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Controlling self-assembling co-polymer coatings of hydrophilic polysaccharide substrates via co-polymer block length ratio

Alberto Scacchi\textsuperscript{a,b,c,d,⇑}, Kourosh Hasheminejad\textsuperscript{a,d}, Sousa Javan Nikkhah\textsuperscript{a,e}, Maria Sammalkorpi\textsuperscript{a,d,f,⇑}

\textsuperscript{a} Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland
\textsuperscript{b} Department of Applied Physics, Aalto University, P.O. Box 11000, FI-00076 Aalto, Finland
\textsuperscript{c} Interdisciplinary Centre for Mathematical Modelling and Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire LE11 3TU, United Kingdom
\textsuperscript{d} Academy of Finland Center of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland
\textsuperscript{e} Department of Physics, Bernal Institute, University of Limerick, V94 T9PX Limerick, Ireland
\textsuperscript{f} Department of Bioproducts and Biosystems, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland

\textbf{Abstract}

Hypothesis: The degree of polymerization of amphiphilic di-block co-polymers, which can be varied with ease in computer simulations, provides a means to control self-assembling di-block co-polymer coatings on hydrophilic substrates.

Simulations: We examine self-assembly of linear amphiphilic di-block co-polymers on hydrophilic surface via dissipative particle dynamics simulations. The system models a glucose based polysaccharide surface on which random co-polymers of styrene and n-butyl acrylate, as the hydrophobic block, and starch, as the hydrophilic block, forms a film. Such setups are common in e.g. hygiene, pharmaceutical, and paper product applications.

Findings: Variation of the block length ratio (35 monomers in total) reveals that all examined compositions readily coat the substrate. However, strongly asymmetric block co-polymers with short hydrophobic segments are best in wetting the surface, whereas approximately symmetric composition leads to most stable films with highest internal order and well-defined internal stratification. At intermediate asymmetries, isolated hydrophobic domains form. We map the sensitivity and stability of the assembly response for a large variety of interaction parameters. The reported response persists for a wide polymer mixing interactions range, providing general means to tune surface coating films and their internal structure, including compartmentalization.

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1. Introduction

Interfacial coatings by, e.g., polymers, are often used to modify surface interactions of materials with their surrounding medium or to protect the underlying substrate. For example, polymer coatings are used as protective layers in biomedical applications [1–5], as anti-corrosion coats protecting metallic surfaces [6], and as preservative layers conserving stone materials in architectural monuments [7].

Specifically interesting are block co-polymers, which consist of blocks differing in their monomer composition, and consequently chemical properties. Block co-polymers self-assemble into a variety of complex morphologies including core−shell particles, cylinders, lamellae and various gyroidal phases [8–10]. The self-assembly response of amphiphilic co-polymers is highly tunable [11], which enables tailoring assembly and composition differences allowing advanced surface modification. Applications exist, e.g., in antifouling, stabilizer, or humidity protection coatings [12–16]. Block co-polymers also self-assemble into compartmentalized aggregates that find use, e.g., in drug delivery [17–21] and as confined, multi-step reactions platforms [22,23].

Particularly important is controlling the assembly of block co-polymers at interfaces in optical and electronic, pharmaceutical, and advanced surface functionalities applications, see Refs. [24–26] for recent reviews. For instance, Yang et al. [27] showed that grafted amphiphilic co-polymers, with controlled architecture, can be used to protect thin film composites membrane surface from fouling. Such films rely on the high precision self-assembly of block co-polymers to desired structures at low cost [28,29]. Related to this, Chen et al. [30] reported that thin self-assembled films of amphiphilic co-polymers can be used to coat and stabilize nanoparticles, such as magnetic iron oxide in aqueous medium, for biomedical applications.

The morphologies and the structure of self-assembling co-polymer films are controlled by altering the chemical composition, the molecular weight distribution, the architecture of the chains, but also by the solvent and the annealing process [31–37]. Methodology such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), small-angle X-ray and neutron scattering (SAXS and SANS, respectively) capture the microphase structures of the block co-polymer films. Ref. [8] provides an extensive review to the topic. At a more detailed level, layer-by-layer assembly of di-block co-polymer films characterization by SEM is covered in Ref. [38] and thin film characterization by grazing incidence small angle scattering methods in Ref. [39]. In general, examining co-polymer film assembly and internal structure is feasible to high accuracy detail, but obtaining systematic assembly dependency data in terms of individual variable remains arduous.

Computer simulations provide an easily up-scaled effective mean to examine the dependencies of block co-polymer assembly on surfaces. In simulations, one can readily change a single variable at the time to predict the assembly response, such as, e.g., the block chemistries, segment and chain lengths, architecture and solvation conditions. For recent reviews on block co-polymer self-assembly modelling and findings, see Refs. [40,41]. Computational work has also focused on block co-polymer film formation and the influence on block length ratio on the assembly. Examination of co-polymer film morphologies in the presence of a substrate have focused on polymer miscibility and substrate selectivity, confinement effects, and substrate patterning, see Refs. [42–49] for examples. Additionally, assembly morphologies of di-block co-polymers in both bulk melts and solutions are well-known to depend strongly on the block segment length ratio, as demonstrated by self-consistent field theory (SCFT) studies [50–52], dissipative particle dynamics (DPD) simulations [53–55], and also molecular dynamics simulations at atomistic and coarse-grained detail level [56,57].

Significantly more rare are studies which involve both a substrate and the variation in the co-polymer block length ratio, see e.g. Ref. [58]. Co-polymer block length dependency in their assembly on nanoplates has been studied [59]. Via coarse-grained molecular dynamics, we examined earlier the effect of block-length on self-assembling amphiphilic coatings on carbon nanotubes, associating the surface coating morphologies with aqueous solubilization [60,61]. Additionally, e.g. Refs. [62,63] examine the effect of block lengths in surface-tethered di-block co-polymer chains, reporting the formation of a laterally uniform double-layered lamellar coating of the substrate with increasing solvophobic block [62] and control of the morphology transitions via block length variations [64,65].

In this work, we employ DPD simulations to focus on the amphiphilic block co-polymer solvophilic-solvophobic block length ratio dependency of self-assembling di-block co-polymer coatings on a solvophilic substrate. A chemically specific substrate and co-polymer system is used as the basis of the study, and DPD parametrization for the setup is presented. We also examine extensively the response of the co-polymer coating to changes in the polymer and substrate chemistries by varying the DPD interaction parameters. The significance of the work is that it provides guidelines for designing from amphiphilic di-block co-polymers efficiently spreading, domain forming, or most stable coatings on solvophilic substrates by simple variation of degree of polymerization (block lengths). Additionally, the presented results match the chemically specified model system, but are also readily generalizable to other polymer chemistries as a stability analysis of the assembly response in terms of the interaction parameters variation is also presented.

2. Methods

2.1. Modelled chemical system

For increased practical significance, we use as our basis model a chemically specific system. As substrate, we use the chemical characteristics of glucose to construct the model coarse-grained (CG) solvophilic substrate which leads to the substrate representing, at GC level, a glucose-based polysaccharide, in practise unmodified cellulose or starch, which at the level of coarse-graining used in the work have similar parameters. The amphiphilic di-block co-polymer that is used as coating material is composed of a starch equivalent hydrophilic block and a hydrophobic block based on a random co-polymer of styrene and n-butyl acrylate (at equal weight ratio). Self-assembling coatings in aqueous solutions are considered.

This particular system is chosen as the chemistry focus of the work because of the following reasons. The glucose-based polysaccharide is used as basis for the substrate model motivated by the general abundance, low cost, renewability, and biocompatibility of cellulose, starch and other glucans. These polysaccharides are also often coated by polymer protective coatings when they are used as fibers, pharmaceutical substrates, and hygiene or paper products [66]. The hydrophilic block chemical equivalent, starch, is an abundant yet cheap natural polysaccharide commonly used in industrial processes and as substrate [67]. The hydrophobic polymer composition is a simple, yet extremely common random co-polymer that is used in e.g., paint binders [68–70], adhesive coatings [71–74], and paper industries [75,76]. Co-polymers of butyl acrylate and styrene are also common in composite latexes and have been used as oil adsorbent membranes [77]. Throughout
2.2. Dissipative particle dynamics simulations and simulations system

DPD simulations method, originally proposed by Hoogerbrugge and Koelman [78], is a mesoscale coarse-grained bead-based molecular simulation technique. It combines aspects of molecular dynamics and lattice-gas automata, acknowledging the idea that different beads may overlap. The non-bonded interactions are modelled via soft repulsive potentials [78,79]. Such soft interaction potentials between beads allow the simulations to reach realistic experimental time- and length-scales for, e.g., block co-polymer self-assembly systems. Each DPD bead represents a coarse-grained region in the molecular system (e.g., several monomers of a polymer, a solvent region, or a group of atoms), which experience a force of the form

\[ F_i = \sum_{j \neq i} \left[ F_{ij}^r + F_{ij}^s + F_{ij}^\lambda \right], \quad i, j = 1, \ldots, N, \]  

(1)

where \( F^r \) describes conservative interactions, \( F^s \) dissipative contributions, \( F^\lambda \) a random contribution, and \( N \) corresponds to the total number of DPD beads in the system. The model assumes pairwise interactions, which are truncated at a cutoff distance \( r_C \).

The conservative contribution is given by a soft repulsive force acting on the centers of two DPD beads, and has the form

\[ F_{ij}^r = a_{ij} (1 - r_{ij}/r_C), \]

(2)

where \( a_{ij} \) is the maximum repulsion between beads \( i \) and \( j \), \( r_{ij} = || \mathbf{r}_i - \mathbf{r}_j || \) is the distance between beads \( i \) and \( j \) in units of \( r_C \), and \( r_C = r_0/r_C \) gives the force direction via a unit vector. The coefficients \( a_{ij} \) are connected to the Flory–Huggins mixing parameter \( \chi_{ij} \) via the relation

\[ \chi_{ij} \approx (a_{ij} - a_{ii})/3.27, \]

(3)

for a fixed number density \( \rho r_C^3 = 3 \) in the system. The choice \( a_{ii} = 25 \) for the repulsion parameter between beads of the same type (i.e., \( \chi_{ii} = 0 \)) is common, and is based on the compressibility of water [78]. An \( a_{ij} \) value exceeding the self-repulsion in magnitude corresponds to a stronger repulsion between beads of different species.

The dissipative force is given by

\[ F_{ij}^s = -\mu \omega^s (r_{ij})(\mathbf{v}_j - \mathbf{v}_i), \]

(4)

where \( \gamma \) is a viscosity related parameter \((\gamma = 4.5)\), \( \omega^s \) is a weight function that takes the value zero at \( r_C \), and the relative velocity is \( \mathbf{v}_j = \mathbf{v}_i - \mathbf{v}_j \).

The random force is described by

\[ F_{ij}^\lambda = \sigma \omega^\lambda (r_{ij}) \xi_{ij}, \]

(5)

where \( \xi_{ij} \) is a zero-mean Gaussian random variable of unit variance, and \( \sigma^2 = 2k_BT \) as the Boltzmann constant and \( T \) the temperature of the system. The weight functions follow the relation \( \omega^s (r_{ij}) = \omega^s (r_0)^2 = (1 - r_{ij}/r_0)^2 \) for \( r_{ij} < r_C \). The dissipative and the random force together act as a thermostat for the system. Additionally, two consecutive beads in the same polymer chain perceive a spring force \( F_{ij}^r \) of the form

\[ F_{ij}^r = -\kappa \sum_j (r_{ij} - r_0) \mathbf{r}_j, \]

(6)

where \( \kappa \) is the spring constant, \( r_0 \) the equilibrium distance, and \( j^* \) refers to the nearest neighbours in the chain. In this work, following Ref. [80], \( \kappa = 80 \) and \( r_0 = r_C \). To simplify the DPD equations and simulations, the cutoff radius \( r_C \), the bead mass \( m \), and the energy \( k_BT \) are reduced to \( r_C = m = k_BT = 1 \), leading to a time unit \( \tau = (m r_C^2/k_BT)^{1/2} = 1 \).

The DPD simulation system is summarized in Fig. 1. The system modelled in this work contains amphiphilic di-block co-polymers \((A_4B_3)\) in a solvent \((S)\). When present, the substrate is a planar surface slab composed of substrate beads \((C)\). The nomenclature A, B refers to the DPD beads such that A is a solvophobic bead, B a solvophobic bead. For model simplicity, S and C are considered identical in mixing characteristics. The subscripts refer to the number of beads in the chain and vary along the work, with the constraints \( k + l = 7 \) and \( k < l \).

The hydrophobic beads B model coarse-grained regions of a random co-polymer composed of styrene (42 wt%) and n-butyl acrylate (58 wt%). The substrate beads C and hydrophilic polymer beads A are parametrized against glucose fragments (for simplicity, identical parameter values). The solvent beads S are parametrized against atomistic detail water. When converting the atomistic polymer structures into DPD beads, it should be noted that the polymeric components are each 5 monomer long chain segments and a DPD water bead contains 33 molecules. These numbers are rounded to closest integer and result from each DPD bead type having the same mass and volume in the simulations. Consequently, the DPD co-polymers of 7 beads are short polymers of 35 monomers in length. It is worth noting that the employed soft core DPD modelling approach omits entanglement considerations. For the short, linear chains considered here, this is a reasonable approximation. However, in assessing the generalization of the findings to longer polymers, the entanglement significance, i.e., dynamics region, should be considered. The DPD coarse-grained solvent bead captures the effective characteristics of the modelled fluid region. Details of the parametrization protocol are provided in the Supplementary Material (SM). The obtained DPD parameters are reported in Table 1. The stability of the self-assembled film structure and the sensitivity of the assembly to the simulation parameters were examined for the co-polymer \( A_4B_3 \) at solids concentration 11.25 %. The examined range was selected to cover a sensible block miscibility range, as well as reasonable values for hydrophilicity and hydrophobicity, and is not comprehensive.

2.3. DPD simulations details

The simulations are performed using the LAMMPS [81] package. The dynamics are implemented via a velocity-Verlet scheme. A time step of \( \Delta t = 0.05 \tau \) is used. The value of \( \tau = (m r_C^2/k_BT)^{1/2} \) in real units varies depending on which monomer chemistry is considered as the reference mass for the conversion. For the base model system here, its value is in the interval 22–26 ps. The system length scale, set by the value of \( r_C \), is uniquely defined by the bead volume and the chosen DPD particle density \( \rho r_C^3 = 3 \). Converted to real units based on molecular volumes in the atomistic detail parametrization, see SM, \( r_C \) corresponds to \( \approx 1.44 \) nm. Throughout, periodic boundary conditions are used in 3D. The co-polymer - solvent system is initialized by placing the co-polymers and the solvent beads randomly (overlap excluded) in a box of \( 40 \times 40 \times 35 r_C^3 \) in the film formation simulations. The co-polymer - solvent system is equilibrated (10⁶ time steps) to obtain an initial configuration for the coating setup, where the co-polymers assemble into particles, following many polymer coating application in experimental protocols. After this, the box is combined with a 5\( r_C \) thick slab of the substrate beads \( (40 \times 40) r_C^2 \) cross-section). This results in a \( 40 \times 40 \times 40 r_C^3 \) total simulation box volume. The substrate beads C are fixed at their random initial
positions, allowing possibility of partial penetration of co-polymer and solvent particles. The simulations are then carried out for \(1.5 \times 10^6\) time steps. For the bulk assembly simulations, a box of \(100 \times 100 \times 100\) \(r^2\) is used and the simulation is run for \(4 \times 10^6\) time steps. An increased simulation box is necessary for the system to exhibit multiple polymer particles. Equilibration was checked by analysing the time evolution of the assembly functions, as well as for bulk assembly, correspond to data analysis performed over the last \(5 \times 10^5\) time steps. VMD [82] has been used for three-dimensional visualizations and Moltemplate [83] for initializing the simulations.

3. Results

3.1. Film formation

We first explore di-block co-polymer substrate adsorption and film formation in our base system by varying polymer concentration and the hydrophilic:hydrophobic ratio \(k: l\) in the \(A_B,\) di-block co-polymers. The total length of the polymer is kept fixed at 7 beads (see Fig. 1). As each bead corresponds to 5 monomers, this corresponds to short polymers of 35 monomers in length. The examined hydrophilic:hydrophobic compositions are in DPD beads \(6:1, 5:2\) and \(4:3\). For all hydrophilic:hydrophobic compositions, self-assembly to the substrate from an aqueous solution with polymer solid content \(\alpha\) ranging from 2% to 11.25% is examined.

Simulation snapshots corresponding to the self-assembly of the di-block co-polymers at the substrate interface are presented in Fig. 2. At low solid concentrations, the most asymmetric co-polymer, \(6:1\), forms distinct droplets when adsorbing (see Fig. 2(a), at \(\alpha = 2\%).\) A relatively high quantity of chains remains absorbed on the surface separate from the larger droplets. Such formed droplets increase in size with increasing solid content (see Fig. 2(b), at \(\alpha = 5\%\)). The channel like geometry in the latter figure is due to the periodic boundary conditions imposed in the simulation. If more material is added, the di-block co-polymer covers an increasing fraction of the surface (see Fig. 2(c), at \(\alpha = 7\%\)). At sufficiently elevated solids concentration, a complete coverage film is formed (see Fig. 2(d), at \(\alpha = 11.25\%\)). For the \(6:1\) polymers, at all examined values of \(\alpha\), some co-polymer chains remain solvated in the bulk aqueous phase, not absorbed to the substrate.

Similar to the \(6:1\) polymer, the \(5:2\) polymer forms droplets at very low values of \(\alpha\) (see Fig. 2(e), at \(\alpha = 2\%).\) With increasing \(\alpha\), the periodic boundary conditions enforce a channel-like geometry to the partial surface coverage (panels (f) and (g) for \(\alpha = 5\%\) and \(\alpha = 7\%,\) respectively). However, similar partial coverage (except for the artificial periodicity) is expected also for larger systems and in the absence of periodic boundary conditions. Again, at \(\alpha = 11.25\%,\) a stable hydrophilic–hydrophobic–hydrophobic lamellar structure is formed (Fig. 2(h)).

For a di-block co-polymer composition of \(4:3\), the low concentration cases exhibit similar equilibrium configurations as the more asymmetric compositions. Also here, at \(\alpha = 2\%\) a single droplet absorbed on the hydrophilic model substrate forms (Fig. 2(i)). The formed droplet is, however, much nearer than for the more asymmetric co-polymers. Increasing the concentration leads to the formation of a much larger (single) spread-out droplet forming on the substrate (see, Fig. 2(j), at \(\alpha = 5\%\)). Increasing the concen-

---

**Table 1**

<table>
<thead>
<tr>
<th>Bead</th>
<th>A</th>
<th>B</th>
<th>S</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25</td>
<td>56.15</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>B</td>
<td>25</td>
<td>107</td>
<td>56.15</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>25</td>
<td>35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Chemical structures of the modelled components, summary of the DPD bead types and examined amphiphilic co-polymers. At top, the basis model for the substrate and the di-block co-polymer are represented in full chemical detail. The substrate models a generic glucose-based polysaccharide substrate (grey background) at a coarse-grained level. The amphiphilic di-block model represents a random co-polymer of styrene and n-butyl acrylate as the hydrophobic block (red background) and starch as the hydrophilic block (blue background). An aqueous solution is considered. At bottom, a summary of the DPD beads used in the study to model the regions corresponding to hydrophilic (blue, A), hydrophobic (red, B), substrate (grey, C) and water (yellow, S). The cartoons present the compositions of the examined di-block amphiphilic co-polymer chains. The ratio \(k : l\) specifies that polymer has \(k\) hydrophilic and \(l\) hydrophobic beads, respectively.
tration shows how the droplet wets the surface with the precise morphology again rising from the periodicity (panel (k), at $\alpha = 7\%$). As before, the concentration of $\alpha = 11.25\%$ results in a very neat (full) layer-by-layer structure (panel (l)).

Let us next analyze the formed films. Fig. 3 presents the average (perpendicular to the surface) probability distribution $P(z)$ (normalized to be unitless), defined via

$$\frac{1}{r_C} \int_0^{L_z} P(z)dz = 1,$$

where $L_z$ is the box dimension along the z axis, for both hydrophobic and hydrophilic beads in the films formed at the highest solid content $\alpha = 11.25\%$ which led to the formation of one full (layer-by-layer) film for all the examined co-polymers. The insets of Fig. 3 show lateral view of the corresponding equilibrium configurations for the three di-block co-polymer compositions. The data shows that the 6:1 co-polymer forms a film in which the two types of beads are mainly mixed. Beads A are slightly enriched at the substrate interface and beads B in the center of the film. $P(z)$ decreases relatively slowly away from the substrate extending into the sol-

Fig. 2. Surface adsorption of di-block co-polymers at different solid concentrations. The substrate beads C are presented in grey, the hydrophilic beads A in blue and the hydrophobic beads B in red. Water beads are not shown in the visualizations for clarity. In all data presentations, matching color intensity difference in the di-block co-polymers is used to differentiate between the block ratio $k : l$.

Fig. 3. Probability distribution perpendicular to the surface $P(z)$ for hydrophilic (A) and hydrophobic (B) beads for films formed by the 6:1, 5:2, and 4:3 polymers at 11.25% polymer concentration. The insets show the cross section cuts of the corresponding equilibrium surface coatings by simulation snapshots. In all data presentations, matching color intensity difference in the di-block co-polymers is used to differentiate between the block ratio $k : l$. Data showing the substrate and water beads probability distributions are presented in Fig. S1 of the SM.
vent phase. This means that the film surface is not well-defined and fluctuations are quite significant. In comparison, the more symmetric co-polymers 5:2 and 4:3 form a film with a clear layer-by-layer internal structure. The data shows a well-defined and strongly confined hydrophobic layer between two hydrophilic slabs. \( \beta(2) \) also decreases more sharply than with the 6:1 co-polymer. This signifies a well-defined, less fluctuating film surface. The stability of the interfaces is more pronounced in the most symmetric co-polymer composition. The data of Fig. 3 allows us to conclude that the composition 4:3 provides the most stable hydrophilic–hydrophobic–hydrophilic film structure. The stability difference is quantified by comparison of the average film height over time \( \langle h \rangle \), and its fluctuation \( \Delta h \). \( \Delta h \) is calculated via

\[
\Delta h = \frac{1}{n} \sqrt{\sum_{i=1}^{n} \Delta h_i^2},
\]

where the terms \( \Delta h_i \) are the values of the standard deviation for the simulation frame \( t \). Here \( n = 50 \), corresponding to the last 33.3% of the simulations. The film height calculation and the fluctuation estimation is done based on considering all polymer mass with \( z < 12r_C \) as part of the film, see Fig. 3 for z-axial probability distributions. Even though the average height of the film changes only marginally with increasing co-polymer symmetry, the fluctuation \( \Delta h \) decreases significantly. This indicates decrease of structural stability, i.e. lower intramolecular adhesion. This data is shown in the first row of Table 2.

In Fig. S1 of the SM, we report the data shown in Fig. 3 complemented by the probability distribution of water and substrate beads. The data shows that water beads can penetrate into the substrate, and readily reside in the hydrophilic region of the film. However, water beads remain absent from the hydrophobic part, as expected based on the degree of immiscibility between water and the hydrophobic component B. We also find that water penetration into the film decreases for the more symmetric co-polymers. This is a direct consequence of the more stratified, more ordered structure.

Table 2

Summary of film formation characteristics for the co-polymers with 6:1, 5:2, and 4:3 compositions. The first row represents the average film height \( \langle h \rangle \) and its fluctuation \( \Delta h \). Next, \( x_{\text{min}} \) correspond to the minimal solid concentration to form a complete film coverage, \( \eta \) the hydrophobic coverage percentage in the fully surface covering film forming at the \( x_{\text{min}} \) concentration, and \( \theta \) the film-substrate contact angle calculated for the droplets forming at \( \sigma = 5\% \).

<table>
<thead>
<tr>
<th>Composition</th>
<th>6:1</th>
<th>5:2</th>
<th>4:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle h \rangle ) \pm ( \Delta h(r_C) )</td>
<td>3.50 ± 0.79</td>
<td>3.62 ± 0.53</td>
<td>3.57 ± 0.45</td>
</tr>
<tr>
<td>( x_{\text{min}} )</td>
<td>9.0 ± 0.5%</td>
<td>9.5 ± 0.5%</td>
<td>10.5 ± 0.5%</td>
</tr>
<tr>
<td>( \eta )</td>
<td>19.3%</td>
<td>34.8%</td>
<td>47.2%</td>
</tr>
<tr>
<td>( \theta )</td>
<td>25.3 ± 8.6</td>
<td>48.4 ± 6.4</td>
<td>63.5 ± 10.3</td>
</tr>
</tbody>
</table>

Each examined co-polymer composition requires a slightly different amount of solid content to produce a film that fully covers the hydrophilic substrate surface. The minimal solid content \( x_{\text{min}} \) to achieve full surface coverage are reported for the examined systems in Table 2. The differences in \( x_{\text{min}} \) can be associated to the fact that, for a fixed solids concentration, the total number of A beads (hydrophilic) in the system decreases when moving towards more symmetric compositions. A larger total solids content is thus needed to shield the hydrophobic layer from the solvent; a too low hydrophilic content leads to preference of the curved (droplet like) assembly. This is seen in the system forming droplets instead of a uniform film at the low concentrations (see Fig. 2).

Although a fully covering film forms, for protective coatings it is useful to assess the efficiency of the formed hydrophobic layer. To this purpose, we calculate the ratio of surface covered by the hydrophobic content, for each co-polymer configuration based on an estimate by Monte Carlo sampling. For this, the xy-plane projection of the coordinates of the B beads are used and the surface coverage \( \eta \) is obtained as the ratio of the number of Monte Carlo sampled coordinate pairs (uniform distribution on the xy-plane) that overlapped with any B bead projections and the total number of sampled coordinate pairs. To determine overlap, we need to define the effective size of the beads (note that the ratio of the covered surface is highly dependent on this choice). As an educated guess (checked for trend consistency in prediction), we set the beads radius to be \( R = 0.2r_C \). The calculation of \( \eta \) considers all co-polymers in the system, as the fraction of co-polymers in the film is at minimum 99.3% in all complete coverage systems. The values are summarized in Table 2.

The hydrophobic layer is further quantified by Fig. 4 which presents a comparison of the projected two-dimensional radial distribution functions (2D-RDF) calculated between the hydrophobic beads in the adsorbed layer on the substrate. The 2D-RDF considers only the \( x \) and \( y \) coordinates in the calculation. The presented data is an average over the entire z-axis thickness of the film and considers the hydrophobic beads of all co-polymers in the system. Notably, the calculation considers also the contributions of the beads in the same polymer chain. Such intra-chain 2D-RDF contributions show at \( r \approx r_C \) in the 5:2 composition and at \( r \approx r_C \) and \( r \approx 2r_C \) in the 4:3 composition (first and second bounded neighbours). The 2D-RDF data of Fig. 4 shows features of a repeating pattern (periodic structure) for the 6:1 and 5:2 co-polymer compositions. The 6:1 co-polymer data shows, in addition to a first peak at \( r \approx r_C \), a clearly visible second bump at \( r \approx 3r_C \). Indicating a relatively short order, the oscillations disappear rather quickly at bead separation distances beyond this. In the 5:2 composition, in addition to the expected intra-chain nearest neighbor peak at \( r \approx r_C \), a significant bump can be found at \( r \approx 4r_C \) and reverberations at \( r \approx 8r_C \) are still clearly visible. The inset of
Fig. 4 shows that this corresponds to a typical distance between the assembly clusters in the film, indicating patterning in the structure. On the other hand, the 4 : 3 composition leads to well-defined peaks but a much faster decay of the radial distribution function. In fact, for \( r > 2r_c \), the oscillations are barely perceived, which is a sign of homogeneity. The homogeneous structure is also clearly visible in the corresponding inset of Fig. 4, where only a few (small) depleted regions can be found.

We note that due to the soft interactions in the DPD model, we observe for the 6 : 1 configuration to a minor degree also some of the co-polymers penetrating the substrate. This results from the very short solvophobic part and soft interactions allowing mixing of the co-polymers penetrating the substrate. This results from the beads probability distributions are presented in Fig. S2 of the SM.

The assembly allows us also to estimate the film-substrate contact angle \( \theta \) of the partially formed film based on geometrical considerations. For this, we choose the concentration \( \alpha = 5\% \) for the three different co-polymer compositions. The contact angle is estimated at 10 different randomly chosen positions at the film boundary and the value reported in Table 2 is the average together with its standard deviation. The results show a correlation between the symmetric nature of the co-polymers and the contact angle, indicating that the tendency of the film to spread decreases as the symmetry of the co-polymer is increased.

So far, we have focused on the structure of the co-polymer films near the minimal complete coverage concentration or on incomplete surface coverage. It is interesting to examine the persistence of the structural assembly features in the presence of excess co-polymer. Fig. 5 shows the z-axial film profiles at concentrations exceeding slightly two times the minimal complete coverage concentration. As expected, the doubled concentration of the 4 : 3 and the 5 : 2 co-polymer compositions lead to formation of a very neat, layered double film. In the 6 : 1 case however, the two layers are barely recognizable. The film formation is quantified by plotting the average perpendicular probability distribution \( \phi(z) \) for beads A and B, respectively, see Fig. 5. The insets of the latter figure report the side view of the corresponding equilibrium configuration snapshots. Fig. 5 shows for the 6 : 1 composition two barely perceivable peaks in the hydrophobic content distribution. For the 5 : 2 composition, two sharp hydrophobic peaks surrounded by three hydrophilic layers are clearly visible. An even more pronounced lamellar structure assemblies on the hydrophilic substrate for the most symmetric 4 : 3 co-polymer and distinct layers together with the sharp drop of \( \phi(z) \) at \( r \approx 13r_c \) indicate both a very well-defined film structure and surface. The well-defined boundary signifies that the film is very stable, i.e. fluctuations are small. Water and substrate beads probability distributions complementing the data shown in Fig. 5 are reported in Fig. S2 of the SM. As shown in the case presented in Fig. S1, water beads penetrate into the substrate, and readily reside in the hydrophilic region of the film. Nevertheless, water beads remain absent from the hydrophobic part. We also find that water penetration into the film decreases for the more symmetric co-polymers, which is a direct consequence of the more stratified and more ordered structure. We conclude that even in the presence of excess solid content, the more even co-polymer composition leads to the nearest layer-by-layer structure.

The results presented above are valid for a specific setup described by the DPD bead interactions in Table 1. To examine the robustness of the findings and the stability range of the film formation on the hydrophilic substrate, we examined the assembly response for a wide range of interaction parameters. As the most symmetric composition, i.e. 4 : 3 co-polymer, resulted in the most stable film, we focused the stability examination on this composition at concentration \( \alpha = 11.25\% \). The range at which the layered structure persisted corresponds to interaction parameters \( a_{AB} \) and \( a_{BC} \) between 46 and 66, \( a_{AB} \) between 30 and 45, and \( a_{BC} \) between 87 and 147. Specifically, we use the basis system as the initial configuration and continue the simulation for additional \( 1.5 \times 10^6 \) time steps with new interaction parameters covering the presented range. Snapshots corresponding to the films forming at the extremum parameter values are presented in the SM, see Fig. S3. The snapshots show the range of structural variation expected within the examined interactions parameter range. As the examined miscibility range is rather wide, and stratified structures persist, we conclude that the stratification response reported here for the symmetric block co-polymer can be considered robust not only in terms of parametrization, but also specific polymer miscibilities. The practical significance is that the findings on film formation and internal structure guided by co-polymer block length ratio can be at qualitative level be generalized to a large variety of polymer systems. This allows tuning the formation of self-assembling hydrophilic surface coatings. Note that for the interaction value \( a_{AB} = 25 \), the film detaches from the substrate. In this case, the solvent, substrate, and hydrophilic beads are indiscernible, i.e. \( a_{AA} = a_{BB} = a_{AB} = a_{BC} = a_{AB} = 25 \). Therefore, no preference to form a film on the substrate can be expected.

3.2. Bulk assembly

The amphiphilic di-block co-polymers examined in this work typically form core–shell particles in bulk solution. We examined the bulk assembly response for \( \alpha \) between 5\% and 11.25\% for the
6 : 1 and the 4 : 3 compositions. Fig. 6 presents final particle configurations in the \((100r_c)^3\) simulation box employed for the bulk assembly simulations. Although an extended simulation system size (in comparison to the systems including a substrate) is used, the snapshots clearly reveal that the assembly response is subject to finite size effects – particle sizes, size distributions, or even assembly morphologies could be influenced by the finite system size the periodic box. However, the formed particles systematically point toward the 6 : 1 composition leading to a smaller particle size polydispersity than the 4 : 3 co-polymer. This is in line with Ref. [84], and likely explained by the fraction of hydrophilic content [85].

We focus further analysis on internal structure of the assemblies, as this can be expected to be relatively independent of finite size effects in the assembly. Fig. 7 presents a comparison of the assemblies by radial average density \(\rho(r)\) of a single representative particle and visualizations of the corresponding particle cross-sections. The density data is normalised by the number of beads per chain of each type, \(N_i, i = A, B, A + B\). Concentrations are \(\alpha = 9.5\%\) for the 6 : 1 composition and \(\alpha = 8\%\) for the 4 : 3 case.

In Fig. 7, the internal structures of the 6 : 1 and 4 : 3 particles differ in the oscillatory behaviour of \(\rho(r)\) rising for the 4 : 3 composition but lacking for the 6 : 1 case. The snapshots (c) and (d) of Fig. 7 reveal that the cross-section of 4 : 3 particle exhibits layering in comparison to the more uniformly mixed 6 : 1 particle. This layering remains imperfect, but the insides of the particle are still sufficiently ordered to give rise to oscillations in \(\rho(r)\), which are due to the more symmetric nature of the co-polymer. Both macroscopic and microphase segregation in bulk assemblies are well-known to be readily tunable by block miscibility and block length. In agreement with our findings, effects include e.g. transitioning from ordered to disordered segregation [86], multicore assembly control [87–90], and length dependent segregation of the block components according to local curvature [91,92]. For more complex architectures, such as H-shaped polymers, an even richer microphase segregation phase landscape arises [93]. Although not observed in this work, longer polymers and polydispersity in the polymer composition, together with polymer block length variation, can be expected to enable tuning assembly morphologies [91,94]. This could, e.g., allow self-assembling micropatterning. The internal structure of the bulk particles also directly connects to the stratified layer-by-layer film coating structure discussed in Section 3.1. Furthermore, indications of analogous surface fluctuations as with the coating structure can be observed for the 6 : 1 particle, while 4 : 3 forms particles with neat, well-defined interface. As expected, the data points toward the particle properties having a direct connection with the surface coating structural characteristics. Naturally, the surface directs the assembly, resulting in more order in the structure than in bulk particles, where the block co-polymers have more freedom to reorganize.

4. Conclusions

In this work, we examined self-assembling amphiphilic di-block co-polymer coatings on a hydrophilic model substrate. While block co-polymer self-assembly is a thoroughly studied topic, with findings covering both bulk and interfacial self-assembly in terms of polymer block miscibility, branching and molecular weight [95], we addressed here the simple, yet so far largely overlooked aspect of using the block length ratio in self-assembling amphiphilic co-

![Fig. 6](image_url) Co-polymer particles formed in \(100 \times 100 \times 100 r_c^3\) simulation box at varying concentrations. From left to right: snapshots corresponding to 6 : 1 composition at (a) 5%, (b) 9.5%, and (c) 11 25% co-polymer concentration and corresponding to 4 : 3 composition at (d) 5%, (e) 9.5%, and (f) 11 25% concentration. The same color intensity difference as in previous data presentations in the di-block co-polymers is used to differentiate between the block ratio \(k \cdot l\).

![Fig. 7](image_url) The radial average density \(\rho(r)\) normalised by the number of beads per chain \(N_i, i = A, B, A + B\), obtained from analysing single particles having 6 : 1 (a) and 4 : 3 (b) co-polymer compositions at \(\alpha = 9.5\%\), and \(\alpha = 8\%\), respectively. The cross sections of the particles are also illustrated for the 6 : 1 (c) and 4 : 3 (d) models. In all data presentations, matching color intensity difference in the di-block co-polymers is used to differentiate between the block ratio \(k \cdot l\).
polymer coatings. In particular, prior studies involving both a substrate and the variation in the di-block co-polymer block length ratio exist, e.g. Refs. [58,62,63,96], but the existing works limit to consideration of surface-tethered co-polymers, thus not capturing the self-assembly aspect of many coating processes, e.g. [28,29], or vesicle spreading [97,98].

We demonstrated that the block length ratio is an easily accessible control of, not only the spreading of the self-assembling polymer coating on substrate, but also the internal structure of the self-assembling film in terms of stratification and domain formation. Our findings are in line with previous experimental studies reporting dramatic effects of block co-polymer chain structure on the equilibrium morphologies. Most related are mixed polymer brushes that show chain length and molar ratio dependent micro-phase separation and surface patterning [96], as well as thin films produced with methods such as solution casting, also structurally highly dependent on the co-polymer block length ratio [99–104]. Furthermore, altering length ratio is well-known to lead to micro-phase separation, providing means to tune the morphologies [105–107,91,94], but also polymeric components segregation and ordering [91,92] with increasing asymmetry in length increasing disorder [86]. The findings of this work show that for surface coatings the experimental observations can actually be generalized to more symmetric di-block co-polymer compositions giving rise to more stable films on a hydrophilic surface. The stable films also have a neat hydrophilic–hydrophobic–hydrophilic layer-by-layer structure that persists over a large range of concentrations and polymer component miscibilities, as long as the amphiphilic di-block copolymer is symmetric in its composition. At high enough concentrations, the layer-by-layer structure turns into well-defined multi-layer lamellar coatings.

We also found a significant block length ratio dependency of cluster (periodic structure) formation in the self-assembled films, mainly in the intermediate block ratio composition, i.e. for the 5:2 di-block co-polymer. Indeed, asymmetry causes such micro-phase separation in bulk co-polymer assemblies [108]. Furthermore, while it has been solidly established that chemical and surface structure guiding patterns can be used to control block co-polymer coatings, see e.g. Ref. [65], the findings here show that confined clustering can be achieved merely by asymmetry and the assembly interface provided by the substrate. This opens possibilities in tuning segregation domains and simple patterning via the interplay between asymmetry in block lengths for co-polymers and the substrate vs solvent interaction energetics of the coating. It is also interesting to speculate that compositional mixtures could lead to advanced patterning in structure.

The significance of this work is that the findings show how the block length ratio in amphiphilic co-polymer coatings provides an easily accessible control to not only the spreading of the self-assembling polymer coating but also the internal structure in terms of stratification and domain formation. Since the CG modelling results were matched to a practical hydrophilic substrate and common amphiphilic co-polymer coating system, and the stability of the reported response mapped over a wide polymer miscibility range, the findings generalize to a large set of practical polymer systems. Furthermore, the match with cellulose-based substrate, e.g. paper, and a common functional coating to it, increases the practical impact of the findings. This is because such materials provide an inexpensive, bio-based, and environmentally friendly alternative to synthetic plastics. Indeed, growing plastic pollution has brought more attention towards replacing plastic packaging materials in industries with sustainable, biodegradable materials, such as paper [109–111]. Altogether, the work contributes toward a better understanding of film formation on solvophilic surfaces, as well as provides insight for engineering coating internal microstructure by simple di-block co-polymer solutions.

5. Data Availability

Data associated with the manuscript is available at https://doi.org/10.23729/178999d8-bd95-4ce2-b5d3-84973c716357. An example of an input script file for the DPD simulations as well as an extract from the initial configuration data file is reported in the SM. If using the inputs or the open data, we request acknowledging the authors by a citation to the original source (this paper).

6. Author contributions

Alberto Scacchi: Conceptualization, Software, Methodology, Formal analysis, Writing - Original Draft, Visualization, Supervision. Kourosh Hasheminejad: Software, Methodology, Formal analysis, Data Curation, Visualization, Writing - Review & Editing. Sousa Javan Nikkhah: Conceptualization, Software, Methodology, Writing - Review & Editing. Maria Sammalkorpi: Conceptualization, Funding acquisition, Project administration, Supervision, Writing - Review & Editing.

Data availability

Simulation script is reported in the SM. Data associated with the manuscript is available at https://doi.org/10.23729/178999d8-bd95-4ce2-b5d3-84973c716357.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2023.02.117.

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