Electronic Supplementary Information to

Interface-Enforced Complexation between Copolymer Blocks

by

Alexander A. Steinschulte, Weinan Xu, Fabian Draber, Pascal Hebbeker, Andre Jung, Dimitri Bogdanovski, Stefanie Schneider, Vladimir V. Tsukruk, Felix A. Plamper*

Experimental Section

Materials

Poly(propylene glycol) (M_n = 4000 g/mol; $Đ$ = 1.1) and methacryloxyethyl thiocarbamoyl rhodamine B was delivered by Polysciences, Warrington, PA, USA. Poly(ethylene glycol) methyl ether (M_n = 5000 g/mol; $Đ$ = 1.1), methanesulfonyl chloride, 2-(*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA; purified by filtration over basic alumina), ethyl α-bromoisobutyrate (EBIB) and *N*,*N*,*N´*,*N´´*,*N´´´*,*N´´´*- hexamethyl triethyltriamine (HMTETA) were delivered by Sigma Aldrich. Chloroform, *n*-hexane, 1,4-dioxane, anhydrous diethylether and anisole were obtained by VWR. *n*-Decane and alumina were obtained from Merck (Darmstadt, Germany). CuCl, $\mathrm{CuCl_2}$ and tetrahydrofuran (THF) and *n*-heptane were delivered by Alpha Aesar.

The synthesis of the polymers PEO_{114}-$(\mathrm{PDMAEMA}_{90})_{3.1}$-$\mathrm{PPO}_{69,}$ PEO_{114}-*b*-PPO_{69}, PPO_{114}-*b*-$\mathrm{PDMAEMA}_{100}$ is described in references (the indexes account for the number-average degree of polymerization per block and the arm number respectively).[1-3] The synthesis of the homopolymer $\mathrm{PDMAEMA}_{138}$ is in accordance to literature.[4] The synthesis of the diblock copolymer PEO_{114}-*b*-$\mathrm{PDMAEMA}_{71}$ is described below.

Synthesis of the $\mathrm{PDMAEMA}_{138}$ homopolymer[4]

Copper(II)chloride (8.0 mg $\mathrm{CuCl_2}$), copper(I)chloride (26.5 mg CuCl), and ethyl α-bromoisobutyrate (47.0 mg EBIB) were added at the approximate molar ratio of 0.25:1:1 into a flask equipped with anisole (6.6 g). This mixture was deoxygenated by purging with nitrogen for 15 min while it was stirred. In another flask, *N*,*N*,*N´*,*N´´*,*N´´´*,*N´´´*- hexamethyl triethylenetetraamine (HMTETA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were mixed and freed from oxygen as well. This monomer−ligand mixture was quickly added to a preheated initiator−catalyst mixture at 80 °C (adding in total 102 mg HMTETA and 6.03 g DMAEMA). After 17 h, the viscous solution was diluted with chloroform (before, a sample was drawn for conversion determination by ^{1}H NMR: 87 % conversion according to the quotient of the NMR peak area of the methylene protons attached to the ester group at 4.1 ppm for PDMAEMA and the NMR peak area of the methylene protons attached to the ester group at 4.25 for DMAEMA; this yields a theoretical degree of polymerization $P_\mathrm{n,theo}\approx 138$) and filtered by a silica gel column to remove the copper traces before it was precipitated in *n*-hexane. The concentrated product was dissolved in 1,4-dioxane, dialyzed, and freeze-dried (3.5 g).

GPC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 7600 g/mol, $Đ$ = 1.23; δ_H(400 MHz; $\mathrm{CDCl_3}$): 4.25-4.00 (O-CH_2-CH$_2$-N; PDMAEMA), 2.80-2.55 (O-CH$_2$-CH_2-N; PDMAEMA), 2.5-2.30 (N-(CH_3)$_2$; PDMAEMA), 2.10-1.70 (PDMAEMA backbone CH_2), 1.35-0.80 (PDMAEMA backbone CH_3).

Synthesis of the PEO_{114}-Br macroinitiator

Poly(ethylene oxide) mono methyl ether (14.565 g, $2.91\cdot10^{-3}$ mol) and 20 mg *N*,*N*-dimethyl-4-pyridinamin (DMAP) were dissolved in 50 g dichloromethane and triethylamine (3.3 g; 0.033 mol). The mixture was dried over molecular sieves under stirring. After 1 h the sieves were removed, the mixture was cooled in ice under stirring and purged for 30 min with nitrogen. Then 2-bromo-2-methyl-propionylbromid (1.395 g, $6.07\cdot10^{-3}$ mol) was added dropwise under nitrogen counterflow. Overnight, the mixture was slowly allowed to warm up to room temperature (RT) under stirring. Further 0.641 g 2-bromo-2-methyl-propionylbromid ($2.79\cdot10^{-3}$ mol) were added and the mixture was heated for 5 h to 50°C. The mixture was filtrated through silica and the filtrate was reconcentrated and precipitated in diethyl ether. The precipitate was separated by centrifugation and dissolved in dichloromethane. The filtration, reconcentration and precipitation steps were repeated two times. The precipitate was then dried under vacuum to yield 10.9 g.

GPC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 4800 g/mol, $Đ$ = 1.04; δ_H(400 MHz; $\mathrm{CDCl_3}$): 3,71-3,61 (m, PEO_{114}), 3,38 (3H, s, CH_3-O-PEO), 1,95 (6H, s, O=C-C(CH_3)$_2$Br)

Synthesis of the PEO_{114}-*b*-$\mathrm{PDMAEMA}_{71}$

Anisole and 2-(*N*,*N*-dimethylamino)ethyl methacrylate were filtrated over basic alumina and deoxygenated by purging with nitrogen. PEO_{114}-Br based macroinitiator (1.00 g; $1.9\cdot10^{-4}$ mol) together with 15.268 g dimethylaminoethyl methacrylate ($8.25\cdot10^{-2}$ mol), 20.4 mg

($2.99 \cdot 10^{-5}$ mol) methacryloxyethyl thiocarbamoyl rhodamine B, 21.2 mg CuCl ($2.14 \cdot 10^{-4}$ mol) and 2.6 mg $CuCl_2$ ($1.93 \cdot 10^{-5}$ mol) were dissolved in 16 ml anisole and further deoxygenated by purging with nitrogen for 30 min. The mixture was heated to 80° C and further deoxygenated by purging with nitrogen for 30 min. Then the ligand *N,N,N´,N´´,N´´´,N´´´*- hexamethyl triethyltriamine (49 mg; $2.1 \cdot 10^{-4}$ mol) was introduced to the macroinitiator mixture at 80°C under stirring and nitrogen counterflow. After 3 h, the reaction was terminated by injection of chloroform (the conversion was determined as 15 % by NMR) and contact with air. Then the polymer solution was filtrated through silica and then reconcentrated, before it was dissolved in THF and precipitated from hexane. Then the precipitate was dissolved in THF, precipitated again in hexane, dissolved in dioxane and lyophilized to yield 1.6 g polymer.

GPC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 21900 g/mol, $Đ$ = 1.11; δ_H(400 MHz; $CDCl_3$): 4.17-3.98 (O-CH_2-CH_2-N; PDMAEMA), 3.73-3.59 (m. PEO_{114}), 3.39 (3H; s; CH_3-O-PEO), 2.66-2.48 (O-CH_2-CH_2-N; PDMAEMA), 2.36-2.20 (N-(CH_3)$_2$; PDMAEMA), 2.10-1.76 (PDMAEMA backbone CH_2), 1.17-0.79 (PDMAEMA backbone CH_3).

Table S 1: Block content of the used polymers

	M_n (PEO) [kg/mol]	M_n (PPO) [kg/mol]	M_n (PDMAEMA) [kg/mol]	M_n (SEC) [kg/mol] ($Đ_M$, SEC)[b]
PEO_{114}-$(PDMAEMA_{90})_{3.1}$-PPO_{69}	5.0	4.0	43.8[a]	58.9 (1.39)[b]
PPO_{69}-*b*-$PDMAEMA_{100}$	-	4.0	15.7[a]	21.9 (1.10)[b]
PEO_{114}-*b*-PPO_{69}	5.0	4.0	-	16.9 (1.10)[b]
PEO_{114}-*b*-$PDMAEMA_{71}$	5.0	-	11.1[a]	21.9 (1.11)[b]
PEO_{114}	5.0	-	-	4.7 (1.04)[b]
PPO_{69}	-	4.0	-	2.6 (1.17)[b]
$PDMAEMA_{138}$	-	-	21.6[a]	7.6 (1.23)[b]

indexes account for the number-average degree of polymerization per block and the arm number respectively according to ^{1}H-NMR

[a] calculated by ^{1}H-NMR (assuming a molar mass of the PPO moiety of 4000 g/mol or by end group analyses)

[b] apparent molecular weight and dispersity as determined by SEC in DMF using PMMA standards

Matching of the compression isotherms

To get a complete picture of the compression isotherm, we measured the isotherms in up to three steps. Each step consists of a compression and an expansion. Before each step, a certain amount of polymer is added to the interface. 6 µL before the first step (leading to 0.6 nmol polymer at the interface), 14 µL (leading to 2.0 nmol polymer at the interface) and finally 30µL (leading to 5.0 nmol polymer at the interface) were applied. By this method we obtained a full overview of the compression isotherm without preparing a new interface for each measurement (see Figure S 1 and Figure S 2).

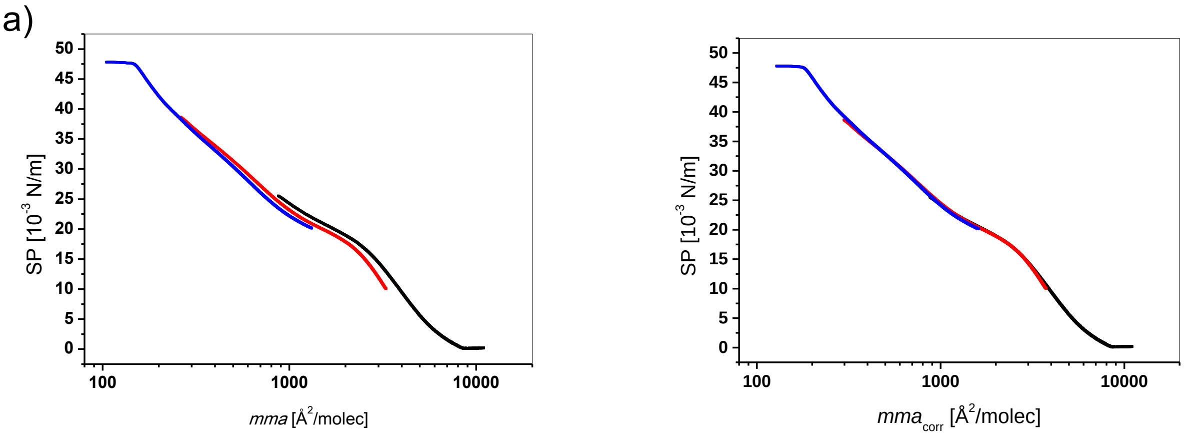

Figure S 1: Compression isotherms of PEO_{114}-*b*-PPO_{69} at an oil-water interface, measured at 35 °C in three following steps, first step is displayed in black, the second step in red, the third in blue; a) before matching: the initial polymer concentrations at the interface are for the first step 0.6 nmol, for the second step 2.0 nmol, for the third step 5.0 nmol; b) after matching: the nominal polymer concentrations at the interface are for the first step 0.6 nmol, for the second step 1.8 nmol, for the third step 4.1 nmol

These three isotherms are then matched by recalculating the *mma* with a reduced assumed polymer concentration at the interface. The assumed polymer concentration at the interface is reduced to e.g. 1.8 nmol for the second step (compression isotherms of following polymers are altered in this way: PEO_{114}-*b*-PPO_{69}, PEO_{114}-*b*-$PDMAEMA_{71}$, PPO_{69}-*b*-$PDMAEMA_{100}$, PPO_{69}) and to 4.1 nmol for the third step (compression isotherm of PEO_{114}-*b*-PPO_{69} is altered in this way). The difference in this measured concentration and the assumed concentration is caused by compression of the polymer to the bulk phase and by a lower spreading efficiency when the polymer is dropped to the interface with an increased surface pressure (due to decreased interfacial tension). The difference between the matched and unmatched compression is shown for PEO-*b*-PPO in Figure S 1 (a) before matching; b) after matching). The compression isotherms of all polymers are shown in Figure S 2 (a) before matching; b) after matching). All compression isotherms shown in the main part of the communication are corrected in this manner. The surface pressure (*SP*; calculated by the subtraction of the interface tension of interface without polymer from the interface tension with polymer) and the *mma* in Table 1 (main part) are determined by the intersection of two tangents added to the corrected isotherms.

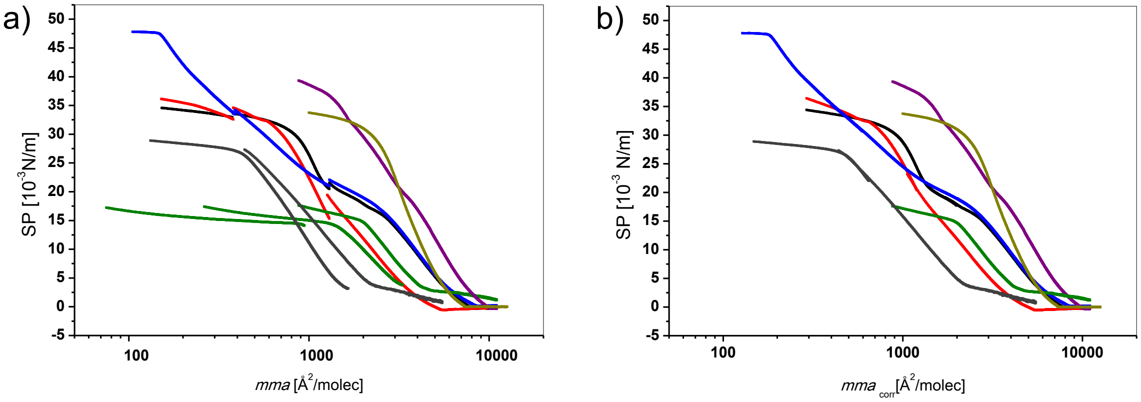

Figure S 2: a) Compression isotherms at an oil-water interface, measured at 35 °C before matching; b) Compression isotherms at an oil-water interface, measured at 35 °C after matching; compression isotherms of diblock copolymers are displayed in following colors: PEO_{114}-*b*-PPO_{69} in blue, PPO_{114}-*b*-$PDMAEMA_{100}$ in red and PEO_{114}-*b*-$PDMAEMA_{61}$ in black; compression isotherms of homopolymers are displayed in following colors: PEO_{114} in green, PPO_{69} in grey and $PDMAEMA_{138}$ in dark yellow; the star polymer PEO_{114}-$(PDMAEMA_{90})_{3.1}$-PPO_{69} is displayed in purple

As a control experiment, the PEO-b-PPO diblock copolymer was measured in three separated steps by preparing always a new interface for each step. This control experiment does not show a significant difference (see Figure S 3 a)). Hence, all other experiments are done by the more timesaving approach described above.

Results and Discussion

General Behavior

All compression isotherms are recorded at an oil-water interface for multiple reasons. The oil-water interface allows us to spread polymers insoluble in chloroform by use of a water/isopropanol mixture (chloroform is typically used for spreading at the water/air interface). More important is the point that all polymers interact with the interface in contrast to the air-water interface (see Figure S 3b). This is especially seen for PEO_{114}-*b*-PPO_{69} that does not show a condensed phase at an air-water interface (see Figure S 3b), probably due to pronounced desorption during compression (as evidenced by the strong “hysteresis” between compression and expansion).

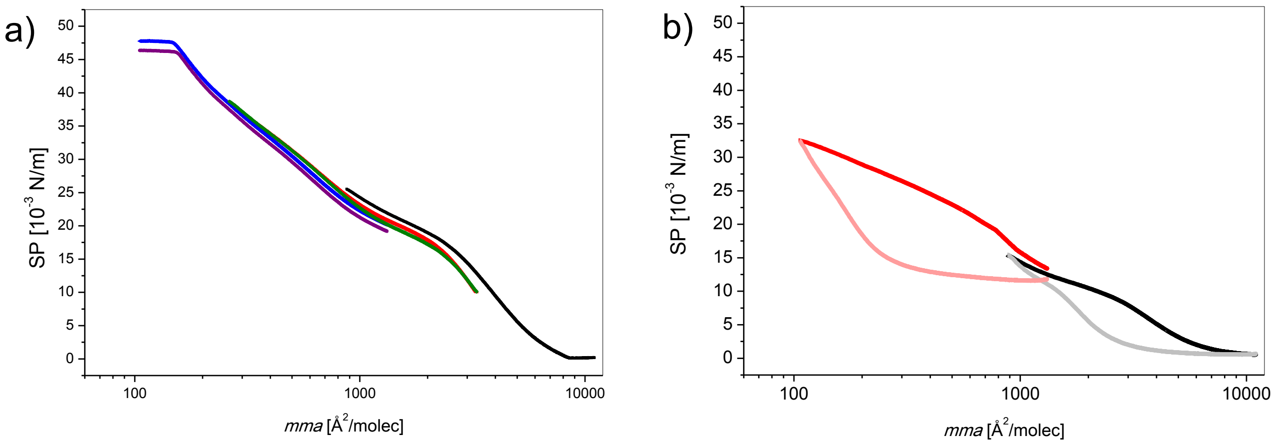

Figure S 3: a) Compression isotherms of PEO_{114}-*b*-PPO_{69} at an oil-water interface, measured at 35 °C in three following steps and in separated steps, 0.6 nmol polymer added to a new interface is displayed in black, 1.4 nmol polymer added to the 0.6 nmol interface is displayed in red, 3.0 nmol polymer added to the 2.0 nmol interface is displayed in blue, 2.0 nmol polymer added to a new interface is displayed in green, 5.0 nmol polymer added to a new interface is displayed in purple; b) PEO_{114}-*b*-PPO_{69} isotherms at an air-water interface (compression in strong colors, expansion in light colours), measured at 35 °C in two following steps, addition of 0.6 nmol polymer is displayed in black (grey), addition of 4.4 nmol polymer is displayed in red (light red)

Charge Effect

Important to notice, the PEO_{114}-*b*-$PDMAEMA_{71}$ shows almost the same behavior as PEO_{114}-*b*-PPO_{69} at higher *mma* values (up to *SP* of 20 mN/m). This superposition of both compression isotherms can be explained by the very similar block lengths in both cases. This comparison shows that charging effects of PDMAEMA are not dominant during these experiments, as the amine-containing block copolymer and the neutral one gives similar behavior. Though the pH of the used deionized water was about pH 6 (indicating protonation in bulk water), this behavior can be explained by restricted protonation at the interface. The confinement of the weak polyelectrolyte into 2D aggravates charging.[5,6]

Compilation of Results

The raw data with compression and expansion isotherms at an oil-water interface of all polymers are displayed in Figure S 4. The most interesting point in the expansion isotherms is the missing shoulder at low *SP* for PPO_{69}-*b*-$PDMAEMA_{100}$. This might indicate that noncomplexed PPO is pressed into the complex and therefore has no influence on the isotherm anymore. In addition, there are also missing PDMAEMA shoulders during expansion at high *SP* for PEO_{114}-$(PDMAEMA_{90})_{3.1}$-PPO_{69} and PPO_{69}-*b*-$PDMAEMA_{100}$. This might also indicate that noncomplexed PDMAEMA is pressed into the complex and therefore has no influence on the expansion isotherm anymore (consider also the rather small plateaus for PDMAEMA, which indicated only limited availability of free PDMAEMA, though PDMAEMA as such can be the majority component). At higher compression, the diblock copolymers desorb most likely in form of unimers, which probably do not self-assemble into micelles due to the lowered interfacial tension of the PPO/PDMAEMA complex and low polymer concentration (below *cmc* in bulk).[3]

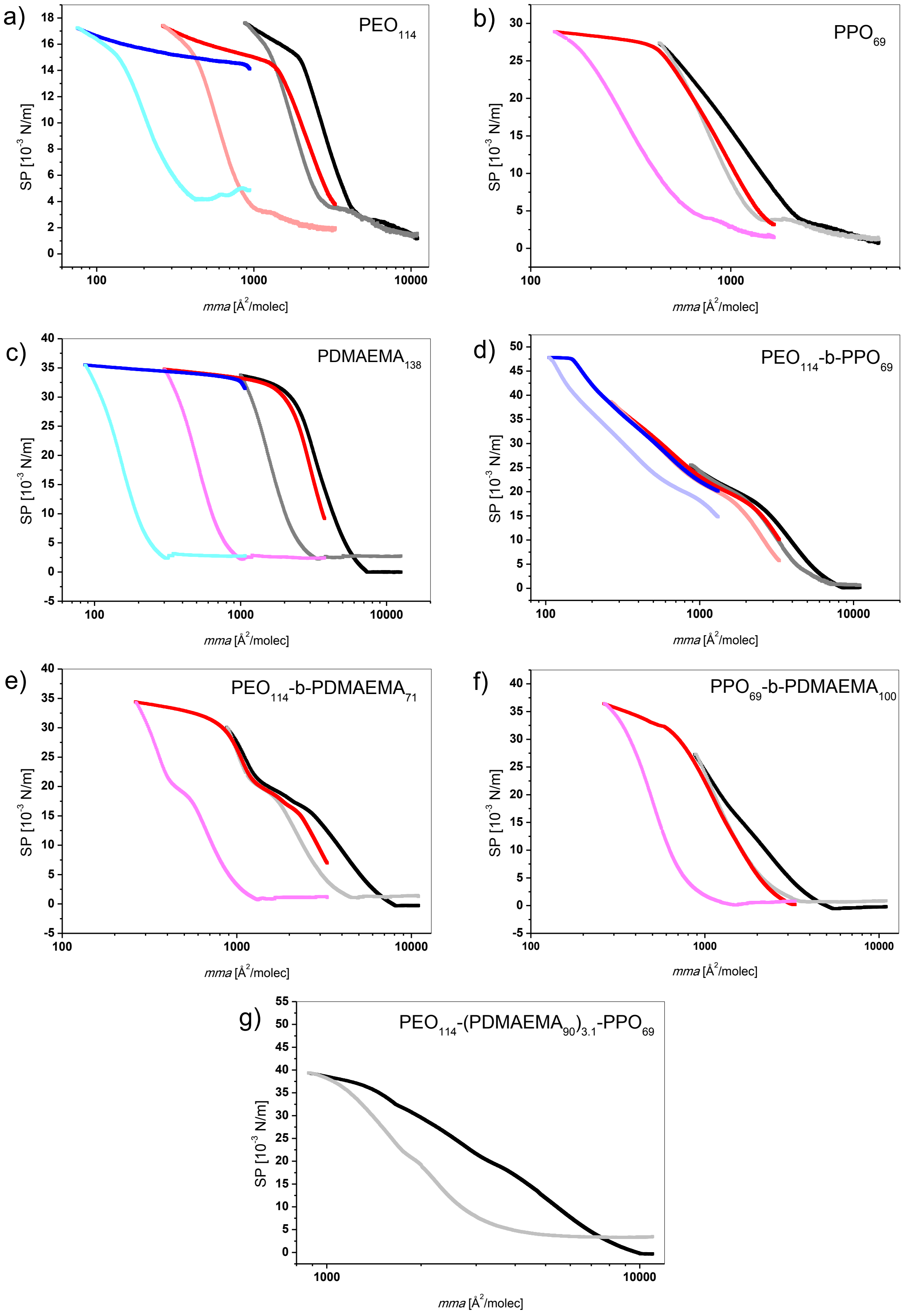

Figure S 4: Compression and expansion isotherms at an oil-water interface, measured at 35 °C, compression isotherms are marked in dark colors, expansion isotherms in light colors, isotherms are recorded stepwise with the first step with 0.6 nmol polymer at the interface is colored in black (and grey for expansion), the second step with 2.0 nmol polymer at the interface is colored in red and the third step colored in blue, a) PEO$_{114}$ homopolymer (last step with 7.0 nmol at the interface) b) PPO$_{69}$ homopolymer (first step with 1.2 nmol at the interface, second step with 4.0 nmol at the interface) c) PDMAEMA$_{138}$-homopolymer (last step with 7.0 nmol at the interface) d) PEO$_{114}$-*b*-PPO$_{69}$ diblock copolymer (third step with 5.0 nmol at the interface) e) PEO$_{114}$-*b*-PDMAEMA$_{71}$ diblock copolymer f) PPO$_{69}$-*b*-PDMAEMA$_{100}$ diblock copolymer g) PEO$_{114}$-(PDMAEMA$_{90}$)$_{3.1}$-PPO$_{69}$ miktoarm star

Snapshots of Selected Systems

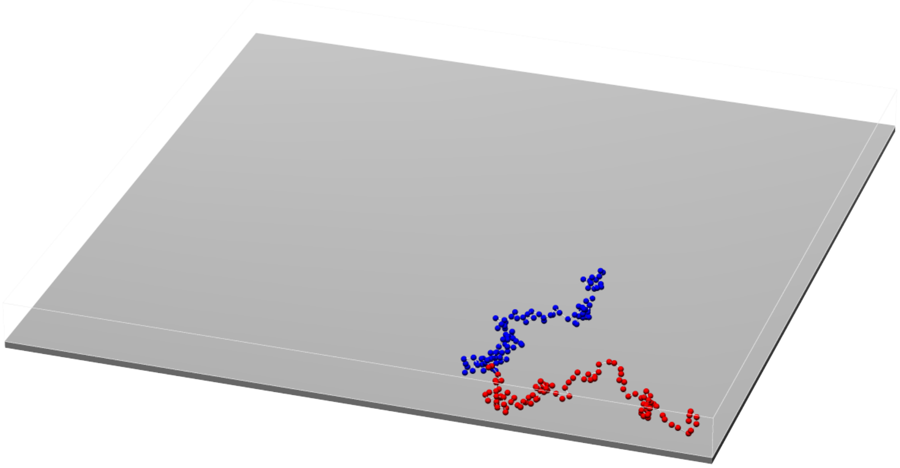

Figure S 1: Snapshot of a diblock copolymer in z confinement with $z = 30\,\mathrm{nm}$ at $\varepsilon = 0.0\,k_\mathrm{B}T$. Click to activate the interactive 3D snapshot (works with Adobe Acrobat Reader).

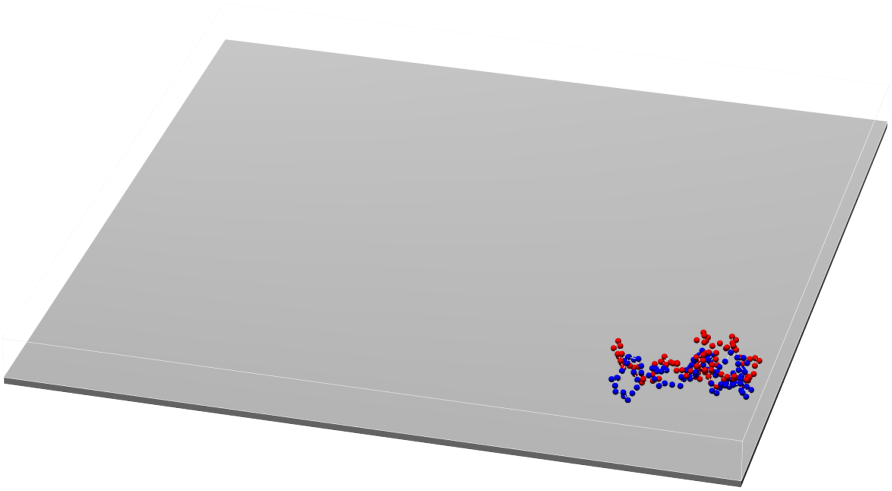

Figure S 2: Snapshot of a diblock copolymer in z confinement with $z = 30\,\mathrm{nm}$ at $\varepsilon = 0.56\,k_\mathrm{B}T$. Click to activate the interactive 3D snapshot (works with Adobe Acrobat Reader).

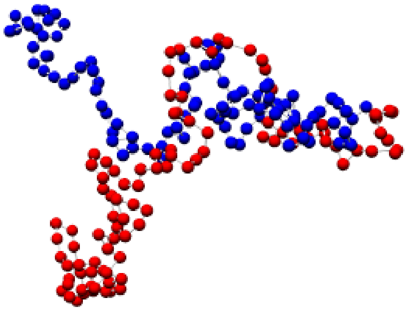

Figure S 3: Snapshot of a diblock copolymer without any z confinement at $\varepsilon = 0.56\,k_\mathrm{B}T$. Click to activate the interactive 3D snapshot (works with Adobe Acrobat Reader).

References

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