The electrostatic co-assembly in non-stoichiometric aqueous mixtures of copolymers composed of one neutral water-soluble and one polyelectrolyte (either positively or negatively charged) block: Dissipative particle dynamics study

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SUPPLEMENTARY INFORMATION

Model and Method

Dissipative Particle Dynamics (DPD)

Since Groot and Warren established a link between the Flory-Huggins interaction parameter \( \chi_{ij} \) and soft-repulsion parameters \( a_{ij} \) used in dissipative particle dynamics (DPD),¹ this coarse-grained simulation method has proven to be a suitable tool for studying polymer systems and a number of neutral polymer systems have been successfully studied.²⁻⁵ Later electrostatics were implemented into the model⁶⁻⁹ and polyelectrolyte (PE) systems were addressed.¹⁰⁻¹³ At present, studies of complex PE systems based on alternative models (“ion-free” and “implicit solvent ionic strength” methods) that do not treat electrostatics explicitly have also been published.¹⁴⁻¹⁸ However, we are of the opinion that the explicit treatment of electrostatic forces should be an intrinsic part of simulations of PEs, because it corresponds to real physics and allows reasonably good emulation of the contribution of counterions to the entropy of the system, which the other approaches do not secure.
In simulations, a DPD particle represents a fluid element which contains a number of solvent molecules, solvated ions or several polymer segments. We thus treated the solvent (S) and counterions (Cl\(^+\) and Cl\(^-\)) as different types of DPD particles. The DPD ions can be regarded as solvated ions. We model the DPD particles as being purely repulsive, i.e., the \( ij \) - pairs of particles interact via a soft repulsive potential\(^1,4 \)

\[
U_{ij}^w = \frac{a_{ij}}{2} r_i \left( 1 - \frac{r_{ij}^2}{r_c^2} \right)^2 \quad (r_{ij} < r_c) \\
= 0 \quad (r_{ij} \geq r_c)
\]

where \( a_{ij} \) is the maximum repulsion between particles \( i \) and \( j \), \( r_{ij} \) is the separation distance, and \( r_c \) is the cut-off radius.

Diblock copolymers \((A^+)_5B_5\) and \((A^-)_5B_5\) consist of two flexible linear strings of DPD particles connected in a chain by harmonic springs:

\[
U_{i,i+1}^{hn} = \frac{K}{2} \left( r_{i,i+1} - r_0 \right)
\]

acting between adjacent particles \( i \) and \( i+1 \) in addition to the soft repulsive interaction. In Eq. (2), \( K \) is the spring constant and \( r_0 \) is the equilibrium distance. A value of \( K/(kT) \) between 2 and 4 (\( k \) is the Boltzmann constant and \( T \) is the temperature) and \( r_0 = 0 \) are typically utilized.\(^1 \)

In the studied systems, the core-forming A\(^+\) and A\(^-\) segments of \((A^+)_5B_5\) and \((A^-)_5B_5\) chains and the counterions are charged. Since the DPD particles are modeled as soft particles, the charge is spread over a finite volume using the Slater smearing charge distribution\(^8 \)

\[
f(r) = \frac{qe}{\pi \lambda^2} \exp \left( -\frac{2r}{\lambda} \right)
\]

In Eq. (3), \( q \) is the relative charge, \( e \) is the electron charge and \( \lambda \) is the decay length of the charge. The electrostatic interaction between charged particles \( i \) and \( j \) is then defined by

\[
U_{ij}^{el} = \frac{q_i q_j}{r_{ij}} \lambda_n kT \left[ - \left( 1 + \beta r_{ij} \right) \exp \left( -2\beta r_{ij} \right) \right]
\]

where \( \lambda_n = e^2/(4\pi \epsilon_0 \epsilon_i kT) \) is the Bjerrum length (\( \epsilon_0 \) is the dielectric constant of a vacuum and \( \epsilon_i \) is the relative permittivity of the reference medium), \( q_i \) and \( q_j \) are their relative charges and \( \beta = 5/(8\lambda) \). The potential expressed by Eq. (4) does not diverge at short
distances which prevents the collapse of beads on top of each other in the case of unlike point charges.\textsuperscript{6-9}

Groot and Warren \textsuperscript{1} mapped the DPD model onto the Flory-Huggins (FH) model and established a link between $a_{ij}$ and the chi-parameter $\chi_{ij}$:

$$\chi_{ij} = 2C\rho r_c^3 \left( a_{ij} - \frac{a_{ii} + a_{jj}}{2} \right) \frac{r_c}{kT}$$

(5)

where $\rho$ is the total particle density and $C$ is a constant depending on $\rho$. Assuming $a_{ii} = a_{jj}$ and using the equation of state for the soft repulsive DPD fluid together with the compressibility value for ambient water, Groot and Warren derived an expression for like-repulsive parameters:

$$\frac{a_{ii}r_c}{kT} = \frac{a_{jj}r_c}{kT} = \frac{75}{\rho r_c^3}$$

(6a)

They further obtained linear relationships between $a_{ij}$ and $\chi_{ij}$ for $\rho r_c^3 = 3$:

$$\frac{a_{ij}r_c}{kT} = \frac{a_{ii}r_c}{kT} + 3.27\chi_{ij}$$

(6b)

We controlled the solvent quality for A and B blocks of $(A^+)_5B_5$ and $(A^-)_5B_5$ by parameters $a_{AS}$ and $a_{BS}$, respectively, and the incompatibility between A and B blocks by parameter $a_{AB}$. Other details regarding the DPD method were given in the Supporting Information of our previous paper.\textsuperscript{10}

\textbf{Simulation Details}

We simulate aqueous solutions of oppositely charged copolymers $(A^+)_5B_5$ and $(A^-)_5B_5$ immersed in a mixture of solvent particles and counterions. In the DPD method, the following reduced units were used: $r_c$ is the unit of length, the unit of mass is the mass of a DPD particle and the unit of energy is $kT$; these terms are used throughout this work. All the DPD simulations were carried out at a total particle density of $\rho = 3$ in a cubic box of $25^3$ (for systems with incompatible A and B blocks) or $32^3$ (for compatible blocks) with periodic boundary conditions applied in all three dimensions, and with noise amplitude $\sigma_y = 3$ and time step $\Delta t = 0.05$. The number of $(A^-)_5B_5$ chains, $N^- = 100$, and their volume fraction, $f_{\nu^-} = 0.021$ remain constant in all simulations, but the number of $(A^+)_5B_5$ chains, $N^+$, varies from 100 to 160 (i.e., ratio $N^+/N^-$ ranges from 1.0 to 1.6, the percentage of positively charged
chains ranges from 50\% to 61.5\% and their volume fraction, $f_V^+$ covers the region 0.021 to 0.034).

Using the reduced units, we set the repulsion parameter between like particles at $a_{ij} = a_{ji} = 25$. This value corresponds to the most common DPD parameterization which defines one solvent (water) bead as a cluster of three molecules. Note that the recalculation of parameters for coarse grained polymer beads, corresponds to a larger number of monomeric units because the Flory-Huggins approach employs in fact the “lattice Kuhn-like segments” that usually represent 5 – 7 units depending on the intrinsic rigidity of the chain. In this study, we performed a series of simulations for block copolymers formed by a water-soluble B block ($a_{BS} = 25$) and a PE block A with varying hydrophobicity ($a_{AS} = 25 – 37.5$) to mimic the fact that the backbone of a number of real PEs is in fact hydrophobic. We also varied the compatibility of blocks A and B and compatibility of counterions with both blocks in the same range because small alkali ions interact with polymers differently than large polarizable ions or ions with organic ligands. The above parameters correspond to the bead-bead $\chi$-interaction parameters $\chi_{AS} = 0 – 3.8$, $\chi_{AB} = 0 – 3.8$, $\chi_{CI-AB} = 0 – 3.8$ and $\chi_{SB} = 0$, respectively. For the harmonic spring potential, we used the spring constant $K = 4$ and equilibrium distance $r_0 = 0$.

In accordance with our earlier studies which mapped the results of our DPD simulations onto our experimental results of the self-assembly of poly(2-vinylpyridine)-block-poly(ethylene oxide), we use the decay length of the charge $\lambda = 0.2$ and Bjerrum length $\lambda_{\infty} \approx 1.10$, which correspond to the aqueous environment.\(^6,7\) The long-range electrostatic interactions were treated using the Ewald sum with cut-off $r_{el}^c = 3$, real-space convergence parameter $\alpha_{ES} = 0.975$ and reciprocal vector range $n_{max} = (5,5,5)$.\(^8\)

Simulations typically started from random configurations but, in a few cases, simulations were also initiated from the associated state. After an equilibration period of $2 \cdot 10^6$ time steps, we typically ran $20 – 50 \cdot 10^6$ time steps for aggregated systems and $5 \cdot 10^6$ time steps otherwise. DPD trajectories were generated using the GNU program DL_MESO,\(^19\) followed by post-processing to evaluate the quantities of interest.
Distribution of exponentially smeared charge

We studied the effect of the charge smearing very carefully and discussed the most important conclusions in our earlier papers. In reference, we actually calibrated the parameters of forces by mapping the simulation results onto experimental data. We found that the value $\lambda = 0.2$, which is the largest value for which the whole charge is localized inside the coarse-grained bead, reproduces nicely the experimental data. In other systematic study, we have shown that the condensation of charges on top of each other for $a_g = 25$ does not occur. Here we present the comparison of the most important features for $\lambda = 0.2$ and also for the value $\lambda = 0.67$ used by some other authors.

Figure 1. Spatial density $g(r)$ of the exponentially smeared charge for different values of the decay constant $\lambda$.

Fig. 1 depicts the distribution of the exponentially smeared charge. It shows that for $\lambda = 0.67$, the charge is delocalized in a very broad region.
**Figure 2.** Sum of the DPD repulsive potential with $a_{ij} = 25$ and the smeared electrostatic potential of two oppositely charged clouds (with charges $+e$ and $-e$) for $\lambda = 0.2$ and $\lambda = 0.67$. Full lines represent the sum of electrostatic and repulsive potential, which are drawn in dashed and dotted lines, respectively.

Fig. 2 shows the effect of charge smearing on pair interactions. It compares the electrostatic potential between two oppositely charged beads (dotted curve – long ticks) with the soft DPD potential for favorably interacting beads with $a_{ij} = 25$ (dotted curve – short ticks). Solid line depicts their combination. The charges of beads are: $+e$ and $-e$. The comparison shows that the resulting soft force is just little less repulsive than that for neutral beads.

**Figure 3.** Radial distribution function, $g$, for the mixture of either positively or negatively charged beads with the same interaction parameter, $a_{AA} = a_{BB} = a_{AB} = 25$. Red lines correspond to $\lambda = 0.2$, while the green lines represent and $\lambda = 0.67$. Full lines are radial distribution functions between oppositely charged particles, $g_{AB}$, and the
dashed ones are radial distribution functions between evenly charged particles, \( g_{AA} \) and \( g_{BB} \).

Fig. 3 compares the radial distribution function in the system containing charged monomer beads. Red curves are for \( \lambda = 0.20 \) and green for \( \lambda = 0.67 \). Full curves show \( g_{AB} \) between oppositely charged beads and dotted curves depict \( g_{AA} \) and \( g_{BB} \) between beads with charges of the same sign.

**Figs. 1 to 3 clearly prove that the use of the decay constant \( \lambda = 0.20 \) secures that (i) whole charge is localized within one bead and local correlation effects are taken into account at the coarse-grained level, (ii) opposite charges do not collapse on the top of each other, and (iii) the resulting force between beads is soft and it is not necessary to shorten the integration step in simulations of charged systems.**

**References**


20. K. Šindelka, MSc Thesis, Charles University in Prague, Faculty of Science, 2014.