Unravelling chain confinement and dynamics of weakly entangled polymers in one component nanocomposites.

Supporting information

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Fitting with friction profiles

We use: **U=1; M=1**; **H=1,** where **U, M, H** are matrices of a dimension given by the segment number.

$$H(i,i)=1/\mathrm{friction}(i) \qquad \text{(S1)}$$

The rest follows the steps described elsewhere [1] , except for the effect of the friction modulation this matches the results of the standard discrete Rouse summation.

In detail the procedure uses the following:

$$M = \left\{ \begin{array}{ccccccc} 1 & -1 & 0 & 0 & 0 & .. & 0 \\ -1 & 1 & -1 & 0 & 0 & .. & 0 \\ 0 & -1 & 1 & -1 & 0 & .. & 0 \\ & & & .. & & & \\ & & & .. & & & \\ .. & & & & & & \\ 0 & 0 & .. & & -1 & 1 & -1 \\ 0 & 0 & .. & & 0 & -1 & 1 \end{array} \right.$$

Then **A = M^t U M = M^t M,** where the unit matrix **U** is only kept to show the mapping to the Guenza-Perico algorithm[1]. To arrive at the chain modes we diagonalize **HA** matrix yielding eigenvectors **E** and eigenvalues **Λ**: **HA = E^{t}ΛE.** With **Cx = AE** and **Cm = E^t Cx = E^t A E** the displacement functions $\varphi_{i,j}(t)$ can be obtained. Here in addition, we introduce a mode p suppression/modulation factor $f_{cross}(p)$ (modelled by Equ. 1, see main text):

$$\varphi_{i,j}(t) = l_0^2 \sum_{p=1}^{N} (E_{i,p}^2 + E_{j,p}^2 - f_{cross}(p)\, 2E_{i,p}E_{j,p}\, exp[-(Wl^4/l_0^4)\Delta_p t])/Cm_{p,p} \qquad \text{(S2)}$$

The mode counting here is obtained by sorting the Eigenvalues, i.e. the slowest modes have the lowest mode numbers p.

Also observing the segmental scattering contrasts a_i we finally arrive at the observable scattering function:

$$S(Q,t) \;=\; \sum_{i,j} a_i\, a_j exp(-\varphi_{i,j}(t)Q^2/6) \qquad \text{(S3)}$$

In order to test more elaborate friction profiles that not only allowed for an increase of friction in the neighborhood of the grafting point but also offered the opportunity to decrease friction at the rim of the shell, we constructed the following function:

$$friction = fric0 + \frac{1}{4}\left(fricpeak * Exp\left[-\frac{4i^2}{narm^2 * wpeak^2}\right] + 1\right)\left(erf\left[\frac{\frac{2*i}{narm}+xcapcut}{wcap}\right] + 1\right)\left(-erf\left[\frac{\frac{2*i}{narm}-xcapcut}{wcap}\right] + 1\right) \qquad \text{(S4)}$$

An example for a possible profile is displayed in Fig. S1:

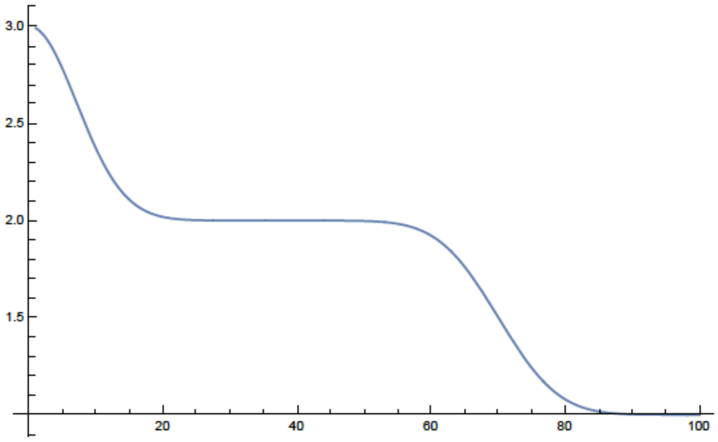


Fig. S1.: Example for a friction profile generated by roufricq. The parameters are: fric0 = 1; fricpeak = 1; narm =100; wpeak = 0.1; xcapcut = 0.7; wcap = 0.1

As is evident from Fig. S1 with the above friction function a wide range of possible friction profiles could be covered. Starting from the best fitted Gaussian profile, various schemes of parameter variation were tested. Fig S2 presents the different friction profiles that resulted from the fitting.

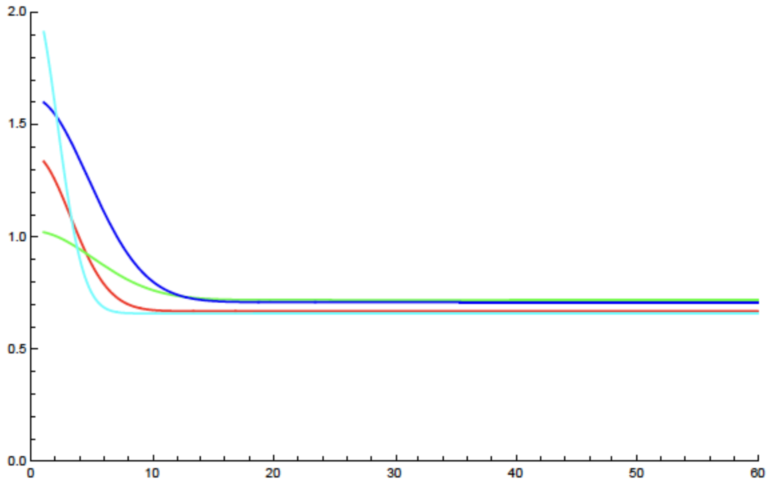
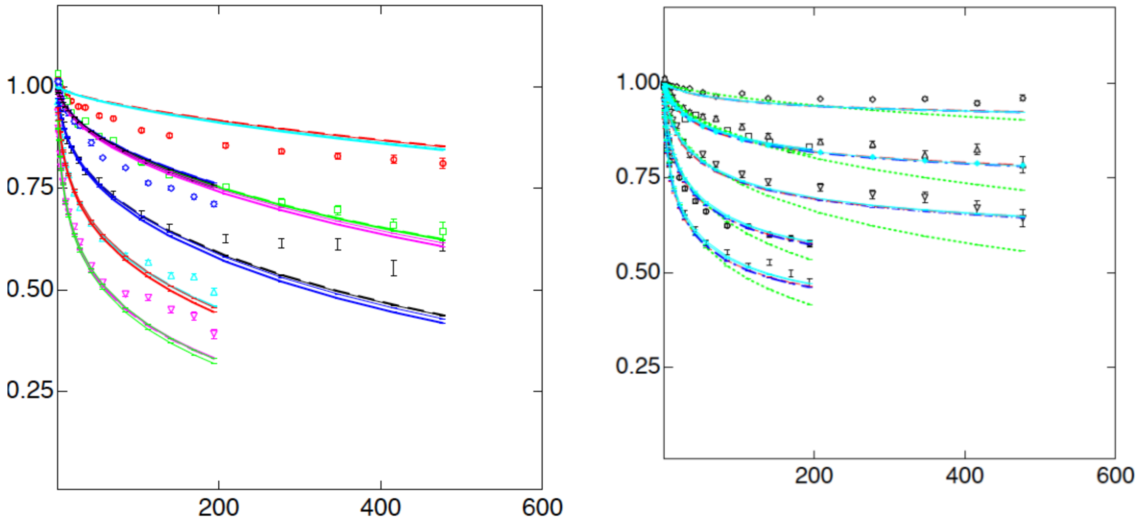


Fig. S2: Results for the friction profile from various fitting attempts to describe the OCNC spectra.

First of all we note that no matter how the fit was conducted (e. g. different initial parameters, or fixed variables) all profiles show an increase of friction close to the grafting point but no reduction of friction towards the rim of the shell. In all cases goodness of the fit compared to the best result from the Gaussian profile (fig. 4d, see the main text) only marginally improved to $\chi^2 = 14.0$. Various friction profiles originating from different fitting attempts are displayed in Fig. S2. Obviously, a significantly better fit cannot be achieved even by a more sophisticated friction profile. Fig. S3 displays the resulting description of the spectra.



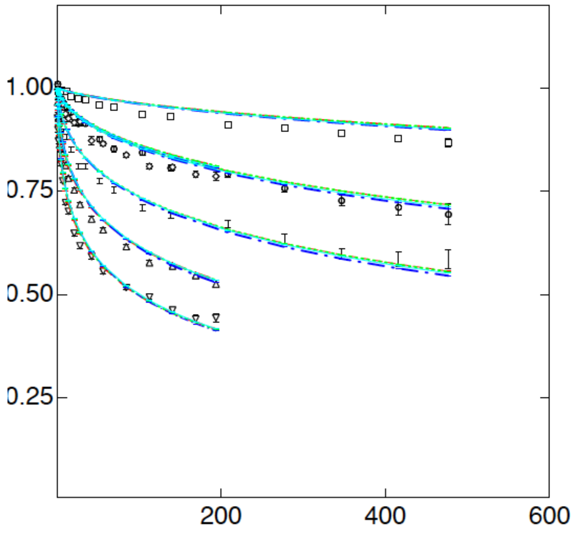


Fig. S3: Fitting results with friction profiles displayed in Fig. S2: upper left: outer part; upper right: inner part; lower left fully labeled; the Q-values from above are: Q = 0.48, 0.77, (0.76), 0.97, 1.14, 1.3 [nm^{-1}]. Line types: dashed (red); dotted (green); dashed-dotted (blue), solid (cyan). The colors correspond to those in Fig. S2

Synthesis of PB-PEO diblocks

All manipulations were carried out at a high vacuum line or in a glove box, filled with argon (M Braun, Unilab). The water level in the glove box was usually below 1 ppm and the oxygen level below 0.1 ppm. The flasks for all manipulations were equipped with Teflon stopcocks that allowed transferring materials between the vacuum line and the glove box without contamination with air. The flasks were pressure tested up to 12 bars.

Materials

THF (≥99.7%) was obtained from VWR. Di-*n*-butylmagnesium (1.0 M solution in heptane), *n*-butyllithium (1.6 M solution in hexanes), *sec*-butyllithium (1.42 M solution in cyclohexane), calcium hydride (CaH_2) (≥90%), naphthalene (99%), potassium (98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99%), 2,2′-(ethylendioxy)diethanthiol (dithiol) (95%), ethylene glycol monovinyl ether (97%) were obtained from Sigma-Aldrich. Ethylene oxide (EO) (≥99.9%) was purchased from Balchem; 1,3-butadiene-d_6 (d-butadiene) (chemical purity 99.8% (GC/MS), isotopic purity 100% (GC/MS)) and ethylene oxide-d_4 (d-EO)(chemical purity 100% (GC/MS), isotopic purity 98.3% (GC/MS)) were purchased from Cambridge Isotope Laboratories.

THF was first degassed using 3 freeze-pump-thaw cycles and then cryo-distilled on potassium metal and a small amount of benzophenone as indicator. After a deep purple color developed, stirring was continued for at least one day. and THF was directly cryodistilled into the reaction flasks. The monomer d-butadiene was first degassed using 3 freeze-pump-thaw cycles and then cryo-distilled on solvent-free di-*n*-butylmagnesium. The mixture was stirred at room temperature for about 12h. Then the monomer was cryo-distilled on solvent-free n-butyllithium, stirred at -10 °C to -20 °C for 20 min. and directly cryo-distilled into the polymerization flasks. EO and d-EO were first degassed using 3 freeze-pump-thaw cycles and then cryo-distilled on CaH_2. In the case of EO the mixture was stirred for two days and the process then repeated once with new CaH_2. In the case of d-EO the mixture was stirred for about two weeks and the process repeated two to three times with new CaH_2. After the drying processes the monomers were cryo- distilled in empty flasks in order to measure the weights and finally transferred into the polymerization flasks.

Sodium naphthalene solution was obtained by mixing 768 mg of naphthalene (5.99 mmol) with 213 mg of potassium metal (5.45 mmol) and 13.63 g of dry THF inside a glove box. After the dissolution of the metal, the mixture was used up within a few hours. The calculated sodium naphthalene concentration was 0.373 mmol/g of solution (solution A). A second sodium naphthalene solution was obtained by mixing 145 mg of naphthalene (1.13 mmol) with 39 mg of potassium metal (1.00 mmol) and 3.197 g of dry THF inside a glove box. After the dissolution of the metal, the mixture was used up within a few hours. The calculated sodium naphthalene concentration was 0.354 mmol/g of solution (solution B). A third sodium naphthalene solution was obtained by mixing 151 mg of naphthalene (1.18 mmol) with 38 mg of potassium metal (0.97 mmol) and 2.631 g of dry THF inside a glove box. After the dissolution of the metal, the mixture was used up within a few hours. The calculated sodium naphthalene concentration was 0.288 mmol/g of solution (solution C).

Polymer Characterization

Size-exclusion chromatography (SEC) experiments were carried out using an Agilent 1260 Infinity SEC instrument equipped with a Wyatt DAWN Heleos II light scattering (LS) detector, an Optilab T-rex differential refractive index (RI) detector and with three PolyPore columns at 50 °C. The solvent was a mixture of THF, DMA, and acetic acid (84:15:1 by volume) at a flow rate of 1 mL/min. NMR spectra were collected on a Bruker Avance III 600 MHz spectrometer equipped with a Prodigy cryoprobe with a 5 mm PFGAutoX DB probe. Samples were measured at 295 K in $CDCl_3$ if not otherwise stated. The microstructure of dPB was calculated from the deuterium NMR spectrum by comparing the signal intensities at 4.8 ppm (2 deuterium atoms 1,2-PB) and at 5.4 ppm (1 deuterium atom 1,2-PB; 2 deuterium atoms, 1,4-PB). The molecular weight and M_w/M_n values of dPB were calculated from the SEC/LS measurements. The ratios of dPEO to dPB in the block copolymers were calculated from the deuterium NMR signal intensities of dPEO at 3.5 ppm and dPB between 1 - 2ppm and 4.8 - 5.4 ppm. These measurements were carried out at 100°C in p-xylene to reduce the signal width. The fractions of hPEO in the block copolymers were calculated by proton NMR using known quantities of the polymer sample and the reference $C_2H_2Br_4$ and comparing the signal intensities of PEO at3.6 ppm and $C_2H_2Br_4$ at 6.0 ppm. MWs of the dPEO and hPEO blocks were calculated from the NMR ratios or fractions and the dPB MW. The M_w/M_n values of the block copolymers was calculated from the SEC/LS measurements.

Polymerization reactions

dPB5k-OH. For the d-butadiene polymerization, the reaction flask was first filled with the *sec*-butyllithium solutions (3.65 mL, 5.18 mmol). Then 31.17 g of dried d-butadiene and 270 mL of dry THF were cryo-distilled into the reaction flask at liquid nitrogen temperature. The mixture was warmed up to -60 °C. After 2.5 h at this temperature, 2.02 g (42.0 mmol) of dry d-EO was added. The yellow color of the reaction mixture disappeared within 2 min. and the mixture was slowly warmed up to room temperature. On the next day about 1/3 of the volume was distilled off under high vacuum conditions to remove the excess of d-EO and possibly still existing d-butadiene monomer. Then 2 g of acetic acid were added, the polymer product dPB5k-OH was precipitated in methanol, washed with methanol and dried under stirring and under high vacuum conditions for several days. The content of 1,2-PB in the polymer was calculated from the deuterium NMR spectrum to be 88%. The molecular weight characterization results are listed in Table 1 in the main text.

dPB5k-hPEO10k. 9.934 g (1.63 mmol) of dPB5k-OH was transferred into a 250 mL reaction flask and degassed under slow stirring. The polymer was dissolved in 200 mL of dry THF and 4.035 g (1.51 mmol) of sodium naphthalene solution (solution A) was added. The slightly yellowish solution was frozen in liquid nitrogen to remove argon gas and 17.24 g of EO were transferred into the reaction flask. The EO polymerization reaction was carried out at 40 °C for 3 days. Then 1 mL of acetic acid was added and THF was removed under reduced pressure. The raw product was dissolved in 1.3 L of chloroform and washed with water to remove salt residues. After removal of the chloroform, washing with hexane and drying under vacuum conditions 24.5 g of product dPB5k-hPEO10k was obtained. The polymer characterization results are listed in Table 1 in the main text.

dPB5k-dPEO10k. The same procedure was applied as described for dPB5k-dPEO10k using 9.757 g (1.60 mmol) of dPB5k-OH, 3.903 g (1.46 mmol) of sodium naphthalene solution (solution A) and 18.31 g of d-EO. After drying 23.5 g of product dPB5k-dPEO10k was obtained. The polymer characterization results are listed in **Table S1**.

dPB5k-hPEO5k-dPEO5k. The same procedure was applied as described for dPB5k-dPEO10k using 2.575 g (0.42 mmol) of dPB5k-OH and 1.15 g (0.41 mmol) of sodium naphthalene solution (solution B). The EO polymerization was carried out by first reacting 2.130 g of EO for 5 days followed by 2.403 g of d-EO for 3 days. After drying 7.06 g of product dPB5k-hPEO5k-dPEO5k was obtained. The polymer characterization results are listed in **Table S1**.

dPB5k-dPEO5k-hPEO5k. The same procedure was applied as described for dPB5k-dPEO10k using 2.234 g (0.37 mmol) of dPB5k-OH and 1.38 g (0.39 mmol) of sodium naphthalene solution (solution C). In this case, most likely not all of the sodium metal had dissolved as the mixture after the addition of the sodium naphthalene solution turned slightly yellowish as for the other reactions. The EO polymerization was carried out by first reacting 2.15 g of d-EO for 3 days followed by 2.02 g of EO for 2 days. The polymer characterization results are listed in **Table S1**.

OCNC synthesis

OCNC sample dh-dd

For the OCNC sample dh-dd 0.957 g of dPB5k-hPEO10k, 2.859 g of dPB5k-dPEO10k and 0.167 g of DMPA were dissolved in 25 mL of benzene and freeze-dried. The obtained mixture (3.948 g) was dispersed in 140 mL of deionized water for overnight. All these processes were carried out in the dark to prevent premature cross-linking of the PB. The obtained slightly turbid micellar solution was then centrifuged to remove solid residues, probably non-dissolved DMPA. After drying, the amount of sold residues was 57 mg. The micellar solution was then degassed under vacuum and 0.433 g of dithiol was added under an argon atmosphere. The mixture was stirred and illuminated with UV-light (Roschwege Star-UV385 UV-LED 385 nm) for 4h. Then, 1.84 g of ethylene glycol monovinyl ether was added and the UV illumination was continued for 1 h to quench residual thiol units. The aqueous dispersion was washed once with 500 mL and then twice with 150 mL of chloroform, the combined chloroform phases were concentrated to 40 mL and precipitated in 400 mL of hexane. After washing with hexane and drying under HV conditions for several hours, 40 mg of hydroquinone was added and the mixture was solubilized in 40 mL of 1,4-dioxane. It was freeze-dried and finally left for an additional day under high vacuum conditions. 4.11 g of the OCNC sample dh-dd was obtained. The sulfur content in the OCNC sample was determined by elemental analysis to be 3.6 mass-%. The calculated value for the sample composition at 100 % incorporation of the cross-linker is also 3.6 mass-%.

OCNC sample hdPEO label

OCNC sample dhd-dd was prepared in the same way by using 2.278 g of dPB5k-hPEO5k-dPEO5k, 1.337 g of dPB5k-dPEO10k and 0.176 g of DMPA for the freeze-drying procedure. 3.790 g of the polymer mixture, 0.417 g of dithiol and 1.792 g of ethylene glycol monovinyl ether were used for the cross-linking experiment. Finally, 3.94 g of the OCNC sample dhd-dd was obtained after the drying process. The sulfur content in the OCNC sample was determined by elemental analysis to be 3.5 mass-%. The calculated value for the sample composition at 100 % incorporation of the cross-linker is 3.6 mass-%.

OCNC sample dhPEO label

OCNC sample ddh-dd was prepared in the same way by using 2.221 g of dPB5k-dPEO5k-hPEO5k, 1.673 g of dPB5k-dPEO10k and 0.191 g of DMPA for the freeze-drying procedure. 4.080 g of the polymer mixture, 0.446 g of dithiol and 1.96 g of ethylene glycol monovinyl ether were used for the cross-linking experiment. Finally, 4.40 g of the OCNC sample dhd-dd was obtained after the drying process. The sulfur content in the OCNC sample was determined by elemental analysis to be 3.5 mass-%. The calculated value for the sample composition at 100 % incorporation of the cross-linker is 3.6 mass-%.

Table S1: molecular weight characterization of the dPB-PEO di-blocks

	dPB block		PEO block		copolymer
			inner part	outer part	
	M_n	M_w/ M_n	M_n		M_w/ M_n
dPB5k-hPEO10k	6,090	1.02	10,400 (h)		1.01
dPB5k-dPEO10k	6,090	1.02	11,100 (d)		1.02
dPB5k-hPEO5k-dPEO5k	6,090	1.02	5,160 (h)	5,950 (d)	1.01
dPB5k-dPEO5k-hPEO5k	6,090	1.02	6,010 (d)	6,380 (h)	1.01

Contrast matching experiment

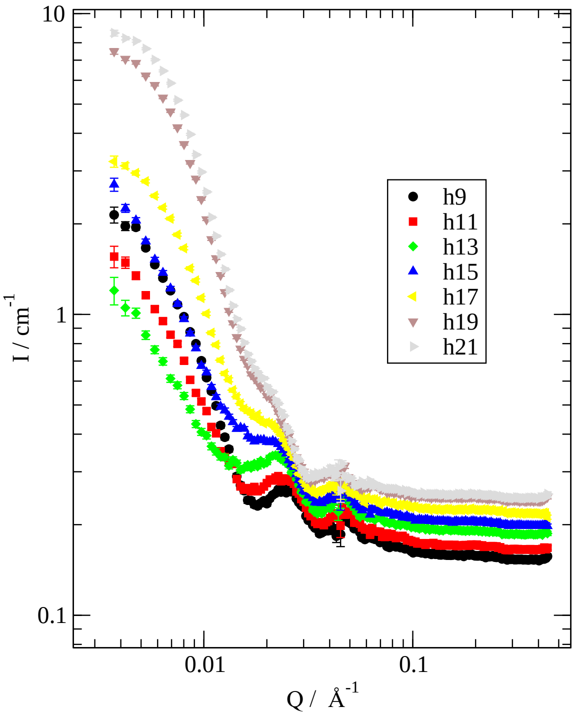


Figure S4. SANS data obtained for the PB-PEO micelles in the mixtures of H2O and D2O of different ratio: content of H2O was varied from 9 to 21 % by volume.

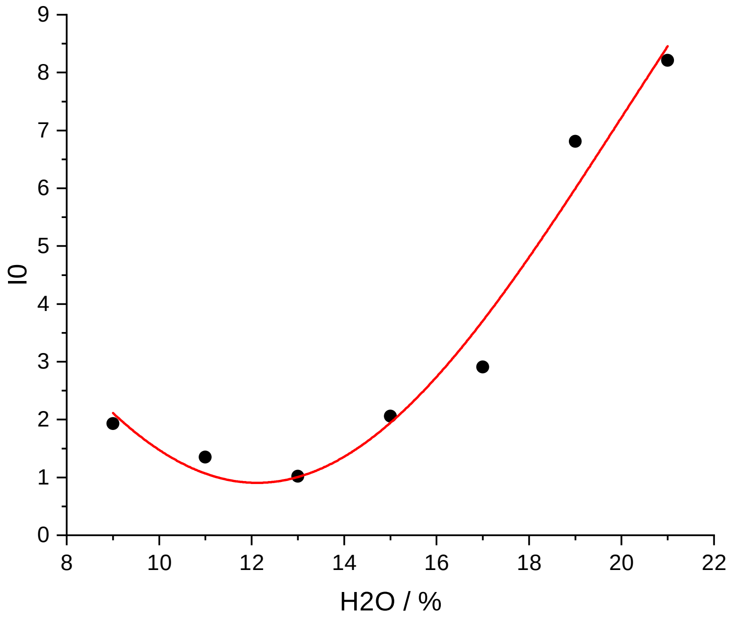


Figure S5. SANS data obtained for the PB-PEO micelles in the mixtures of H2O and D2O of different ratio: content of H2O was varied from 9 to 21 % by volume. The intensity at lowest values of the momentum transfer ($Q \rightarrow 0$) was used to determine the proper matching condition and estimate the scattering density of the core. Minimum of scattering intensity corresponds to 12.2 % (by volume) of H2O.

References

1 M. Guenza, M. Mormino and A. Perico, A Local Approach to the Dynamics of Star Polymers, *Macromolecules*, 1991, **24**, 6168–6174.