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Interface-enforced complexation between copolymer blocks†

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Binary diblock copolymers and corresponding ternary miktoarm stars are studied at oil–water interfaces. All polymers contain oil-soluble poly(propylene oxide) PPO, water-soluble poly(dimethylaminoethyl methacrylate) PDMAEMA and/or poly(ethylene oxide) PEO. The features of their Langmuir compression isotherms are well related to the ones of the corresponding homopolymers. Within the Langmuir-trough, PEO-*b*-PPO acts as the most effective amphiphile compared to the other PPO-containing copolymers. In contrast, the compression isotherms show a complexation of PPO and PDMAEMA for PPO-*b*-PDMAEMA and the star, reducing their overall amphiphilicity. Such complex formation between the blocks of PPO-*b*-PDMAEMA is prevented in bulk water but facilitated at the interface. The weakly-interacting blocks of PPO-*b*-PDMAEMA form a complex due to their enhanced proximity in such confined environments. Scanning force microscopy and Monte Carlo simulations with varying confinement support our results, which are regarded as compliant with the mathematical random walk theorem by Pólya. Finally, the results are expected to be of relevance for e.g. emulsion formulation and macromolecular engineering.

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Introduction

Amphiphilic copolymers are well known and understood for their self-assembly in bulk solution.¹ The formation of star-like (core-corona), worm-like or vesicular morphologies depend on e.g. the respective block lengths and the interfacial tension between the insoluble component and the solvent.^{2,3} At the same time, many amphiphilic block copolymers exhibit surface activity, i.e. the polymers can be anchored at water–air or water–oil interfaces.

One important tool to investigate the properties of interfaces is the Langmuir-trough experiment. Compression and expansion isotherms give information on the spatial demands of adsorbed polymers along with their ability to stabilize the interface. In previous studies amphiphilic diblock copolymers,^{4–6} colloidal particles like microgels,^{7,8} thermoresponsive polymers^{9,10} and star-shaped molecules have been investigated.^{11–14}

Interfaces also operated as templates for complexation between different components.^{15–19,50} In most reported studies, the dominant attractive forces would also act in common

solvents, allowing complexation not only at interfaces.^{19,20} Even without such attractive forces, immiscible branched polymers can intermingle at the bottom and top of fluid interfaces due to steric effects upon compression (though they are still immiscible on local chain level).²¹ Hence, interfaces provide platforms for unexpected properties of surface-active entities, being unparalleled in bulk.^{22,23,49}

We have reported on the prevention of self-assembly of so-called miktoarm stars by architecture-induced complexation in bulk water.²⁴ Within one molecule,²⁵ different poly(propylene oxide) (PPO) and poly(dimethylaminoethyl methacrylate) (PDMAEMA) arms interacted due to the increased mutual segment density close to the center of these star-shaped polymers. The complexation led to a reduction of interfacial tension between the complex and bulk water: the rather hydrophilic PDMAEMA shields the more hydrophobic (PPO-rich) interior of the PPO–PDMAEMA complex.²⁶

In contrast, linear PPO-*b*-PDMAEMA block copolymers exhibit hardly any complexation in bulk water but initiate “conventional” micellization toward constructs possessing hydrophobic PPO cores and hydrophilic PDMAEMA coronas.²⁴ The connectivity as such is not sufficient to promote complexation but chain segregation dominates. This was also found for other copolymers: statistical copolymers show a synergistic depression of cloud points whereas block copolymers are unaffected.²⁷ In sum, there is a prerequisite of high mutual segment density and spatial proximity between weakly interacting partners. Only by aid of certain

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† Electronic supplementary information (ESI) available: Details about the synthesis, the matching of the compression isotherms, the expansion isotherms and the interactive simulation snapshots of selected systems. See DOI: 10.1039/c5sm00242g

Scheme 1 Interface as catalyst for complex formation between the two weakly interacting polymers in PPO-*b*-PDMAEMA; complexation is aided by the proximity of PPO and PDMAEMA within interfacial pancakes (bottom) while no complexation for PPO-*b*-PDMAEMA is seen in bulk water (top).

measures, such as advanced macromolecular architecture, the effect of weak interaction of PPO and PDMAEMA can be amplified in bulk H₂O.

Within this report, we add an unprecedented interface-stimulated complexation as an additional measure: the interface directs each of the two weakly interacting partners of PPO-*b*-PDMAEMA toward the phase boundary and therefore into spatial proximity, facilitating their complexation also at the oil–water interface (see Scheme 1). Due to varying degrees of freedom, such complexation occurs in a 2D environment but not in 3D, as being rationalized by Monte Carlo simulations under varying confinement and by Pólya's mathematical approach.²⁸ Recent simulations on polymers in confined space have not addressed intramolecular polymer complexation.^{29–31,51} Hence, simulations are regarded within this manuscript to understand the interfacial properties of PPO-*b*-PDMAEMA.

Experimental section

Materials

Poly(propylene glycol) ($M_n = 4000 \text{ g mol}^{-1}$; $D = 1.1$) was delivered by Polysciences, Warrington, PA, USA. Poly(ethylene glycol) methyl ether ($M_n = 5000 \text{ g mol}^{-1}$; $D = 1.1$) was delivered by Sigma-Aldrich. *n*-Decane and alumina were obtained from Merck (Darmstadt, Germany).

The synthesis of the polymers PEO₁₁₄-(PDMAEMA₉₀)_{3,1}-PPO₆₉, PEO₁₁₄-*b*-PPO₆₉, PPO₁₁₄-*b*-PDMAEMA₁₀₀ is described in references (the indexes account for the number-average degree of polymerization per block and the arm number respectively).^{24–26} The synthesis of the homopolymer PDMAEMA₁₃₈ is in accordance with literature (for an exact description see ESI†).³² The synthesis of the diblock copolymer PEO₁₁₄-*b*-PDMAEMA₇₁ is described in the ESI†.

The block content and dispersity (D_M) of the analysed polymers is shown in the ESI† (Table S1).

Preparation of the monolayer

The compression and expansion experiments were measured with a KSV Nima Liquid/Liquid Langmuir trough. The trough and the barriers are made of polyoxymethylene (POM). The trough has a length of 737 mm. The width is 54 mm and therefore it has an area of approximately 400 cm². The used Wilhelmy plate has a perimeter of 39.24 mm. The temperature was set to 35 °C for all experiments to ensure the hydrophobicity of PPO. The trough was placed in a custom-built box to prevent disturbing air flows causing measurement errors.

Millipore water was used as an aqueous subphase. *n*-Decane, which was filtered three times over basic and neutral aluminium oxide, was used as an oil phase. After addition of each phase, the interface was compressed and cleaned with a vacuum nozzle to ensure a clean interface.

The examined polymer was dissolved in a water : isopropanol mixture (4.5 : 1 v : v) to facilitate the spreading of the polymer at the interface.⁸ The concentration used for all polymer samples was 0.1 mmol L⁻¹. The polymer solution was added drop wise to the oil–water interface using a Hamilton Gastight[®] Syringe (50 µL). 45 min of equilibration time was given before each compression. The interface was compressed with a barrier speed of 10 mm min⁻¹. The available surface for one polymer molecule is given by the mean molecular area (mma), which is defined by the following:

$$\text{mma} = (A \cdot M) / (m \cdot N_A) \quad (1)$$

A is the actual area of the trough enclosed by the two barriers, M the respective molecular weight of the polymer and m the mass of polymer at the interface. It is assumed for this formula that all polymer remains at the interface.

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 30 µL (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 ESI†). These three isotherms are then matched by recalculating the mma with a reduced assumed polymer concentration at the interface (see ESI† for more detailed information about the matching).

Fabrication and characterization of monolayers after Langmuir–Blodgett transfer

The Langmuir–Blodgett (LB) studies were conducted using a KSV 2000 minitrough according to the usual procedure adapted in the lab.³³ The temperature was set to 35 °C for all experiments by using a temperature controller (PolyScience, Model 9106) with an accuracy of ± 0.1 °C. Millipore water was used as an aqueous subphase, and *n*-heptane was used as an oil phase in order to have a faster drying. Freshly cut silicon substrates with dimensions of 1 cm × 2 cm and [100] orientation

(semiconductor processing) with a native silicon dioxide layer (2 nm) were cleaned with piranha solution (3 : 1 concentrated sulfuric acid and hydrogen peroxide mixture) in accordance with the usual procedure. Subsequently, it was thoroughly rinsed with Millipore water and dried with a dry nitrogen stream. The freshly cleaned silicon wafers were immersed in 10 wt% HF solution for 3 min, and then dried with nitrogen stream again. The HF treatment is used to transform the Si wafer surface from hydrophilic (contact angle close to 0°) to hydrophobic (contact angle of 75°).

The block copolymer was dissolved in a water : isopropanol mixture (4.5 : 1 v : v) with a concentration of 0.01 mmol L⁻¹, and 4.8 μL polymer solution was added drop wise to the oil–water interface. The concentration and volume of the samples are chosen to make sure that the block copolymers are in gas state at the interface and the chains are well dispersed on the substrate after transferring. 45 min of equilibration time was given after spreading the polymer solution. The Langmuir–Blodgett monolayer was transferred from the oil–water interface by vertically dipping the substrate from air down to the water subphase at a rate of 1 mm min⁻¹.

Atomic force microscopy (AFM) images of the monolayers were obtained with an Icon Bruker atomic force microscope. The AFM images were generated in the “light” tapping mode with an amplitude ratio within 0.90–1.00 to avoid monolayer damage. The AFM cantilevers had spring constants in the range of 40–60 N m⁻¹, and the scanning rate was 0.5 Hz. AFM section analysis was performed with a NanoScope Analysis software, and the average height of the granules was obtained by averaging at least 50 different points from several AFM images of the same sample.

Model and simulation details

The linear diblock copolymer is modeled as a bead-spring chain with monomers represented as hard spheres. The chain contains two distinct blocks composed of one particle type each, representing the PPO and PDMAEMA monomers of the real system. Both particle types are identical in radius ($r_{\text{HS}} = 0.2$ nm) and all particles interact through a hard sphere potential. An additional Lennard-Jones-(12,6) (LJ) interaction potential is applied between two particles of different types representing attractive interactions.

$$u_{ij} = \begin{cases} \infty & r_{ij} < \sigma \\ 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] & r_{ij} \geq \sigma \end{cases} \quad (2)$$

with σ being the particle diameter. The depth of the potential well ϵ was varied from 0.0 to approx. 1.2 $k_{\text{B}}T$ in all simulation sets for a temperature of $T = 298$ K. No LJ potential is applied between particles of the same type. Furthermore, all particles are connected *via* a harmonic potential representing the bond with a force constant $k_{\text{bond}} = 0.4$ N m⁻¹ and an equilibrium bond length of $r_{\text{eqv}} = 0.5$ nm.

Two distinct cases were investigated. In case one, the polymer chain is contained in a cubic simulation cell with $L_x = L_y = L_z = 50$ nm

and periodic boundary conditions in all directions, representing an unconfined system. In case two, periodic boundaries are only applied in xy -directions ($L_x = L_y = 50$ nm) and in the z direction hard wall potentials are applied at $z \leq -L_z/2$ and $z \geq L_z/2$. The length of the cell in z -direction is varied in the interval $L_z = [3, 24]$ nm with an increment of 3 nm. The second case represents a pseudo-2D geometry as a model of the interface of the experimental system.

Monte Carlo simulations were performed in the canonical ensemble (NVT) using single particle moves and pivot moves. The maximal translational displacement values of a single particle were chosen to yield an acceptance ratio of approx. 20–30%. Each calculation started with an equilibration run of 5×10^6 MC steps to achieve thermodynamic equilibrium followed by a production run of 5×10^6 steps.

The error bars (one standard deviation of the mean) in Fig. 3 are smaller than the data symbols and therefore omitted.

Results and discussion

The preparation of the polymers is reported elsewhere or adapted to previous reports (see Experimental section and ESI†).^{24,25,32} To highlight the role of the different polymer components and the architectural effect on the interfacial properties, different diblock copolymers (PEO₁₁₄-*b*-PPO₆₉, PEO₁₁₄-*b*-PDMAEMA₇₁, PPO₆₉-*b*-PDMAEMA₁₀₀), their corresponding homopolymers (PEO₁₁₄, PPO₆₉, PDMAEMA₁₃₈) and a miktoarm star uniting all components (PEO₁₁₄-(PDMAEMA₉₀)_{3.1}-PPO₆₉) have been studied in a Langmuir trough and compared (indices assign their degree of polymerization and arm number, respectively). All compression isotherms are recorded at an oil–water interface. Such liquid/liquid interface allows the spreading of polymers which are 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 ESI†, Fig. S2b).

We shortly describe the general processes involved during compression.^{34,35} Before the pancake/coil transition, the polymer allows multiple contacts with the interface and their chain moieties. Per unit area, the number of contact points increase with compression, leading to a slight increase in surface pressure (SP) with decreasing mean molecular area (mma). Upon first contact of the polymers due to compression (equal to mma_0) the SP increases strongly with decreasing mma as the interface is completely covered and the contact points per area still increase. After a certain compression, the gain in interfacial energy per contact point cannot compensate the constraints of the increasingly compressed polymer chains at the 2D plain. More favorable, a detachment of surface-bound moieties takes place, allowing a gradual release of the rather confined polymer into 3D space (B in Fig. 1). In case of the homopolymers, the polymers start to detach from the interface due to the reduction in number of contact points during compression. This finally leads to the removal of polymer at already rather high mma values. Still, the number of contact points per unit area stays

Fig. 1 Compression isotherms of (block) copolymers (linear PEO₁₁₄-b-PPO₆₉, PPO₆₉-b-PDMAEMA₁₀₀, PEO₁₁₄-b-PDMAEMA₇₁ and star-shaped PEO₁₁₄-(PDMAEMA₉₀)_{3.1}-PPO₆₉) at an *n*-decane–water interface at 35 °C: surface pressure SP against mean molecular area mma (see ESI†; the capital letters refer to Scheme 2; inset shows PDMAEMA-related “plateaus”).

rather constant during this conformational transition, as manifested in the rather constant SP. For real amphiphilic diblock copolymers, the number of amphiphilic junctions (amphiphilic connections between the blocks) at the interface increases per unit area, leading to an effective stabilization of the interface up to high SP. At a critical value, the monolayer collapses under formation of a multilayer and partial detachment of polymer, manifested in a real plateau (for PEO-*b*-PPO D in Fig. 1).

Related to the homopolymers (see Table 1 and ESI†), the corresponding copolymers show similarities at an oil–water interface. The SP at the plateaus of the diblock copolymers resembles the one of the homopolymers. Fig. 1 suggests independent transitions of one block after the other. The PEO-interface contact points provide the weakest stabilization of all homopolymers, as seen by the low SP value in Table 1. Along with the PEO length, this gives reason why PEO detaches first also in the corresponding diblock copolymers. The copolymers containing PEO show both a plateau at a similar SP as the PEO homopolymer, analogously to other PEO-based copolymers.⁴ At the same time, the mean molecular area (mma) of the PEO-related

plateau of both PEO-based diblocks is shifted similarly to a higher mma value (compared to the PEO homopolymer) due to larger spatial demands (both blocks contact the interface from different sides, avoiding sandwich conformation for maximum coverage). Also PDMAEMA-containing copolymers show a plateau at a similar SP as the homopolymers. Generally, these plateaus are connected to conformational transitions at the polymer-decorated interface. The pancake-like⁴ conformations in the expanded state experience a transition to more extended coil- or mushroom-like conformations.

The ability of the bishydrophilic PEO₁₁₄-*b*-PDMAEMA₇₁ to increase the surface pressure is given by the ability of its homopolymers, providing two respective plateaus. The surface detachment of block/interface contacts occurs on the same side for both blocks (Scheme 2). Hence, PEO₁₁₄-*b*-PDMAEMA₇₁ desorbs into the bulk water upon compression. This is especially seen for the expansion isotherms, which deviate strongly from the compression isotherms still at high mma (≤ 10 nm² per molec; see ESI†) due to ineffective anchoring. This is actually the case for all polymers, except PEO₁₁₄-*b*-PPO₆₉.

PEO₁₁₄-*b*-PPO₆₉ shows parallel compression and expansion isotherms down to low mma values (~ 2 nm² per molec). Hence it can be regarded as an effective amphiphile as it remains anchored at the interface in contrast to the respective homopolymers and bishydrophilic species. Only below mma ~ 2 nm² per molec, the monolayer collapses under formation of multilayers and/or partial polymer detachment, manifested in a real plateau. Before, the polymer chains eventually adapt an almost fully stretched conformation (brush), effectively stabilizing the interface up to high SP (48 mN m⁻¹, being close to the interfacial tension of ~ 51 mN m⁻¹ for water/*n*-decane).³⁶ Therefore, this plateau is probably caused by the point where the interface tension between water and *n*-decane is decreased to nearly 0 and no further stabilization is possible.

PPO₆₉-*b*-PDMAEMA₁₀₀ does not act as such an effective amphiphile, allowing a considerable mismatch of expansion and compression isotherms already at high mma values (ESI†). This can be explained by interfacial desorption, stimulated by complex formation between PPO and PDMAEMA²⁴ which prevents effective anchoring to the interface. Hence, the maximum SP rises only slightly above the SP of pure PDMAEMA (a plateau

Table 1 Surface pressure (SP in 10^{-3} N m⁻¹) assigned in *italics* and mma (mean molecular area in [nm² per molec] in black) of the used polymers at the water–oil interface (oil: *n*-decane)

Onset shoulder as marked in Fig. 1	PEO ₁₁₄	PPO ₆₉	PDMAEMA ₁₃₈	PEO ₁₁₄ - <i>b</i> -PPO ₆₉	PEO ₁₁₄ - <i>b</i> -PDMAEMA ₇₁	PPO ₆₉ - <i>b</i> -PDMAEMA ₁₀₀	PEO ₁₁₄ -(PDMAEMA ₉₀) ₃ -PPO ₆₉
A ^a	48	27	60	68	68	42	84
A ^b						19.5	
B				26	28	12	39
				17	15	6.8	18
C				6.5		32	21
				29			29
D ^c	20	4.6	24	1.8	9.4	4.5	14
	15	28	31	48	31	34	37

^a mma at the intercept of tangents around the first rise in SP (mma₀). ^b Slight shoulder only observed for PPO₆₉-*b*-PDMAEMA₁₀₀ at first compression. ^c Collapse of monolayer.

Scheme 2 Illustration of the diblock copolymers and the miktoarm star at the oil–water interface upon compression.

at $\sim 32 \text{ mN m}^{-1}$ is seen in the inset of Fig. 1) into a (pseudo-) plateau with onset at $\sim 34 \text{ mN m}^{-1}$. This is considerably below the SP of the real amphiphile $\text{PEO}_{114}\text{-}b\text{-PPO}_{69}$ (Fig. 1) and unexpectedly close to the one of bishydrophilic $\text{PEO}_{114}\text{-}b\text{-PDMAEMA}_{71}$. The interfacial complex, which is promoted by the close proximity of the interacting chains at the interface, provides only a limited amphiphilic character due to the presence of hydrophobic PPO and hydrophilic PDMAEMA: the surface of the complex can adapt to the surroundings.²⁶ Hence the complex can also reduce its ability to stabilize interfaces. Due to excess PDMAEMA in $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$, one hardly discerns any characteristics related to the PPO homopolymer. Only the slight shoulder at 12 mN m^{-1} might be caused by some PPO being favorably compressed into the induced PDMAEMA–PPO complex (A' in Fig. 1) as evidenced by its disappearance during the second compression (ESI†). A more detailed investigation by block length variation is planned.

Importantly, the mma_0 values (mma at the first rise in SP upon compression) are related to the spatial demands of the respective pancake-like conformations. They indicate a rather compact structure at the interface for $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$ compared to e.g. $\text{PEO}_{114}\text{-}b\text{-PPO}_{69}$ (Table 1), though both have comparable block lengths and hydrodynamic radii in molecularly

dispersed solution.²⁴ The compactness of these $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$ pancake/sandwich-like structures can be visualized by Langmuir–Blodgett transfer onto silica wafers, followed by scanning force microscopy in the dry state.³³ $\text{PEO}_{114}\text{-}b\text{-PPO}_{69}$ and $\text{PEO}_{114}\text{-}b\text{-PDMAEMA}_{71}$ exhibit only flat pancakes (height of granules $\sim 0.36 \text{ nm}$, corresponding to a single chain conformation; Fig. 2). $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$ shows more globular structures (height $\sim 0.64 \text{ nm}$: sandwich conformation). Again, this suggests an interfacial complexation for $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$.

Such compaction can be understood in terms of Monte Carlo simulations (Fig. 3 and ESI†).³⁷ This compaction was qualitatively demonstrated by introducing two hard wall confinements in z -direction. The confinement in z -direction mimics the close proximity of the PPO and PDMAEMA pancakes at the interface which are typically confined in a layer in the range of nanometers.⁵ With decreasing gap size (stronger 2D confinement), the normalized end-to-end distance decreases at lower interaction energy ϵ of the two blocks (especially at $0.4k_{\text{B}}T < \epsilon < 0.7k_{\text{B}}T$). The increased proximity is sufficient to trigger the complexation between the weakly interacting partners PPO and PDMAEMA. Demonstrated by a comparison with simulations³⁸ and experimental results,^{24,26} this interfacial effect is similar to the architectural effects responsible for the induced complexation within miktoarm stars in bulk solution.

At the interface, the miktoarm star has analogous properties as $\text{PEO}_{114}\text{-}b\text{-PDMAEMA}_{71}$ and $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$ (Fig. 1). The collapse of the monolayer is at a slightly higher SP than the one of the collapse of the $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$ monolayer. The absent increase of the SP to even higher values indicates that also the star lacks a pronounced amphiphilic character due to complexation. Though parts of the miktoarm star are hydrophobic, the internal complexation prevents the benefits of a Janus-like structure^{39,40} by a reduction of interfacial tension between complex and bulk medium.

Fig. 2 AFM height images (top) of $\text{PEO}_{114}\text{-}b\text{-PPO}_{69}$ (left), $\text{PEO}_{114}\text{-}b\text{-PDMAEMA}_{71}$ (center), $\text{PPO}_{69}\text{-}b\text{-PDMAEMA}_{100}$ (right; scan size: 500 nm , Z range: 1.0 nm ; obtained from expanded state A after Langmuir–Blodgett transfer onto HF-treated silicon wafer) and the statistical height distribution of the block copolymers obtained from AFM section analysis (bottom)

Fig. 3 Normalized end-to-end distance $[(R_{ee}^2(\epsilon))^{0.5} - \langle R_{ee}^2(\epsilon = 1.21 k_B T) \rangle^{0.5}] / [\langle R_{ee}^2(\epsilon = 0) \rangle^{0.5} - \langle R_{ee}^2(\epsilon = 1.21 k_B T) \rangle^{0.5}]$ of a diblock copolymer with interacting blocks (100 beads each) as a function of the interaction energy ϵ and confinement (varied by gap size z : $z = \infty$ in $\bullet$, $z = 12$ nm in $\blacktriangledown$, $z = 9$ nm in $\blacktriangle$, $z = 6$ nm in $\blacklozenge$, $z = 3$ nm in $\blacksquare$) obtained by use of simulations (top) and exemplary simulation snap shots (bottom; see ESI,† also for interactive snapshots).

The *n*-decane close to the interface appears to have only negligible effects on the general mechanism of interaction between the blocks. Complexation would require limited immersion of parts of PDMAEMA into the oil phase and parts of PPO into the water phase. Hence, this unfavorable contribution is more than outweighed by the complexation as such. Once bound to the interface, the different monomeric units tend to complex irrespective of the surrounding solvent hemispheres. Additionally, the interface might even help to orient the complexing partners beneficially.

Besides Langmuir–Blodgett/AFM technique, supplementary techniques for structure determination are available for the air–water interface, like reflectometry.^{41,42} However the structural analysis of the oil–water interface is much less developed. Hence we concentrate on the Langmuir technique at this stage. In future we aim to gain spectroscopic evidence for complexation by *e.g.* sum frequency generation spectroscopy (SFG),^{43–46} which will be still a challenge at liquid/liquid interfaces. The same is true for structure determination, as in the case of *e.g.* neutron reflectometry.^{47,48}

Conclusions

The characteristic features of the Langmuir compression isotherms of the PEO₁₁₄–(PDMAEMA₉₀)_{3.1}–PPO₆₉ miktoarm terpolymer and the corresponding diblock copolymers, PPO₆₉-*b*-PDMAEMA₁₀₀, PEO₁₁₄-*b*-PPO₆₉ and PEO₁₁₄-*b*-PDMAEMA₇₁ at the oil–water interface are compared to the compression isotherms of the corresponding homopolymers. Unless PPO and PDMAEMA are simultaneously present in the polymer, each block detaches independently from the interface in the order of the stabilizing abilities of the involved homopolymers. This happens by removing interfacial contacts of the pancake-like conformations (as seen in isotherm plateaus). While all PPO-containing copolymers are supposed to show a compression behavior of a truly amphiphilic copolymer, only the PEO₁₁₄-*b*-PPO₆₉ does. This is caused by the complexation of PPO with PDMAEMA in PPO₆₉-*b*-PDMAEMA₁₀₀ and in the miktoarm star. This kind of complex was already found for the star in bulk water but not for the diblock copolymer.²⁴ The complexation is facilitated by the close proximity of PPO and PDMAEMA at the oil–water interface before and during compression. Finally, this macromolecular system can be regarded as compliant with the mathematical Pólya's random walk theorem,²⁸ which states that a random walker always returns to its origin in 1D and 2D but not necessarily in a 3D system. In our case, the complexation between the weakly-attractive components can be considered as a sensor for the return of the “random” chain toward its origin/complexant. Hence, both the mathematical approach of Pólya and the simulations help to understand why this return and therefore complexation does take place in a pseudo-2D environment but hardly in 3D.

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Notes and references

- 1 E. B. Zhulina and O. V. Borisov, *Macromolecules*, 2012, **45**, 4429–4440.
- 2 F. A. Plamper, A. P. Gelissen, J. Timper, A. Wolf, A. B. Zevin, W. Richtering, H. Tenhu, U. Simon, J. Mayer, O. V. Borisov and D. V. Pergushov, *Macromol. Rapid Commun.*, 2013, **34**, 855–860.
- 3 Y. Mai and A. Eisenberg, *Chem. Soc. Rev.*, 2012, **41**, 5969–5985.
- 4 H. D. Bijsterbosch, V. O. de Haan, A. W. de Graaf, M. Mellema, F. A. M. Leermakers, M. A. C. Stuart and A. A. V. Well, *Langmuir*, 1995, **11**, 4467–4473.
- 5 M. Kraska, M. Gallei, B. Stuehn and M. Rehahn, *Langmuir*, 2013, **29**, 8284–8291.
- 6 F. Rehfeldt, R. Steitz, S. P. Armes, R. von Klitzing, A. P. Gast and M. Tanaka, *J. Phys. Chem. B*, 2006, **110**, 9171–9176.

- 7 C. Said-Mohamed, J. Niskanen, M. Karesoja, P. Pulkkinen, H. Tenhu, M. Daoud and L.-T. Lee, *Soft Matter*, 2011, **7**, 7112–7122.
- 8 K. Geisel, L. Isa and W. Richtering, *Angew. Chem., Int. Ed.*, 2014, **53**, 4905–4909.
- 9 A. M. P. S. Gonçalves da Silva, S. I. C. Lopes, P. Brogueira, T. J. V. Prazeres, M. Beija and J. M. G. Martinho, *J. Colloid Interface Sci.*, 2008, **327**, 129–137.
- 10 P. C. D. S. Claro, M. E. Coustet, C. Diaz, E. Maza, M. S. Cortizo, F. G. Requejo, L. I. Pietrasanta, M. Ceolin and O. Azzaroni, *Soft Matter*, 2013, **9**, 10899–10912.
- 11 R. Kodiyath, I. Choi, B. Patterson, C. Tsitsilianis and V. V. Tsukruk, *Polymer*, 2013, **54**, 1150–1159.
- 12 I. Choi, R. Gunawidjaja, R. Suntivich, C. Tsitsilianis and V. V. Tsukruk, *Macromolecules*, 2010, **43**, 6818–6828.
- 13 J. L. Logan, P. Masse, Y. Gnanou, D. Taton and R. S. Duran, *Langmuir*, 2005, **21**, 7380–7389.
- 14 J. L. Logan, P. Masse, B. Dorvel, A. M. Skolnik, S. S. Sheiko, R. Francis, D. Taton, Y. Gnanou and R. S. Duran, *Langmuir*, 2005, **21**, 3424–3431.
- 15 G. Decher, *Science*, 1997, **277**, 1232–1237.
- 16 H. Monteillet, F. Hagemans and J. Sprakel, *Soft Matter*, 2013, **9**, 11270–11275.
- 17 S. Yang, S. Ma, C. Wang, J. Xu and M. Zhu, *Aust. J. Chem.*, 2014, **67**, 11–21.
- 18 L. A. Bimendina, S. E. Kudaibergenov and E. A. Bekturov, *J. Macromol. Sci., Polym. Rev.*, 2003, **C43**, 27–44.
- 19 S. Le Tirilly, C. Tregouët, S. Bône, C. Geffroy, G. Fuller, N. Pantoustier, P. Perrin and C. Monteux, *ACS Macro Lett.*, 2014, **4**, 25–29.
- 20 N. Higashi, T. Matsumoto and M. Niwa, *Langmuir*, 1994, **10**, 4651–4656.
- 21 S. S. Sheiko, J. Zhou, J. Arnold, D. Neugebauer, K. Matyjaszewski, C. Tsitsilianis, V. V. Tsukruk, J.-M. Y. Carrillo, A. V. Dobrynin and M. Rubinstein, *Nat. Mater.*, 2013, **12**, 735–740.
- 22 N. Du, R. Song, X. Zhu, W. Hou, H. Li and R. Zhang, *Chem. Commun.*, 2014, **50**, 10573–10576.
- 23 S. Jordens, E. E. Riley, I. Usov, L. Isa, P. D. Olmsted and R. Mezzenga, *ACS Nano*, 2014, **8**, 11071–11079.
- 24 A. A. Steinschulte, B. Schulte, S. Rütten, T. Eckert, J. Okuda, M. Möller, S. Schneider, O. V. Borisov and F. A. Plamper, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4917–4932.
- 25 A. A. Steinschulte, B. Schulte, N. Drude, M. Erberich, C. Herbert, J. Okuda, M. Möller and F. A. Plamper, *Polym. Chem.*, 2013, **4**, 3885–3895.
- 26 A. A. Steinschulte, B. Schulte, M. Erberich, O. V. Borisov and F. A. Plamper, *ACS Macro Lett.*, 2012, **1**, 504–507.
- 27 F. A. Plamper, A. A. Steinschulte, C. H. Hofmann, N. Drude, O. Mergel, C. Herbert, M. Erberich, B. Schulte, R. Winter and W. Richtering, *Macromolecules*, 2012, **45**, 8021–8026.
- 28 G. Pólya, *Math. Ann.*, 1921, **84**, 149–160.
- 29 A. Milchev and K. Binder, *Eur. Phys. J. B*, 1998, **3**, 477–484.
- 30 J. Paturej, A. Milchev, S. A. Egorov and K. Binder, *Soft Matter*, 2013, **9**, 10522–10531.
- 31 P. Romiszowski and A. Sikorski, *J. Chem. Phys.*, 2002, **116**, 1731–1736.
- 32 T. Thavanesan, C. Herbert and F. A. Plamper, *Langmuir*, 2014, **30**, 5609–5619.
- 33 I. Choi, D. D. Kulkarni, W. Xu, C. Tsitsilianis and V. V. Tsukruk, *Langmuir*, 2013, **29**, 9761–9769.
- 34 K. Kita-Tokarczyk, M. Junginger, S. Belegirinou and A. Taubert, in *Self Organized Nanostructures of Amphiphilic Block Copolymers II*, ed. A. H. E. Müller and O. Borisov, Springer, Berlin, Heidelberg, 2011, vol. 242, pp. 151–201.
- 35 G. T. Barnes and I. R. Gentle, *Interfacial science: an introduction*, Oxford University Press, Oxford, 2nd edn, 2011.
- 36 R. Aveyard and D. A. Haydon, *Trans. Faraday Soc.*, 1965, **61**, 2255–2261.
- 37 P. Linse, *MOLSIM*, Lund University, Lund, Sweden, 2014.
- 38 P. Hebbeker, F. A. Plamper and S. Schneider, *Macromol. Theory Simul.*, 2015, **24**, 110–116.
- 39 A. Walther and A. H. E. Müller, *Chem. Rev.*, 2013, **113**, 5194–5261.
- 40 A. Kumar, B. J. Park, F. Tu and D. Lee, *Soft Matter*, 2013, **9**, 6604–6617.
- 41 M. Reinhardt, J. Dzubiella, M. Trapp, P. Gutfreund, M. Kreuzer, A. H. Gröschel, A. H. E. Müller, M. Ballauff and R. Steitz, *Macromolecules*, 2013, **46**, 6541–6547.
- 42 T. Ortmann, H. Ahrens, F. Lawrenz, A. Gröning, P. Nestler, J.-U. Günther and C. A. Helm, *Langmuir*, 2014, **30**, 6768–6779.
- 43 P. B. Miranda and Y. R. Shen, *J. Phys. Chem. B*, 1999, **103**, 3292–3307.
- 44 M. M. Knock, G. R. Bell, E. K. Hill, H. J. Turner and C. D. Bain, *J. Phys. Chem. B*, 2003, **107**, 10801–10814.
- 45 D. Lis, J. Guthmuller, B. Champagne, C. Humbert, B. Busson, A. Peremans and F. Cecchet, *ChemPhysChem*, 2013, **14**, 1227–1236.
- 46 K. Laß and G. Friedrichs, *J. Geophys. Res.: Oceans*, 2011, **116**, C08042.
- 47 M. Campana, J. R. P. Webster and A. Zarbakhsh, *Langmuir*, 2014, **30**, 10241–10247.
- 48 A. Zarbakhsh, J. R. P. Webster and K. Wojciechowski, *Langmuir*, 2009, **25**, 11569–11575.
- 49 C.-S. Hsieh, M. Okuno, J. Hunger, E. H. G. Backus, Y. Nagata and M. Bonn, *Angew. Chem., Int. Ed.*, 2014, **53**, 8146–8149.
- 50 L. V. Sigolaeva, S. Y. Gladys, A. P. H. Gelissen, O. Mergel, D. V. Pergushov, I. N. Kurochkin, F. A. Plamper and W. Richtering, *Biomacromolecules*, 2014, **15**, 3735–3745.
- 51 B.-Y. Ha and Y. Jung, *Soft Matter*, 2015, **11**, 2333–2352.