Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information (ESI)

Molecular Weight Prediction with No Dependence on Solvent Viscosity. A Quantitative Pulse Field Gradient Diffusion NMR Approach.

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CONTENTS

Samples and reagents. Polystyrene samples (P1 to P7) were from Polymer Standards Service (Mainz, Germany). Tetrahydrofuran-d_8 (THF-d_8), toluene-d_8 (Tol-d_8) benzene-d_6 (C_6D_6) and chloroform-d_1 ($CDCl_3$) were purchased from Eurisotop (Saint-Aubin, France). THF-d_8 and Tol-d_8 were dried over K/benzophenone, reflux and vacuum transferred onto 3 Å molecular sieves prior to use. C_6D_6 and $CDCl_3$ were dried over CaH_2 and vacuum transferred onto 3 Å molecular sieves prior to use. All other reagents and solvents were of commercial quality and were used without further purification.

NMR Spectroscopy. All measurements were performed on a Bruker Avance III 500 spectrometer equipped with a microprocessor-controlled gradient unit and a third radiofrequency channel using an indirect 5 mm TBI $^1H/^{31}P/BB$ triple probe with an actively shielded Z-gradient coil. The spectral reference used was internal tetramethylsilane for ^1H The shape of the gradient pulse was sinusoidal, and its strength varied automatically in the course of the experiments. The calibration of the gradients on each spectrometer was carried out via a diffusion measurement of HDO in D_2O at ambient temp. The D value of each sample can then be calculated according to the following equation, where $D_{HDO} = 1.9\ 10^{-9}\ m^2\ s^{-1}$.[1]

$$D_{P1-P7} = \frac{m_t}{m_{HDO}} D_{HDO}$$

The m_t parameter is calculated for each measurement from the observed slope, slope, with the help of the next equation, which takes into account the settings for the diffusion delay Δ, the gradient length δ, as well as the nature of the observed nucleus $\gamma_{P1\text{-}P7}$, with respect to the calibration with HDO.

$$m_t = \frac{slope}{\left(\frac{\gamma_{P1-P7}}{\gamma_{HDO}}\right)^2 \left(\frac{\delta_{P1-P7}}{\delta_{HDO}}\right)^2 \frac{\left(\Delta - \frac{\delta}{4}\right)_{P1-P7}}{\left(\Delta - \frac{\delta}{4}\right)_{HDO}}}$$

For polystyrene standard samples (P1 to P7), each NMR tube contained 0.9 mg and 1 mL C_6D_6. The Δ values were 150 ms for P1-P6 and 200 ms for P7. The δ values were 2.75 (P1), 3.2 (P2), 3.75 (P3), 5.0 (P4), 8.0 (P5) and 11 ms (P6-P7), respectively. The gradient strength was incremented in 4% steps, so that 23 points could be used for regression analysis. The recovery delay was set to 10s. The number of scans per increment were 64 and typical experimental times were around 6.5 h. All experiments were run without spinning to avoid convection. The standard Bruker pulse program, stegp1s, employing a stimulated echo sequence with monopolar pulses and 1 spoil gradient was utilized. Gradient recovery delays were 0.2 ms. To check reproducibility, three different measurements with the same parameters (δ and Δ) were always carried out. All LMS diffusion processing was performed by using the DiffAtOnce software package available at www.diffatonce.com.[2] All of the data leading to the reported *D* values afforded lines whose correlation coefficients were above 0.9999. ITAMeD solutions were obtained by the use of the algorithm provided by Urbanczyk et al.[3] In the ITAMeD the numer of iterations was set to 10.000 and the sparsity-promoting l1 to 10-5.

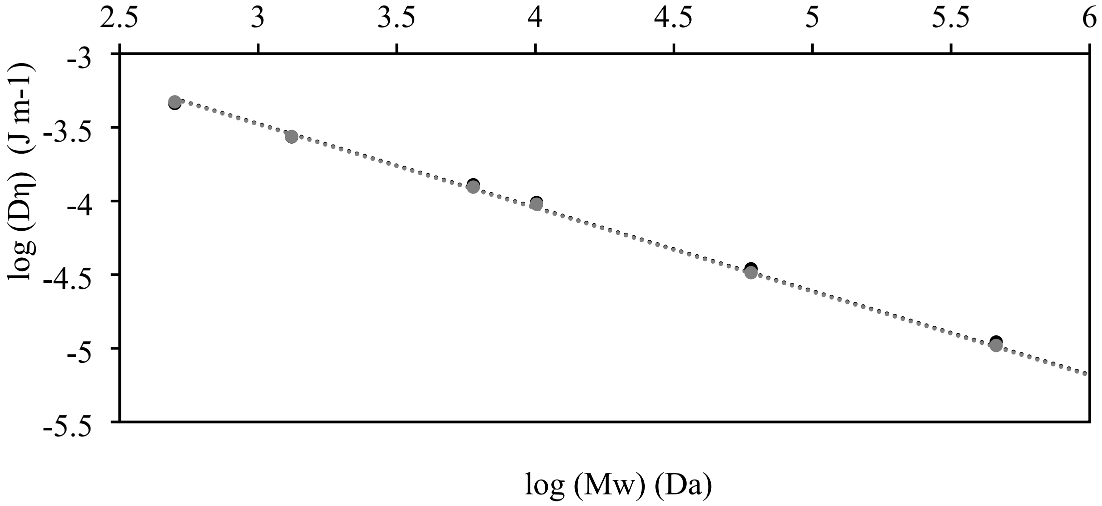


Figure S1. Universal Calibration Curves (UCC) for Mw prediction.

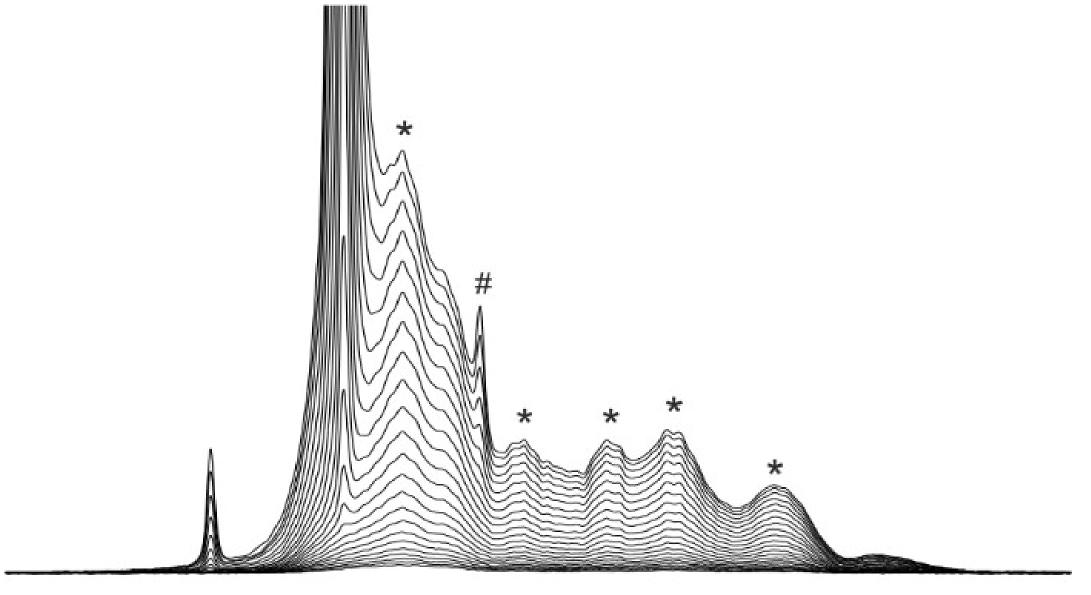


Figure S2. Raw PFG-STE data showing the aromatic region of sample P2 in benzene-d_6, showing with an asterisk the five monitored signals and with # the one overlapped with the benzene satellite.

Table S1. ITAMeD Diffusion values (m^2 s^{-1}) and Mw UCC-predicted for P2 and P6 in four different solvents.

	Mw predicted (Da)[a]	**D (10^{-9}) ITAMeD**	**diff (%)[a]**
P2$_{\text{BENZENE}}$	1396	0.4245	5.8
P2$_{\text{THF}}$	1260	0.5978	4.5
P2$_{\text{CDCL3}}$	1386	0.4902	5.0
P2$_{\text{TOLUENE}}$	1409	0.4745	6.7
P6$_{\text{BENZENE}}$	437746	0.0162	4.8
P6$_{\text{THF}}$	422510	0.0222[b]	8.1
P6$_{\text{CDCL3}}$	422712	0.0192[b]	8.1
P6$_{\text{TOLUENE}}$	414482	0.0190[b]	9.8

[a] Molecular weight of commercial P2 is 1320 Da and molecular weight of commercial P6 is 460000 Da. These measurements were done at 295 K.

Table S2. Predicted Mw for the residual non-deuterated solvent for each sample of P2.

Solvent	**D (10^{-10} m^2 s^{-1})[a]**	**Dη (10^{-3}) (J m^{-1})**	**Mw (Da)[b]**	**diff (%)**
Benzene-d_6	21.19	1.3687	82.5	5.6
THF-d_8	28.14	1.4127	82.5	8.1
$CDCl_3$	25.20	1.414	77.72	34.9
Toluene-d_8	22.04	1.2667	94.43	2.5

a ^1H PFG-STE measurements were performed at room temperature. b Estimated via the ITAMeD universal calibration curve $y = -0.5682x - 1.775$ ($R^1 = 0.9993$).

Table S3. Viscosity values at 21ºC employed in all the calculations.[a]

	A	**B**	**C**	**D**	**T (K)**	**η (kg $m^{-1}s^{-1}$)**
Benzene-d_6	-7.4005	1181.5	0.014888	-0.000013713	294	0,000645628
THF-d_8	-2.7860	476.81	0.004917	-0.000006881	294	0.000486048
$CDCl_3$	-4.7831	699.02	0.010929	-0.000012244	294	0.000561465
Toluene-d_8	-5.1649	810.68	0.010454	-0.000010488	294	0.000574712

a log η = A + B/T + CT + DT2, from www.knovel.com.

Formulation of equation 5 (manuscript)

The Einstein-Stokes equation is

$$D = \frac{k_B T}{6\pi\eta r_H} \qquad \text{(S1)}$$

Equation S1, is actually a simplified law which applied in the particular case of spherical particles of colloidal dimension (much higher than that of the solvent) in a fluid continuum.[4] The general Stokes-Einstein law is given by S2 where $c(r_{sl}, R_h)$ is a coefficient that depends on the ratio between the hydrodynamic radius of the solvent, r_{sl}, and that of the particle, R_h, whereas fs is a correction factor that takes into account the shape of the molecule. When the radius of the molecule is at least five times larger than that of the solvent, the $c(r_{sl},R_h)$ coefficient equals 6.[5]

$$D = \frac{k_B T}{c(r_{sl}, R_h) f_s \pi\eta r_H} \qquad \text{(S2)}$$

Since the variations in enthalpy are due to thermal differences, the Stokes-Einstein equation can be rewritten as

$$\eta D \propto \frac{k_B T}{r_H} = cte \qquad \text{(S3)}$$

According to Pollack's relationship S4 between the viscosity and the diffusion coefficient,[6] which is an empirical relation between diffusion coefficient and viscosity in the diluted concentration regime, we can derived equation S4 in energy terms

$$D = K\eta^{-\beta} \qquad \text{(S4)}$$

$$\eta^{\beta} D = \frac{k_B T}{c(r_{sl}, r_H) f_s(a,b) r_H} \qquad \text{(S5)}$$

Operating in the left side of equation S5 in order to give $(\eta D)^{\beta}$ as a function of the hydrodynamic radius, and employing equation S4, we obtain equations S6 and S7

$$\eta^{\beta}D = \eta^{\beta}D\frac{D^{\beta}}{D^{\beta}} = \eta^{\beta}D^{\beta}\frac{D}{D^{\beta}} = \eta^{\beta}D^{\beta}\frac{K\eta^{-\beta}}{(K\eta^{-\beta})^{\beta}} = (\eta D)^{\beta}\frac{(K\eta^{-\beta})}{(K^{\beta}\eta^{-\beta^{2}})} = (\eta D)^{\beta}(K^{1-\beta}\eta^{\beta(\beta-1)}) \tag{S6}$$

$$(\eta D)^{\beta} = \frac{k_BT}{c(r_{sl},r_H)f_s(a,b)K^{1-\beta}\eta^{\beta(\beta-1)}r_H} \tag{S7}$$

To estimate molecular weights we need to write the hydrodynamic radius as function of molecular weight as has been already reported (equation S8),[7] to get equation S8

$$M_W = N_A\rho V = N_A\rho\frac{4}{3}\pi R_h^3;\ r_H^3 = \frac{3M_w}{4\rho N_A\pi} \tag{S8}$$

$$(\eta D)^{\beta} = \frac{k_BT}{c(r_{sl},r_H)f_s(a,b)K^{1-\beta}\eta^{\beta(\beta-1)}\left(\frac{3M_W}{4\rho N_A\pi}\right)^{1/3}} \tag{S9}$$

Flory scaling relationship (equation S10 and S11)[8] is probably the most direct relation between Mw and diffusion coefficient.[9] Delsuc and coworkers have checked the validity of this power law equation for a large set of molecular types and molecular weights, introducing α as a measure of the fractal dimension d_F (= 1/α).[10]

$$D = AM_w^{-\alpha} \tag{S10}$$

$$\log(D) = -\alpha\log(M_w) + A \tag{S11}$$

If we apply logarithms in both sides of equation S9, we obtain the equation S12 derived in this contribution, allowing the straightforward representation of log(□D) versus logMw.

$$\log(\eta D) = -\frac{1}{3\beta}\log(M_W) - \frac{1}{\beta}\log\left(\frac{c(r_{sl},r_H)f_s(a,b)K^{1-\beta}\eta^{\beta(\beta-1)}\left(\frac{3}{4\rho N_A\pi}\right)^{1/3}}{k_BT}\right) \tag{S12}$$

To give parallelism between the Flory scaling relationship and our equation S12 we can write the following equivalences:

$$\eta D = \left(\frac{k_B T}{c(r_{sl}, r_H) f_s(a,b) K^{1-\beta} \eta^{\beta(\beta-1)} \left(\frac{3}{4\rho N_A \pi}\right)^{1/3}}\right)^{1/\beta} M_w^{-1/(3\beta)} \equiv A' M_w^{-\frac{1}{3\beta}} \equiv A' M_w^{-\alpha}$$

In equation S12 one can substitute the c(r_{sl}, r_H) factor of the second term by a function of r_{sl} and r_H based on microfriction theory (equations S14 or S15), and as a function of MW and MW_{sl} based on equation S8.

$$c = 6\left[\left[\frac{3r_{sl}}{2r_H}\right] + \left(1 + \frac{r_{sl}}{r_H}\right)^{-1}\right]^{-1} \qquad \text{(S14)}$$

$$c = 6\left[1 + 0.695\left(\frac{r_{sl}}{r_H}\right)^{2.234}\right]^{-1} \qquad \text{(S15)}$$

When one uses S15, the aforementioned substitutions yield equation S16.

$$\log(\eta D) = -\frac{1}{3\beta}\log\left(\frac{M_W}{\left(1 + 0.695\left(\frac{M_{Wsl}\rho_H}{M_W\,\rho_{sl}}\right)^{\frac{2.234}{3}}\right)^3}\right) - \frac{1}{\beta}\log(6\pi H)$$

$$H = \frac{f_s(a,b) K^{1-\beta} \eta^{\beta(\beta-1)} \left(\frac{3}{4\rho N_A \pi}\right)^{1/3}}{k_b T} \qquad \text{(S16)}$$

Using equation S16, for large molecules such as polymers (MW >> MW_{sl}) the c factor is 6 as has been described previously, and the equation is reduced to S17.

$$\log(\eta D) = -\frac{1}{3\beta}\log(M_W) - \frac{1}{\beta}\log\left(\frac{6\pi f_s(a,b) K^{1-\beta} \eta^{\beta(\beta-1)} \left(\frac{3}{4\rho N_A \pi}\right)^{\frac{1}{3}}}{k_b T}\right) \qquad \text{(S17)}$$

For small molecules such as solvents (MW ~ MW_{sl}), the ratio (MW_{sl} / MW) in S16 is approximately 1, and we obtain S18, where again, there is no dependence with the molecular weight in the second term.

$$\log(\eta D) = -\frac{1}{3\beta}\log(M_W) - \frac{1}{\beta}\left(\log\left(\frac{6\pi}{1.695}H\right)\right) \qquad \text{(S17)}$$

In both situations only the first term meets dependence with the molecular weight as it is mentioned in the manuscript.

Table S4. LMS D-values (m^2 s^{-1}) for polymers P1-P7, predicted molecular weight (Da) and errors (%).

	Mw	**Log(Mw)**	**D (10^{-9}) DiffAtOnce**	**LOG(Dη)**	**Mw Predicted**	**diff (%)a**
P1	500	2.69897	0.7119	-3.33759845	572	14.4
P2	1320	3.12057	0.4224	-3.56429353	1438	8.7
P3	5970	3.77597	0.1997	-3.88963938	5369	10.1
P4	10100	4.00432	0.1512	-4.01046565	8763	13.2
P5	60000	4.77815	0.0537	-4.46004316	54267	9.6
P6	460000	5.66276	0.0171	-4.95702133	407271	11.5
P7	1020000	6.0086	0.0088	-5.24553477	1312362	28.7

a Average error of 13.7 %.

Table S5. ITAMeD D-values (m^2 s^{-1}) for polymers P1-P7, predicted molecular weight (Da) and errors (%).

	Mw	**Log(Mw)**	**D (10^{-9}) ITAMeD**	**LOG(Dη)**	**Mw Predicted**	**diff (%)a**
P1	500	2,69897	0.7299	-3.32675408	538	7.6
P2	1320	3,12057	0.4245	-3.56213975	1397	5.8
P3	5970	3,77597	0.1926	-3.90536116	5612	6.0
P4	10100	4,00432	0.1474	-4.02151996	8986	11.0
P5	60000	4,77815	0.0505	-4.48672606	59190	1.3
P6	460000	5,66276	0.0162	-4.98050243	437746	4.8
P7	1020000	6,0086	0.0094	-5.21688959	1140853	11.8

a Average error of 6.9 %.

Table S6. LMS D-values ($m^2\ s^{-1}$) for polymer P1.

ppm	Slope	Correction factor[a]	D (10^{-9})[b]	R^1
7.10	-5.1969	0.134422	0.70394	0.9999
7.08	-5.2805	0.134422	0.71526	0.9999
7.07	-5.3265	0.134422	0.72150	0.9999
7.05	-5.3449	0.134422	0.72400	0.9999
6.96	-5.5150	0.134422	0.74703	0.9999
6.94	-5.0140	0.134422	0.67917	0.9999
6.88	-5.1145	0.134422	0.69278	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.71195 $10^{-9}\ m^2\ s^{-1}$.

Table S7. ITAMeD D-values ($m^2\ s^{-1}$) for polymer P1.

ppm	Slope	Correction factor[a]	D (10^{-9})[b]
7.10	-5.2786	0.134422	0.7150
7.08	-5.2786	0.134422	0.7150
7.07	-5.2786	0.134422	0.7150
7.05	-5.2786	0.134422	0.7150
6.96	-5.7674	0.134422	0.7812
6.94	-5.6696	0.134422	0.7680
6.93	-5.2786	0.134422	0.7150
6.88	-5.2786	0.134422	0.7150

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.7299 $10^{-9}\ m^2\ s^{-1}$.

Table S8. LMS D-values ($m^2\ s^{-1}$) for polymer P2.

ppm	Slope	Correction factor[a]	D (10^{-9})[b]	R^1
7.10	-4.1844	0.099348	0.41891	0.9999
7.08	-4.2157	0.099348	0.42204	0.9999
7.07	-4.2019	0.099348	0.42065	0.9999
7.05	-4.1855	0.099348	0.41902	0.9999
6.96	-4.2023	0.099348	0.42076	0.9999
6.94	-4.1939	0.099348	0.41986	0.9999
6.93	-4.2679	0.099348	0.42727	0.9999
6.88	-4.2995	0.099348	0.43043	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.42237 $10^{-9}\ m^2\ s^{-1}$.

Table S9. ITAMeD D-values (m^2 s^{-1}) for polymer P2.

ppm	**Slope**	**Correction factor**[a]	**D (10^{-9})**[b]
7.10	-4.2033	0.099348	0.4208
7.08	-4.2033	0.099348	0.4208
7.07	-4.2033	0.099348	0.4208
7.05	-4.1056	0.099348	0.4208
6.96	-4.1056	0.099348	0.4208
6.94	-4.3011	0.099348	0.4306
6.93	-4.3988	0.099348	0.4404
6.88	-4.2033	0.099348	0.4208

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.4245 10^{-9} m^2 s^{-1}.

Table S10. LMS D-values (m^2 s^{-1}) for polymer P3.

ppm	**Slope**	**Correction factor**[a]	**D (10^{-9})**[b]	**R^1**
7.10	-2.66254	0.072409	0.19427	0.9999
7.08	-2.69912	0.072409	0.19694	0.9999
7.07	-2.71807	0.072409	0.19832	0.9999
7.05	-2.77177	0.072409	0.19976	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.19973 10^{-9} m^2 s^{-1}.

Table S11. ITAMeD D-values (m^2 s^{-1}) for polymer P3.

ppm	**Slope**	**Correction factor**[a]	**D (10^{-9})**[b]
7.10	-2.6393	0.072409	0.1926
7.08	-2.6393	0.072409	0.1926
7.07	-2.6393	0.072409	0.1926
7.05	-2.7370	0.072409	0.1927
6.96	-2.7370	0.072409	0.1927
6.94	-2.7370	0.072409	0.1927

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.1926 10^{-9} m^2 s^{-1}.

Table S12. LMS D-values (m^2 s^{-1}) for polymer P4.

ppm	**Slope**	**Correction factor**[a]	**D (10^{-9})**[b]	**R^1**
7.10	-3.62695	0.006359	0.149175	0.9999
7.08	-3.66879	0.006359	0.150896	0.9999
7.07	-3.67748	0.006359	0.151254	0.9999
7.05	-3.68478	0.006359	0.151554	0.9999
6.71	-3.65978	0.006359	0.150526	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.15121 10^{-9} m^2 s^{-1}.

Table S13. ITAMeD D-values (m^2 s^{-1}) for polymer P4.

ppm	**Slope**	**Correction factor**^{a}	**D (10^{-9})**^{b}
7.10	-3.6168	0.006359	0.1488
7.08	-3.6168	0.006359	0.1488
7.07	-3.6168	0.006359	0.1488
7.05	-3.6168	0.006359	0.1488
6.95	-3.7146	0.006359	0.1447
6.71	-3.7146	0.006359	0.1447

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.14743 10^{-9} m^2 s^{-1}.

Table S14. LMS D-values (m^2 s^{-1}) for polymer P5.

ppm	**Slope**	**Correction factor**^{a}	**D (10^{-9})**^{b}	**R**^{1}
7.10	-3.23001	0.00858	0.052158	0.9999
7.08	-3.29689	0.00858	0.053237	0.9999
7.07	-3.30974	0.00858	0.053445	0.9999
7.05	-3.34107	0.00858	0.053951	0.9999
6.96	-3.38193	0.00858	0.054610	0.9999
6.94	-3.39453	0.00858	0.054615	0.9999
6.71	-3.32081	0.00858	0.054814	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.05369 10^{-9} m^2 s^{-1}.

Table S15. ITAMeD D-values (m^2 s^{-1}) for polymer P5.

ppm	**Slope**	**Correction factor**^{a}	**D (10^{-9})**^{b}
7.10	-3.0792	0.00858	0.0497
7.08	-3.4213	0.00858	0.0521
7.07	-3.4213	0.00858	0.0521
6.96	-3.0792	0.00858	0.0497
6.94	-3.0792	0.00858	0.0497
6.71	-3.0792	0.00858	0.0497

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.0505 10^{-9} m^2 s^{-1}.

Table S16. LMS D-values (m^2 s^{-1}) for polymer P6.

ppm	**Slope**	**Correction factor**^{a}	**D (10^{-9})**^{b}	**R**^{1}
7.10	-1.91895	0.006359	0.016473	0.9999
7.08	-1.96214	0.006359	0.016844	0.9999
7.07	-1.99802	0.006359	0.017152	0.9999
7.05	-2.02832	0.006359	0.017412	0.9999
6.71	-2.04627	0.006359	0.017566	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.017089 10^{-9} m^2 s^{-1}.

Table S17. ITAMeD D-values (m^2 s^{-1}) for polymer P6.

ppm	**Slope**	**Correction factor[a]**	**D (10^{-9})[b]**
7.10	-2.0528	0.008519	0.0176
7.08	-2.0528	0.008519	0.0176
7.07	-1.7107	0.008519	0.0147
6.71	-1.7107	0.008519	0.0147

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is is 0.0162 10^{-9} m^2 s^{-1}.

Table S18. LMS D-values (m^2 s^{-1}) for polymer P7.

ppm	**Slope**	**Correction factor[a]**	**D (10^{-9})[b]**	**R[1]**
7.10	-1.27292	0.006359	0.0081574	0.9999
7.08	-1.31067	0.006359	0.0083993	0.9999
7.07	-1.34919	0.006359	0.0086458	0.9999
7.05	-1.37937	0.006359	0.0088396	0.9999
6.71	-1.33708	0.006359	0.0085686	0.9999

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.008522 10^{-9} m^2 s^{-1}.

Table S19. ITAMeD D-values (m^2 s^{-1}) for polymer P7.

ppm	**Slope**	**Correction factor[a]**	**D (10^{-9})[b]**
7.10	-1.4663	0.006359	0.0094
7.08	-1.4663	0.006359	0.0094
7.07	-1.4663	0.006359	0.0094
7.05	-1.4663	0.006359	0.0094
6.71	-1.4663	0.006359	0.0094

a The correction factor is defined by (D_{HDO}/m_{HDO}) × (m_t/slope). b Average diffusion value is 0.0094 10^{-9} m^2 s^{-1}.

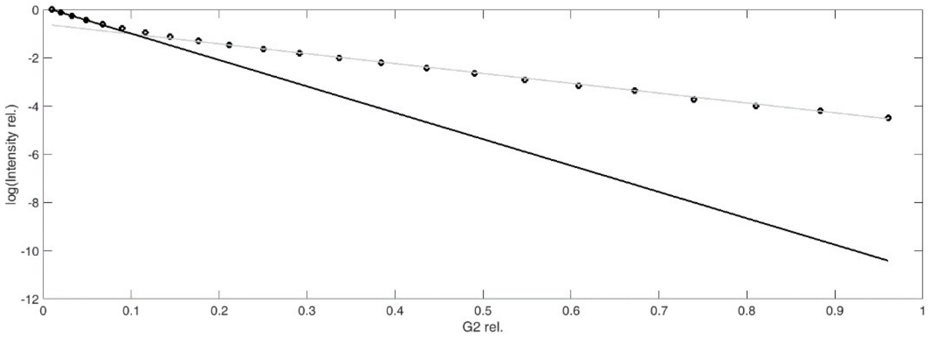


Figure S3. Ln(I/I$_0$) vs G^2 plot of signal at δ$_H$ 7.00 ppm (labelled with # in Figure S2) that is sum of polystyrene P2 and the benzene satellite.

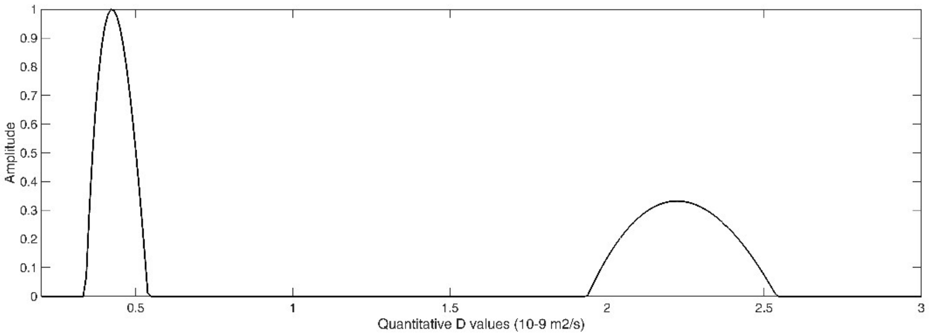


Figure S4. ITAMeD solution of signal at δ$_H$ 7.00 ppm (labelled with # in Figure S2) that is sum of polystyrene P2 and the benzene satellite. The obtained D values are 4.208 10^{-10} m^{2}s^{-1} for P2 and 22.215 10^{-10} m^{2}s^{-1} for chloroform.

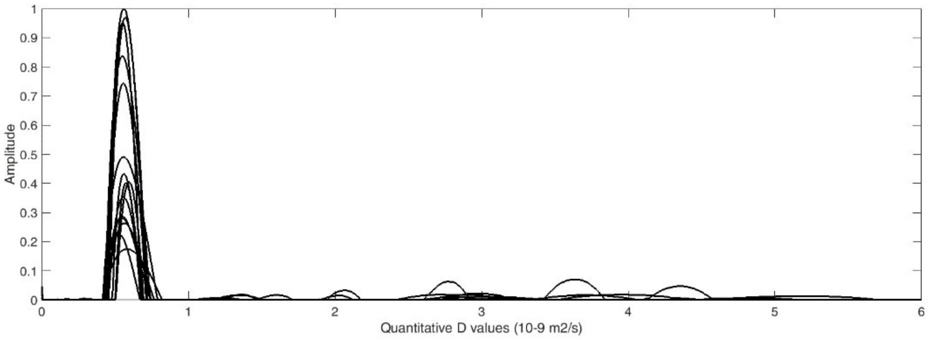


Figure S5. ITAMeD solution for P1 (500 Da), D-value of 0.7299 10^{-9} m^2s^{-1}. Minor peaks are due to polymeric entities of low polymer weight present at very low concentration that the ITAMeD algorithm can detect.

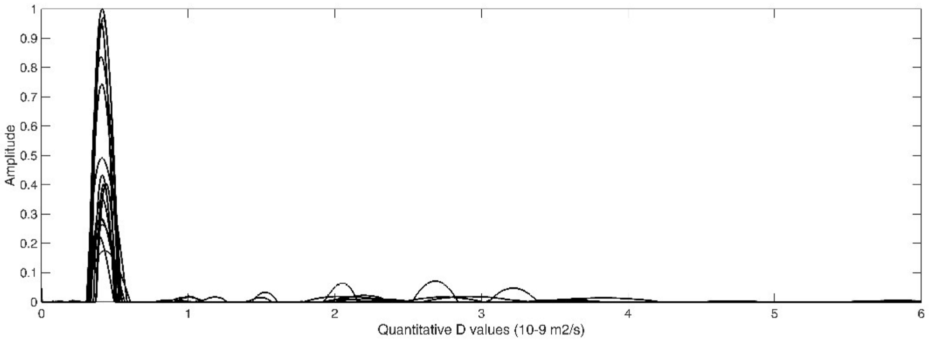


Figure S6. ITAMeD solution for polymer P2 (1320 Da), D-value of 0.4245 10^{-9} m^2s^{-1}. Minor peaks are due to polymeric entities of low polymer weight present at very low concentration that the ITAMeD algorithm can detect.

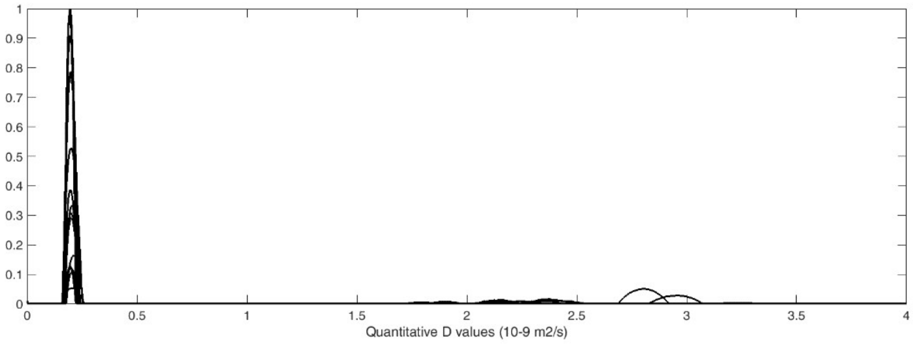


Figure S7. ITAMeD solution for polymer P3 (5970 Da), D-value of 0.1926 10^{-9} m^2s^{-1}. Minor peaks are due to polymeric entities of low polymer weight present at very low concentration that the ITAMeD algorithm can detect.

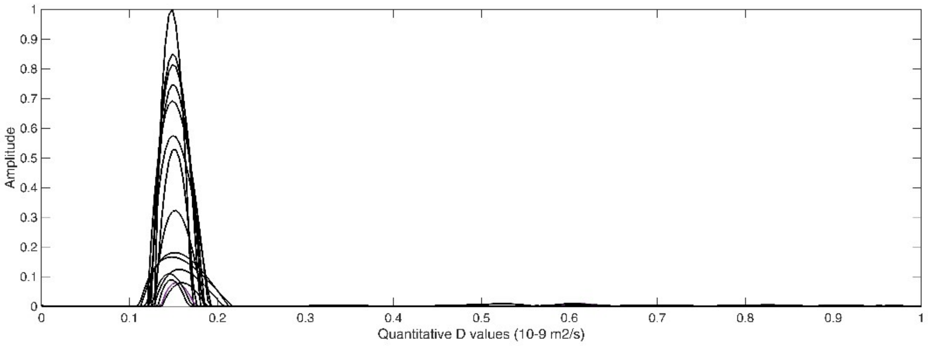


Figure S8. ITAMeD solution for polymer P4 (10100 Da), D-value of 0.1474 10^{-9} m^2s^{-1}. Minor peaks are due to polymeric entities of low polymer weight present at very low concentration that the ITAMeD algorithm can detect.

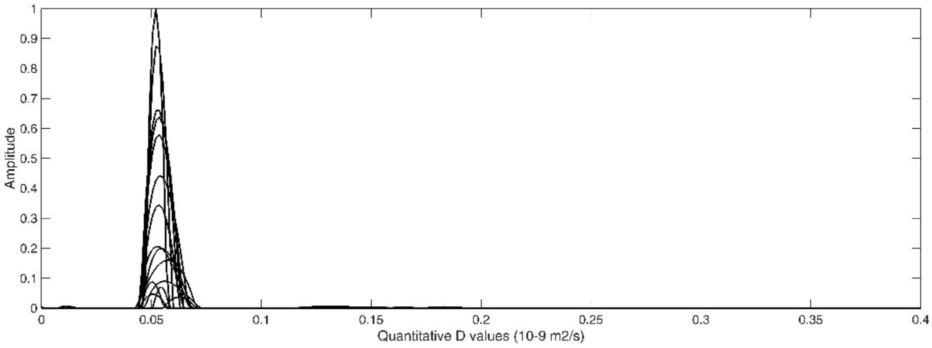


Figure S9. ITAMeD solution for polymer P5 (60000 Da), D-value of 0.0505 10^{-9} m^2s^{-1}.

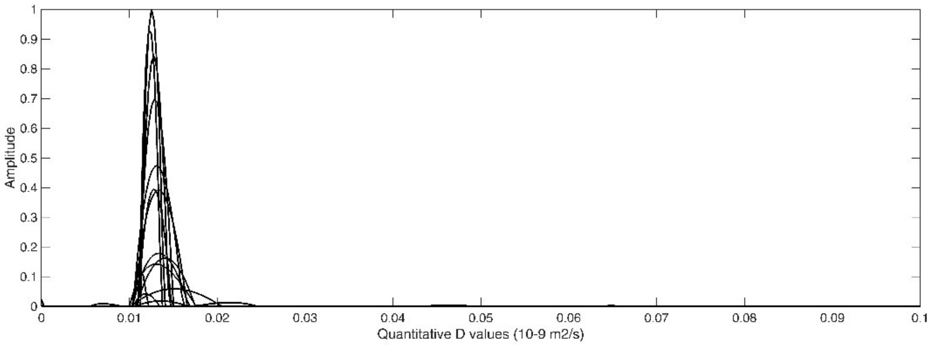


Figure S10. ITAMeD solution for polymer P6 (460000 Da), D-value of 0.0162 10^{-9} m^2s^{-1}.

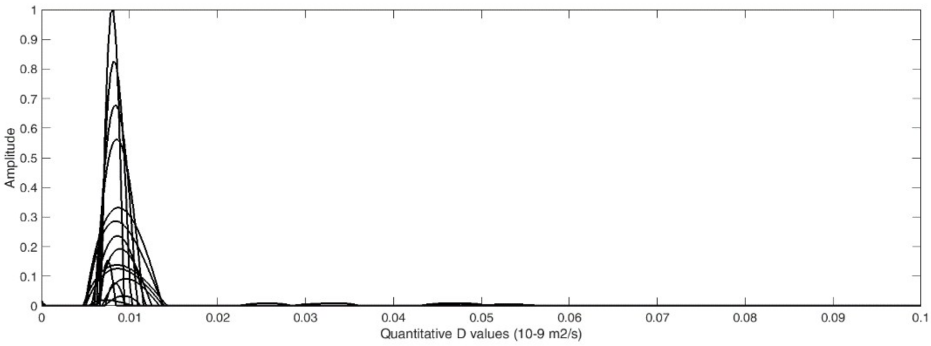


Figure S11. ITAMeD solution for polymer P7 (1020000 Da), D-value of 0.0094 10^{-9} m^2s^{-1}. Minor peaks are due to polymeric entities of low polymer weight present at very low concentration that the ITAMeD algorithm can detect.

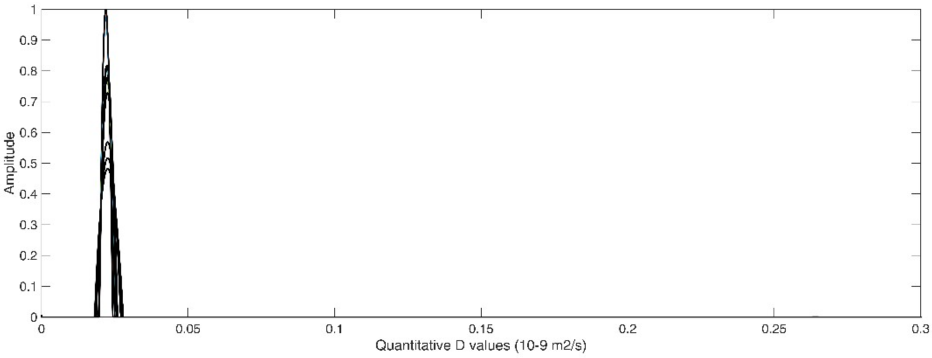


Figure S12. ITAMeD solution for polymer P6 (460000 Da) in tetrahydrofuran-d_8, D-value of 0.0222 10^{-9} m^2s^{-1}.

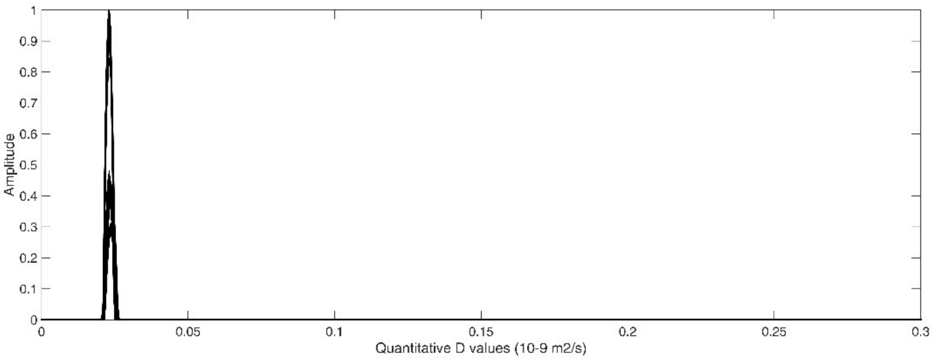


Figure S13. ITAMeD solution for polymer P6 (460000 Da) in chloroform-d_8, D-value of 0.0192 10^{-9} m^2s^{-1}.

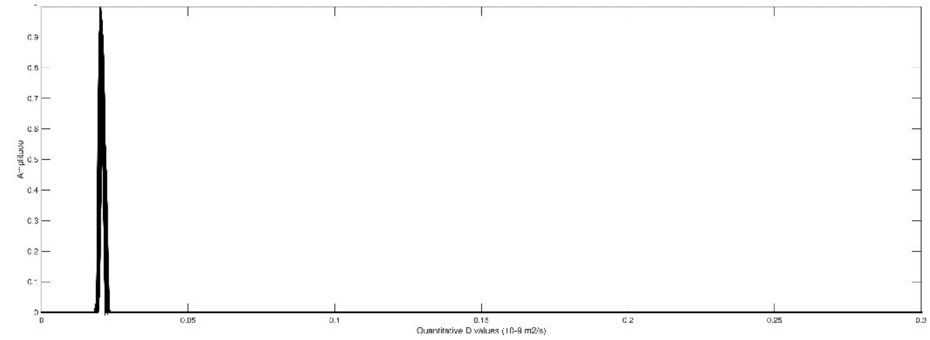


Figure S14. ITAMeD solution for polymer P6 (460000 Da) in toluene-d_8, D-value of 0.0190 10^{-9} m^2s^{-1}.

Table S20. UCC-predicted Mw (Da) for PS samples (above 20 kDa) in $CDCl_3$ according to the Cr (28) and d_F (1.63) provided by Delsuc and coworkers.[10]

Mw	Estimated D (10^{-9} m^2 s^{-1})	Dη (J m^{-1})	Predicted Mw	error (%)a
25000	0.09479	5.322E-05	25981	3.9
30000	0.08546	4.798E-05	30760	2.5
45000	0.06788	3.811E-05	44779	0.5
50000	0.06393	3.59E-05	49369	1.3
55000	0.06056	3.4E-05	53925	2.0
60000	0.05764	3.236E-05	58451	2.6

a Average error of 2.1 %.

Table S21. UCC-predicted Mw (Da) for PS samples in Tol-d_8 according to the Cr (4.3) and d_F (2.446) provided by Delsuc and coworkers.[10]

Mw	Estimated D (10^{-9} m^2 s^{-1})	Dη (J m^{-1})	Predicted Mw	error (%)a
25000	0.09261	5.322E-05	20403	18.4
30000	0.08349	4.798E-05	26288	12.4
45000	0.06631	3.811E-05	46183	2.6
50000	0.06246	3.59E-05	53466	6.9
55000	0.05917	3.4E-05	61039	10.9
60000	0.05631	3.236E-05	68886	14.8

a Average error of 11.0 %.

Table S22. UCC-predicted MW (Da) for PS samples (above 30 kDa) in THF-d_8 according to the Cr (29.3) and d_F (1.608) provided by Delsuc and coworkers.[10]

Mw	Estimated D (10^{-9} m^2 s^{-1})	Dη (J m^{-1})	Predicted Mw	error (%)a
25000	0.10950	5.322E-05	26151	4.6
30000	0.09872	4.798E-05	30891	2.9
45000	0.07841	3.811E-05	44742	0.6
50000	0.07385	3.59E-05	49263	1.5
55000	0.06996	3.4E-05	53745	2.3
60000	0.06658	3.236E-05	58193	3.0

a Average error of 2.5 %.

Table S23. UCC-predicted MW (Da) for PS samples (below 30 kDa) in THF-d_8 according to the Cr (8.09) and d_F (2.014) provided by Delsuc and coworkers.[10]

Mw	Estimated D (10^{-9} m^2 s^{-1})	Dη (J m^{-1})	Predicted Mw	error (%)a
5000	0.27325	0.0001328	4271	14.6
10000	0.18430	8.958E-05	11321	13.2
15000	0.14637	7.115E-05	16398	9.3
20000	0.12430	6.042E-05	21327	6.6
25000	0.10950	5.322E-05	26151	4.6
29000	0.10064	4.892E-05	29948	3.3

a Average error of 8.6 %.

Table S24. UCC-predicted MW (Da) for PMMA samples (above 25 kDa) in $CDCl_3$ according to the Cr (17.3) and d_F (1.836) provided by Delsuc and coworkers.[10]

Mw	Estimated D (10^{-9} m^2 s^{-1})	Dη (J m^{-1})	Predicted Mw	error (%)a
25000	0.09479	5.322E-05	24443	2.2
30000	0.08546	4.798E-05	29564	1.4
45000	0.06788	3.811E-05	45130	0.3
50000	0.06393	3.59E-05	50373	0.7
55000	0.06056	3.4E-05	55639	1.2
60000	0.05764	3.236E-05	60926	1.5

a Average error of 1.2 %.

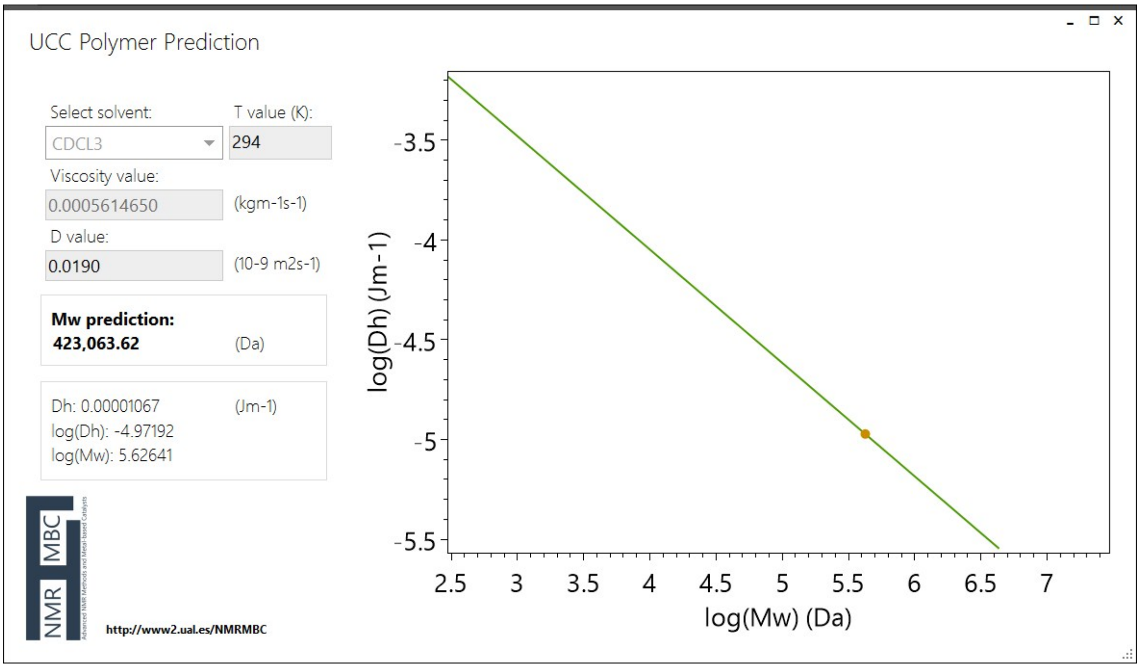
Table S25. UCC-predicted MW (Da) for PEO samples in $CDCl_3$ according to the Cr (12.36) and d_F (1.7342) provided by Delsuc and coworkers.[10]

Mw	Estimated D (10^{-9} m^2 s^{-1})	Dη (J m^{-1})	Predicted Mw	error (%)[a]
10000	0.15954	8.958E-05	10162	1.6
20000	0.10760	6.042E-05	20118	0.6
30000	0.08546	4.798E-05	29999	0.003
40000	0.07257	4.075E-05	39831	0.4
50000	0.06393	3.59E-05	49626	0.7
60000	0.05764	3.236E-05	59393	1.0

[a] Average error of 0.7 %.

Table S26. Mw, Mn and PDI data for the polystyrene samples (P1-P7) used in this study.

Samples	Mw	Mn	PDI
P1	500	439	1.14
P2	1320	1224	1.07
P3	5970	5853	1.02
P4	10100	9661	1.03
P5	60000	61571	1.03
P6	460000	438443	1.04
P7	1020000	1070500	1.05



UCC Polymer Prediction

Select solvent: CDCL3

T value (K): 294

Viscosity value: 0.0005614650 (kgm-1s-1)

D value: 0.0190 (10-9 m2s-1)

Mw prediction:
423,063.62 (Da)

Dh: 0.00001067 (Jm-1)
log(Dh): -4.97192
log(Mw): 5.62641

Figure S15. Interface of the desktop application for UCC polymer prediction available at http://www2.ual.es/NMRMBC/downloads/UCCPolymerPrediction.rar.

References

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[1] H. J. V. Tyrrell; K. R. Harris, *Diffusion in Liquids*, Butterworths, London, 1984.

[2] DiffAtOnce® is a registered program developed by I. Fernández and F. M. Arrabal-Campos in the University of Almería. 2013, and available at www.diffatonce.com.

[3] Urbanczyk, M.; Bernin, D.; Kozminski, W.; Kazimierczuk, K. *Anal. Chem*. **2013**, *85*, 1828-1833.

[4] An ideal character of the medium, in particular, implies that experiments are carried out at infinite dilution where the interaction between diffusing species is negligible. This condition is often not met in conventional experiments at finite concentrations.

[5] Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. *Chem. Soc. Rev*. **2008**, *37*, 479-489.

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[7] Li, D.; Keresztes, I.; Hopson, R.; Williard, P. G. *Acc. Chem. Res*. **2009**, *42*, 270−280

[8] a) Flory, P. *Principles of Polymer Chemistry*, New York: Cornell University, 1953; b) Edwards, S. F.; Doi, M. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.

[9] Where A is a molecule dependent constant and α is a coefficient that depends highly on the shape of the particle.

[10] a) Auge, S.; Schmit, P.-O. Crutchfield, C. A.; Islam, M. T.; Harris, D. J.; Durand, E.; Clemancey, M.; Quoineaud, A.-A.; Lancelin, J. M. Prigent, Y.; Taulelle, F.; Delsuc, A. *J. Phys. Chem. B* **2009**, *113*, 1914-1918; b) Floquet, S., Brun, S., Lemonnier, J. F., Henry, M., Delsuc, M. A., Prigent, Y.; Cadot, E.; Taulelle, F. *J. Am. Chem. Soc*. **2009**, *131*, 17254–17259.