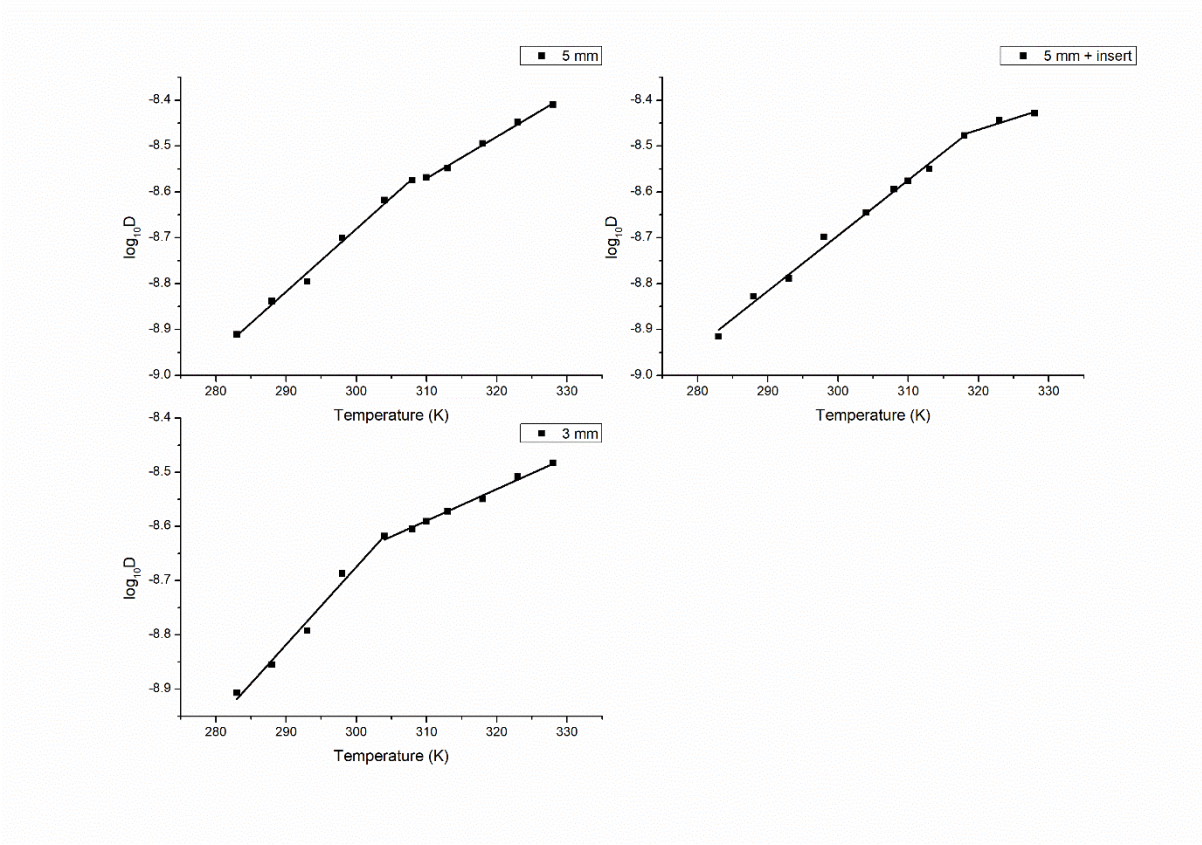
Supplementary Figures



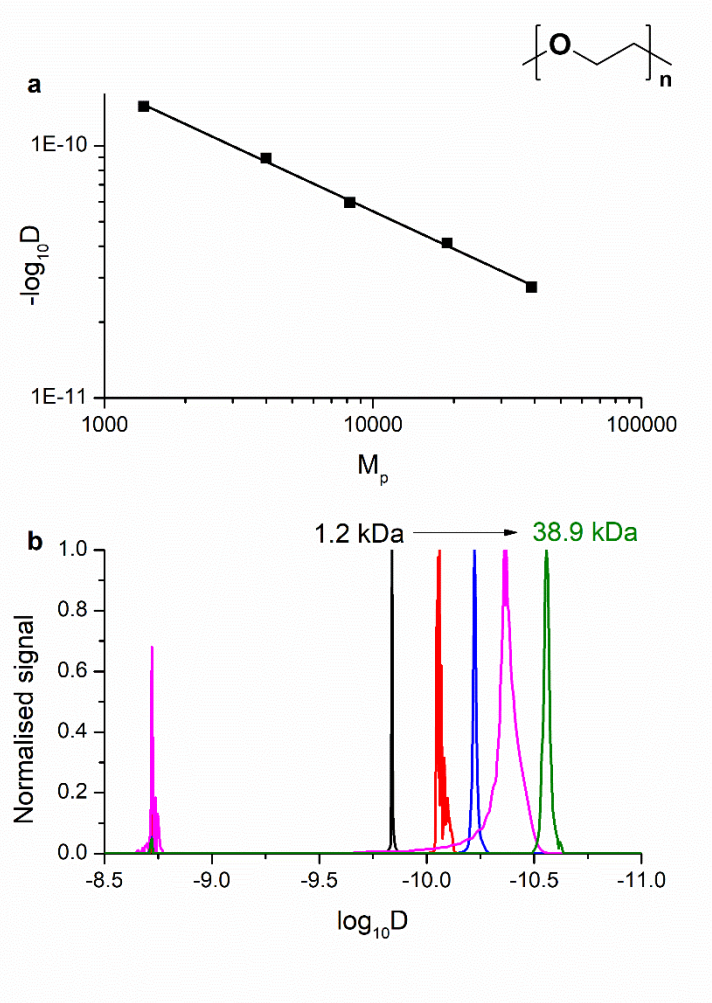
Supplementary Figure S1: The pulse sequence (ledbpg2s) used in this work.



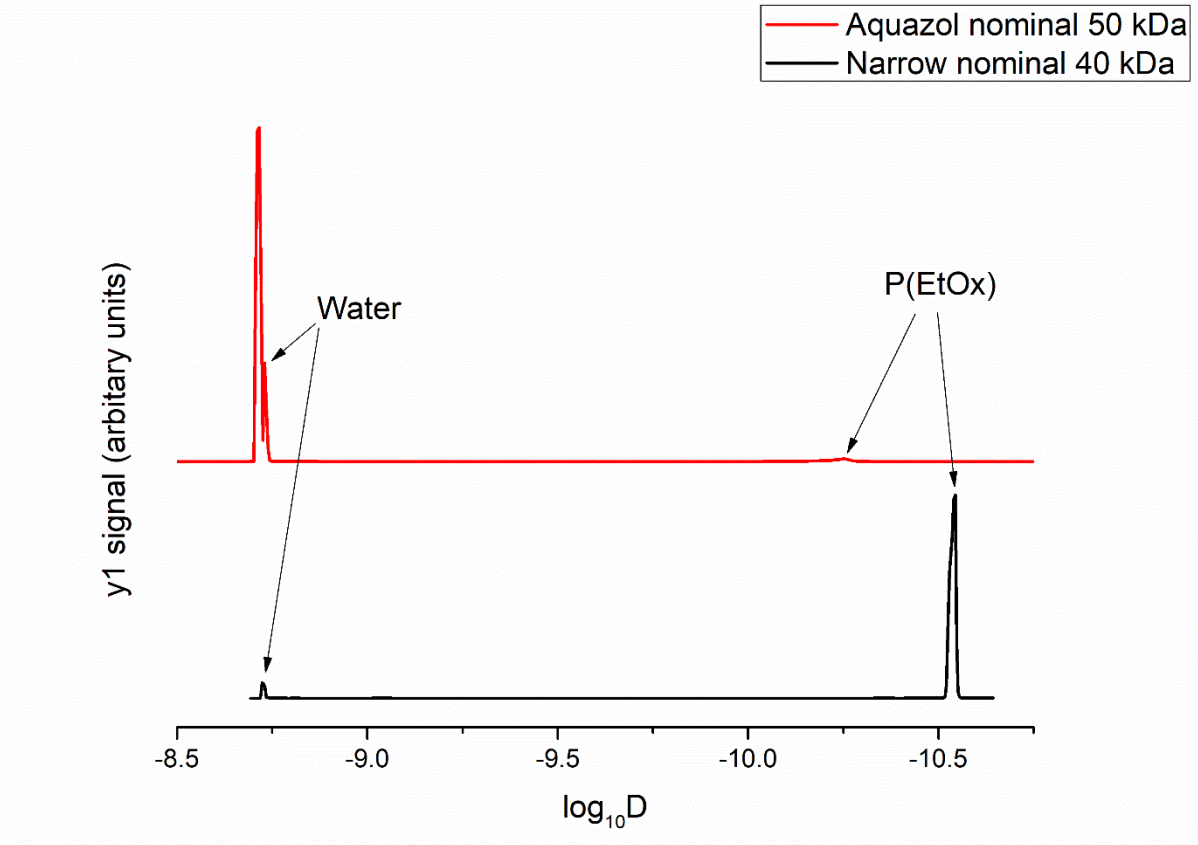
Supplementary Figure S2: Stejskal-Tanner plot for all P(EtOx) at 298 K. The slope is the diffusion coefficient. M_W are nominal.



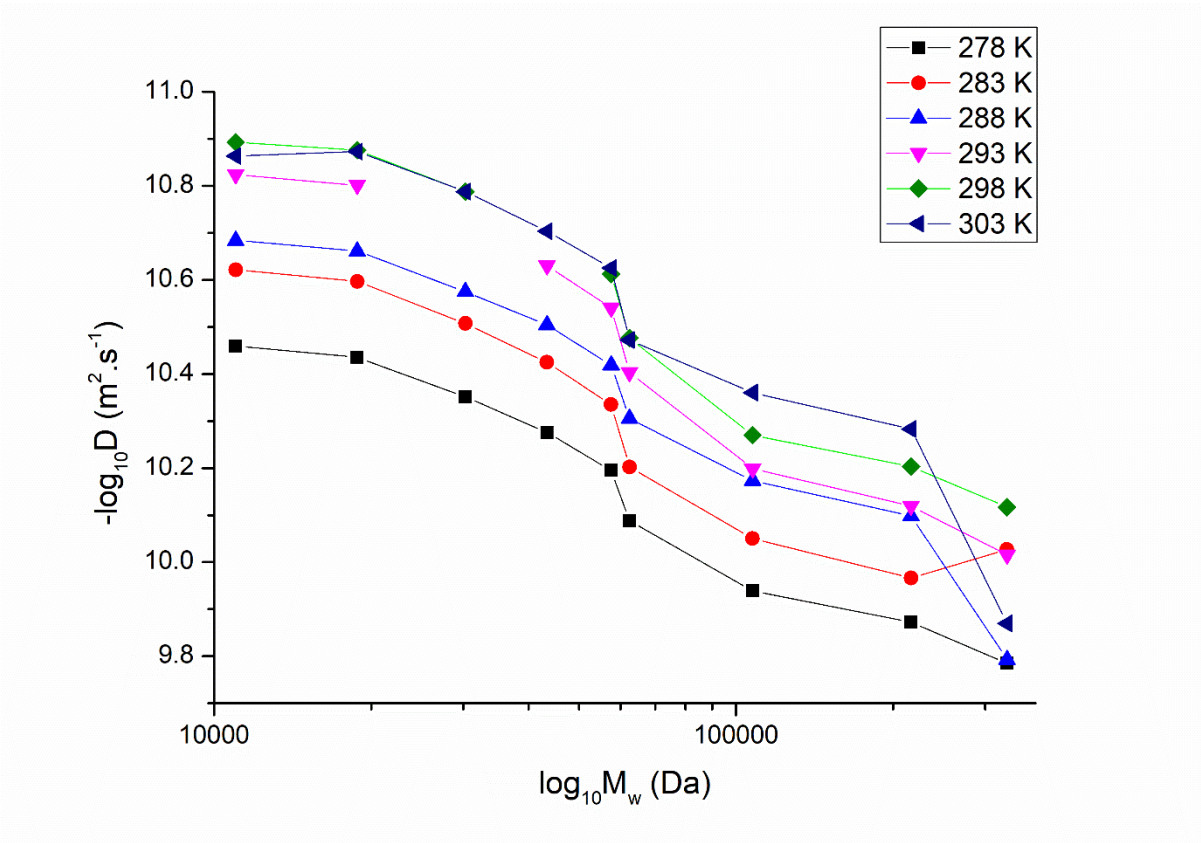
Supplementary Figure S3: Effect of tube size and type on the self-diffusion coefficient of water at varying temperatures. In all cases and inflexion point was observed, which was interpreted as the onset of convection currents.



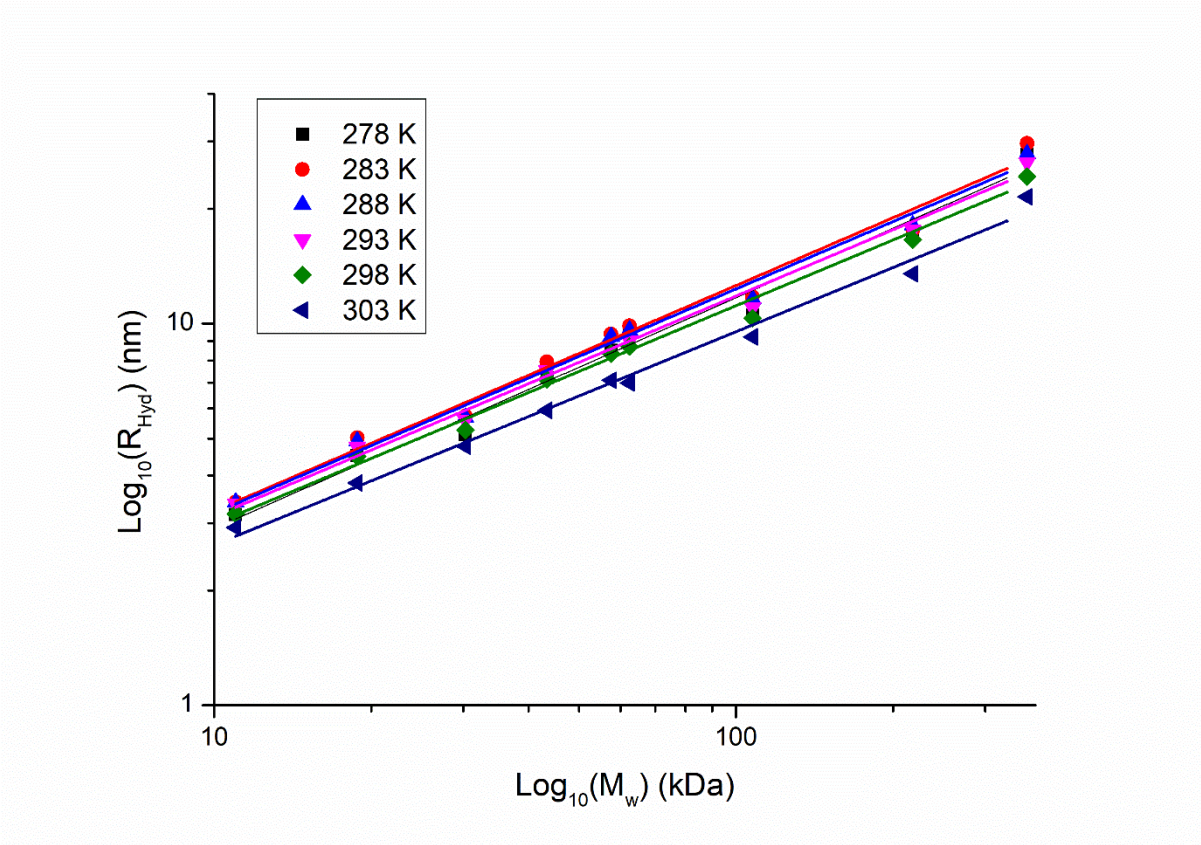
Supplementary Figure S4: Equivalent figure to fig. 4 for PEG at 25 °C. (a) Relationship of D with M_p (adj. r^2 = 0.9978, intercept = -8.2789, slope = 0.4952). (b) The positive projection along the x1 axis of DOSY for PEG of M_p 1.2 kDa to 38.9 kDa. High resolution DOSY was not performed with PEG, as the dispersity was not a primary concern.



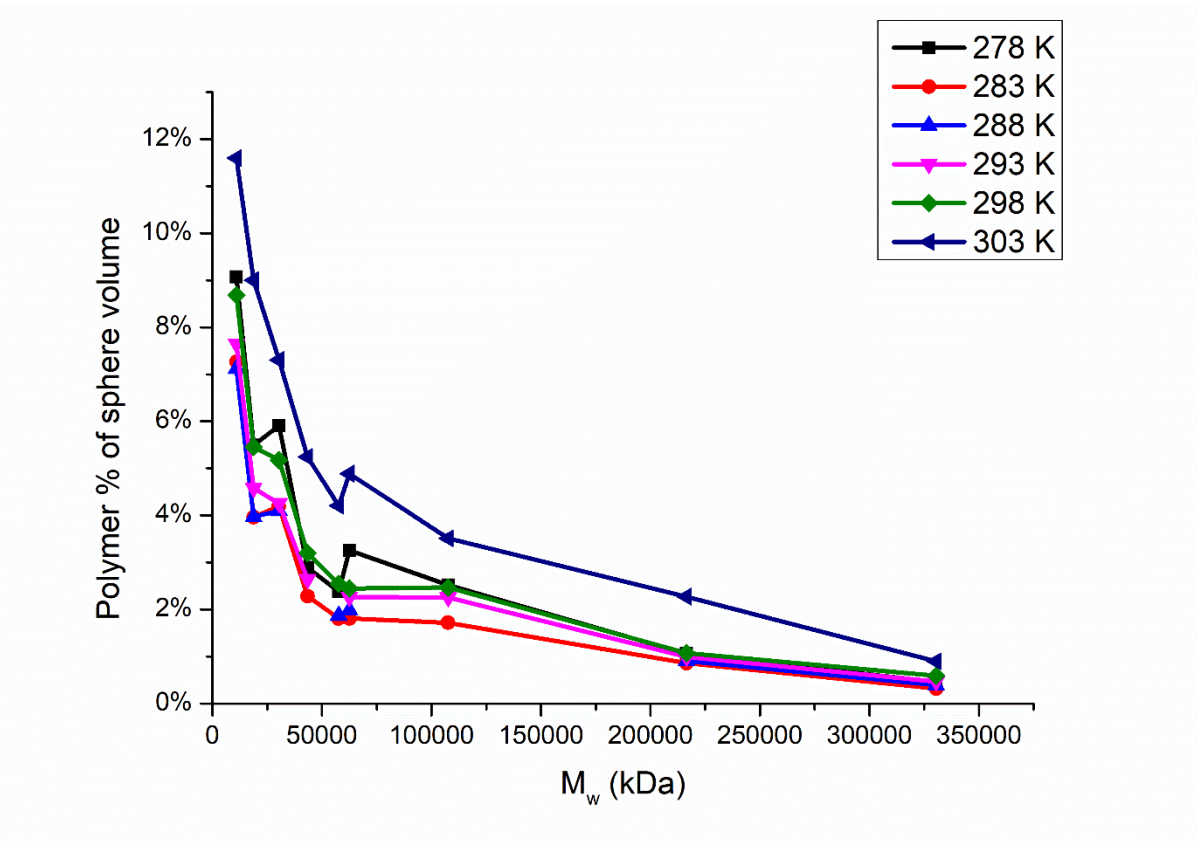
Supplementary Figure S5: Comparison of the weak and broad Aquazol 50 signal in the y1 (diffusion) dimension and a narrow dispersity P(EtOx) of nominally 40 kDa.



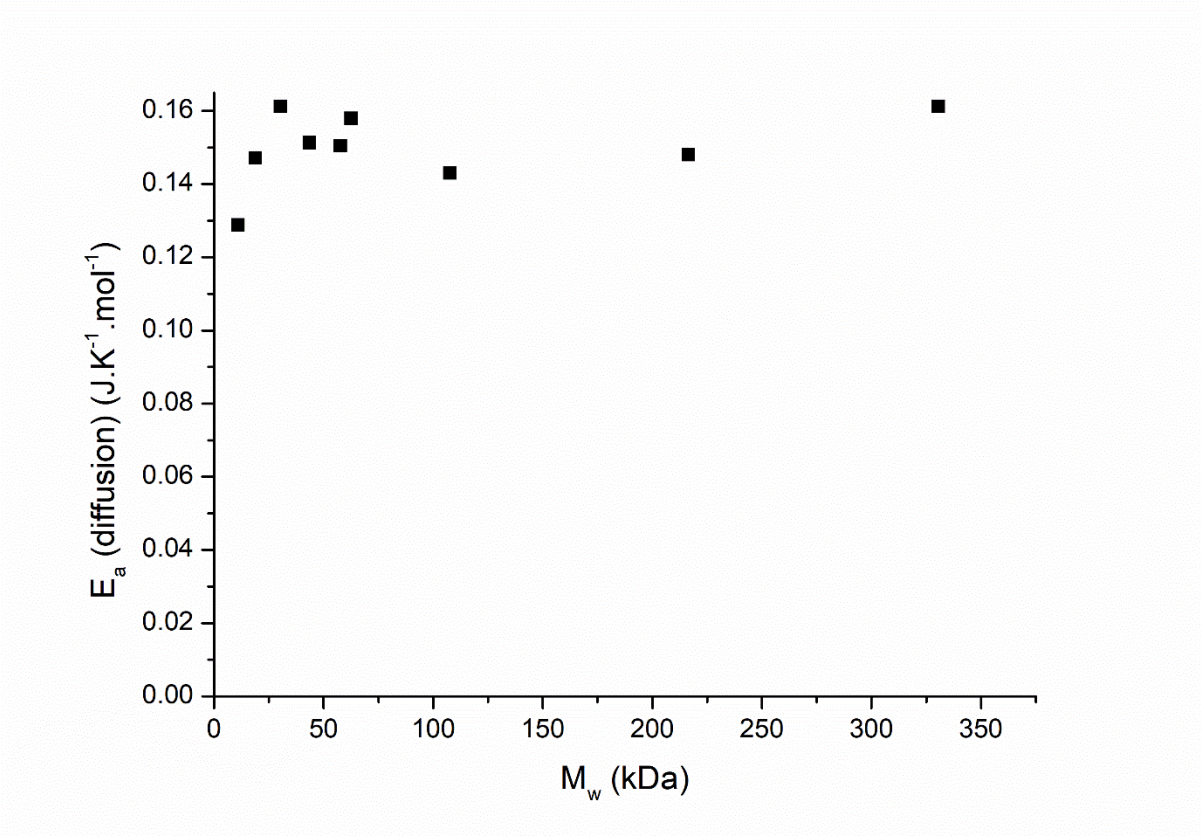
Supplementary Figure S6: $-\log_{10}D$ plotted against M_w for varying temperatures. A linear fit is not reasonable.



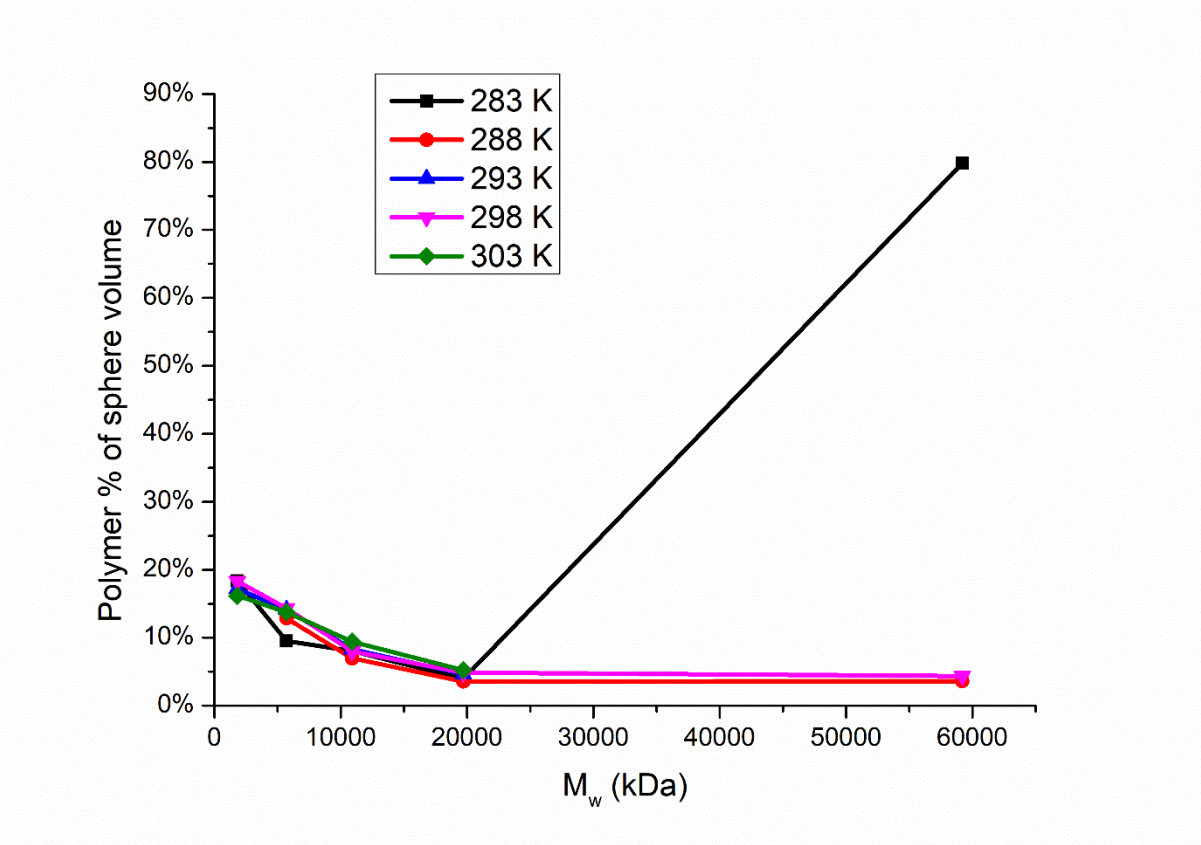
Supplementary Figure S7: Relationship of log(M_w) of a series of P(EtOx) to their hydrodynamic radius



Supplementary Figure S8: Assuming a spherical volume, the volume of the sphere that is P(EtOx), with the remainder being water.



Supplementary Figure S9: Activation energy of diffusion determined by the Arrhenius equation plotted against M_w.



Supplementary Figure S10: Assuming a spherical volume, the volume of the sphere that is PEG with the remainder being water. The M_w = 59.2 kDa PEG behaved anomalously at 283 K, which is attributed to helix formation.