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# Dissipative particle dynamics simulations of H-shaped diblock copolymer self-assembly in solvent

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# ABSTRACT

We examine the self-assembly of H-shaped block-copolymers as the function of the middle block to branch length ratio and interaction between the middle and branch blocks differing in their solvophobicity. The work shows that the examined H-shaped polymers readily transition from uniform mixing of the polymer species to domain formation and a variety of advanced assembly configurations including vesicles, onion-like, and multicompartment aggregates. We identify the polymer conformational and packing changes involved to extract governing interactions and molecule features giving rise to the different assembly structures. The findings are discussed in terms of the H-shaped polymer architecture and polymer assemblies. We conclude that the assembly structure is governed by the molecular level local curvature induced by the varying conformations of the polymers. The findings highlight that for H-shaped polymers the degree of polymerization and polymer chemistries in terms of solvation and mixing characteristics of the blocks are keys to controlling the assembling structures.

# 1. Introduction

Block copolymers provide access to a wide range of well-defined, self-assembling supramolecular structures including lamellar, hexagonal, cuboid and various particle and micellar assembly phases [1–3]. Block composition, length of the copolymer chains, polymer architecture and functionalizations, as well as, system composition provide a variety of readily available parameters that enable optimizing the self-assembly response, aggregate shape and the assemblies response to environment, see e.g. Refs. [4–11] for examples.

Particularly interesting for applications are the self-assembling, finite size particle-like assemblies with internal composition differences or compartments, such as polymer micelles and vesicles. Micelles of block copolymers have applications, for example as drug delivery devices [12,13], microreactors [14,15], in dispersant technology [16], in viscosity modification [17] and in encapsulation or immobilization of enzymes and other biospecies [18,19]. Self-assembling polymer vesicles attract special attention in nanomedicine, including drug delivery and gene therapy, but also as model biomembranes and solubilization because of the hydrophobic-hydrophilic layered membrane and hollow

core that may entrap solvent and other molecules, see for example [8, 20–25]. Block copolymers also readily self-assemble into supramolecular structures consisting of multiple compartments that differ in their chemical environment [2,3]. For example, alternating solvophilic and solvophobic microphase separated domains have applications as multi-drug carriers [26–29] or as a catalysis platform in sequential chemical reactions including artificial cell constructs [24,30–32].

For applications, the assembly morphology and guidelines for controlling it are important. One means to control the self-assembling structures is by using advanced polymer architectures, such as star, miktoarm, Y-shaped, or H-shaped polymers. In this work, we focus on self-assembly of block copolymers with H-shaped architecture. An Hshaped block copolymer refers to a non-linear polymer consisting of a central linear polymer chain terminated at both ends by two polymeric chains called branches, see Fig. 1. Such architecture was first synthesized by Roovers et al. [33] in 1981 from polystyrene, and has later attained significant interest, see e.g. Refs. [34–39]. This is because the H-shaped architecture allows a wide range of assembly morphologies and feasible tunability. Assemblies of H-shaped polymers have attracted interest, for example as candidates for drug-delivery systems in

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**Fig. 1.** a) A schematic illustration of an H-shaped  $A_{2x3}B_5A_{2x3}$  polymer showing the two parameters investigated and b) representation of the species in the system as colored beads. The subscript notation 2x3 refers to two branches of beads *A*, each with three beads, and the 5 refers to the number of *B* beads in the middle block in the example polymer.

controlled drug release applications because of their stimuli responsive behavior, see e.g. Refs. [39,40]. They have also been demonstrated as promising candidates for self-healing materials, if constructed from hard-soft-hard block combinations, see Ref. [41].

Experimental studies have thus demonstrated that H-shaped block copolymers self-assemble into a variety of different structures including vesicles, multicompartment micelles, cylindrical aggregates, and spherical micelles [36,38,42,43]. Besides assembly morphology, also other features of self-assembly behavior of H-shaped polymers have been studied: For example, Iatrou et al. [34] and Pispas et al. [35] showed that the unique H-shaped architecture decreases the critical micellization concentration (cmc) and aggregation number in comparison with linear diblock copolymers. Zou et al. [38] synthesized A2BA2 type H-shaped block copolymers where the A block is hydrophobic and B block hydrophilic. The abbreviation A2BA2 refers to a polymer in which the middle block B is capped at both ends by two branch blocks A. Their results revealed that large complex micelles form with large hydrophobic/hydrophilic ratios, while multilayer and unilamellar vesicles formed at smaller hydrophobic/hydrophilic ratios. In a subsequent paper [44], the large complex vesicles were successfully used to disperse and stabilize multiwalled carbon nanotubes in water solvent via encapsulating them into the vesicles.

Experimental studies have demonstrated that H-shaped polymers can be effectively synthesized, with relatively high control over block length and variety of polymer species. The studies also cover selfassembly into micellar structures on specific H-shaped polymer systems. However, the mechanisms and factors controlling the selfassembly and morphologies rising from this architecture remain poorly understood. Computer simulations provide a powerful tool to gain insight on polymer self-assembly and the involved structure formation. Block-copolymer self-assembly response in solution has been examined with various computational approaches including selfconsistent field theory (SCFT) [45-51], Monte Carlo approaches [52, 53] Brownian dynamics modelling [54-57] but also dissipative particle dynamics (DPD) simulations [57-64]. Coarse-grained and atomistic molecular dynamics simulations capture more microscopic detail but especially atomistic detail models are limited in chain length due to system size limits and relaxation times in comparison to readily accessible simulation durations [65-70].

Computational studies have also addressed specifically H-shaped polymers [55,71–73]. Moultos et al. [55] used Brownian dynamics simulation to study the self-assembly behavior of A2BA2 and A2BC2 type H-shaped copolymers, where A and C are solvophilic and B a solvophobic block, to assess the cmc response and assembly morphology change when hydrophobic/hydrophilic fraction was changed. Huang et al. [71] used DPD simulations to compare the microphase separation behavior of Y- (AB2), H- (A2BA2), and  $\pi$ - (B(A)B(A)B) -shaped diblock copolymer melts. Shao et al. [72] charted the changes in self-assembly when varying the copolymer block arrangements. Jeong et al. employed Brownian dynamics combined with a Rouse model to examine rheological behaviors of H-shaped long-chain branched polymers under shear and uniaxial elongational flows [73]. Wang et al. examined

separation of linear and H-shaped polymers [74]. However, a systematic investigation of factors affecting the self-assembly structures of A2BA2 type diblock H-shaped polymers, where the middle block B is solvophobic and the branches A are selective to solvent remains lacking.

In the current study, we explore the morphologies rising for H-shaped polymers as function of middle block length which affects the hydrophobic/hydrophilic ratio and the chemical compatibility between the blocks of the A2BA2 copolymer via dissipative particle dynamics (DPD) [75] simulations. Previously, DPD has been succesfully used to explore the parameter space and determine the factors affecting the self-assembly of various polymer architectures such as linear di- and multi-block [76-78], *n*-, Y-, and H-shaped [72,79,80], hyperbranched multiarm [81,82], and comb-like [25,83] copolymers demonstrating the practical power of the approach to extract assembly guidelines and control features. We demonstrate by systematic variation of the middle block to branch length ratio and interactions between the middle and branch blocks that the H-shaped polymer architecture readily self-assembles into a number of useful assemblies differing in their internal composition and domain formation: we report the polymer system transitioning from uniform mixing of the polymer species to domain formation and a variety of advanced assembly configurations including vesicles, onion-like, and multicompartment aggregates. While these assembly morphologies are all well-known morphologies for block-copolymer systems in general, in this work, we focus on the H-shaped polymer system to analyze the transitions in solution. Via analyzing the structures, we extract governing interactions and guidelines for tuning it. We discuss the self-assembly in terms of molecular curvature and effective packing shape of the polymers at molecular level. The significance of the work is that the presented systematic characterization of assembly dependence on both solvation and mixing characteristics but also block length sensitivity provides practical guidelines for tuning experimental H-shaped A2BA2 polymer systems so that the full potential of them can be more readily pursued.

# 2. Methods

# 2.1. Dissipative particle dynamics simulation method

Dissipative particle dynamics (DPD) is a coarse-grained bead-based simulation method that uses soft interaction potentials to model hydrodynamic behavior of complex liquids. Successful usage regimes include also e.g. liquid-liquid [84] and liquid-solid interfaces [85]. The mesoscale simulation technique was originally introduced by Hoogerbrugge and Koelman in 1992 [75]. One bead in a DPD model represents a cluster of atoms or molecules and the time evolution of the bead system follows Newton's equations of motion. In general, the total force  $\vec{F}_i$ 

tem follows Newton's equations of motion. In general, the total force  $F_i$  exerted on bead *i* by the other beads *j* in the system is

$$\vec{F}_{i} = \sum_{j \neq i} (\vec{F}_{ij} + \vec{F}_{ij} + \vec{F}_{ij})$$
(1)

where  $\vec{F}_{ij}^{C}$  is the conservative force,  $\vec{F}_{ij}^{D}$  the dissipative force and  $\vec{F}_{ij}^{R}$  the random force. The forces are pairwise additive. The conservative force is based on a soft repulsion model:

$$\vec{F}_{ij}^{C} = \begin{cases} a_{ij} (1 - r_{ij} / r_c) \hat{r}_{ij} & (r_{ij} < r_c) \\ 0 & (r_{ij} \ge r_c) \end{cases}$$
(2)

where  $a_{ij}$  is the interaction parameter that defines the maximum repulsion between beads *i* and *j*,  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$  the distance vector between *i* and *j*,  $r_{ij} = |\vec{r}_{ij}|$ , and  $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$  the corresponding distance unit vector.  $r_c$  is the cutoff radius that limits the range of the forces. The dissipative and random force are coupled such that they act as a thermostat:

$$\vec{F}_{ij}^{D} = -\gamma \omega^{D}(r_{ij})(\hat{r}_{ij} \cdot \vec{v}_{ij})\hat{r}_{ij}$$
(3)

$$\vec{F}_{ij}^{R} = \sigma \omega^{R}(r_{ij})\xi_{ij}\Delta t^{-1/2}\hat{r}_{ij}$$
(4)

where  $\vec{v}_{ij}$  is the relative velocity between bead *i* and *j*.  $\gamma$  and  $\sigma$  are the friction and noise amplitudes, and  $\xi_{ij}$  is a random number with zero average and a unit variance.  $\omega^D$  and  $\omega^R$  are weight functions for the dissipative force and random force. To be consistent with the fluctuation-dissipation theorem, two conditions are set on the weight functions and amplitudes of the dissipative and random forces:

$$\omega^{D}(r_{ij}) = [\omega^{R} r_{ij}]^{2}$$
(5)

$$\sigma^2 = 2\gamma k_{\rm B} T \tag{6}$$

In this,  $k_{\rm B}$  is the Boltzmann constant. We follow here the form of  $\omega^D$  and  $\omega^R$  proposed by Groot and Warren [86]:

$$\omega^{D}(r_{ij}) = [\omega^{R} r_{ij}]^{2} = \begin{cases} (1 - r_{ij} / r_{c})^{2} & (r_{ij} < r_{c}) \\ 0 & (r_{ij} \ge r_{c}) \end{cases}$$
(7)

The bonded interactions between the consecutive beads are modelled by the spring force  $\vec{F}_{ii}$ , defined by

$$\vec{F}_{ij}^{S} = -C(r_{ij} - r_0)\hat{r}_{ij}$$
(8)

A force constant of C = 20 was used and the equilibrium separation is  $r_0 = r_c = 1$ . This force is sufficient to ensure the adjacent beads of the polymer remain connected as a string of beads. The pair-wise forces  $\vec{F}_i$  (Eq. (1)) act both between those beads that are connected by the springs and those that are not subject to the spring force.

A modified velocity-Verlet algorithm is used to integrate the equations of motion. The time step for the simulation was chosen to be  $\Delta t = 0.05\tau$ . Unit normalization follows reduced units such that the cutoff radius  $r_c$ , the bead mass m and the Boltzman constant times absolute temperature  $k_BT$  are used as the distance, mass, and energy units. The unit reduction follows  $r_c = m = k_BT = 1$  which leads to the time unit  $\tau = (mr^2/k_BT)^{1/2} = 1$ . The number density is set to  $\rho = 3$ . The interaction parameter  $a_{ij}$  can be connected to experimental polymer mixing data using the Flory-Huggins parameter  $\chi_{ij}$  for the species i and j. At  $\rho = 3$  density, the connection is an empirical equation  $a_{ij} = a_{ii} + 3.27\chi_{ij}$  [86]. Here  $a_{ii} = 25$  is used for the interaction between same type of beads.

### 2.2. Polymer model, simulations conditions and analysis details

A schematic illustration of the investigated H-shaped polymer and the DPD bead types in the simulations are shown in Fig. 1. The polymer consists of a solvophobic middle block (purple *B* beads) with two slightly solvophobic branches at each end (green *A* beads). Additionally, the system contains solvent, *S* beads. The length of middle block denoted by  $L_{\rm MB}$  is varied to study the effect of the middle block length on selfassembly behavior. For identifying the examined polymers, we adopt a notation where the number and length of the blocks is identified by subscripts, see Fig. 1. Polymers with the following block configurations are considered:  $A_{2x3}B_5A_{2x3}$ ,  $A_{2x3}B_6A_{2x3}$ ,  $A_{2x3}B_7A_{2x3}$ ,  $A_{2x3}B_{10}A_{2x3}$ ,  $A_{2x3}B_{15}A_{2x3}$  and  $A_{2x3}B_{20}A_{2x3}$ .

The interaction parameter values between beads *A* and *S* and beads *B* and *S* are selected to be  $a_{AS} = 30$  and  $a_{BS} = 60$ , respectively. This implies slight solvophobicity to bead *A* and high solvophobicity to bead *B*, i.e that the solvent (bead *S*) is selective towards beads *A* but incompatible with bead *B*. The interaction parameter between the branch and middle block  $a_{AB}$  is varied between 30 and 80. Other interactions are kept constant and the complete interaction parameter matrix is

$$\begin{pmatrix} A & B & S \\ A & 25 & a_{AB} & 30 \\ B & a_{AB} & 25 & 60 \\ S & 30 & 60 & 25 \end{pmatrix}$$
(9)

Simulations were performed in a cubic box with periodic boundary conditions applied in all three dimensions. For systems with  $A_{2x3}B_5A_{2x3}$ ,  $A_{2x3}B_6A_{2x3}$ ,  $A_{2x3}B_7A_{2x3}$  and  $A_{2x3}B_{10}A_{2x3}$  architecture, a cubic box of  $40 \times 40 \times 40 r_c^3$  was used while for  $A_{2x3}B_{15}A_{2x3}$  and  $A_{2x3}B_{20}A_{2x3}$  architectures the cubic box size was increased to  $60 \times 60 \times 60 r_c^3$ . System size dependency was examined comparing assemblies formed at same polymer concentration in the  $(40r_c)^3$  and  $(60r_c)^3$  systems, as well as, for the polymer with middle bead length  $L_{\rm MB}=20$ , also in a  $(100r_{\rm c})^3$  box. The bead density of  $\rho = 3$  results in  $1.92 \times 10^5$ ,  $6.48 \times 10^5$ , and  $3 \times 10^6$ beads for the  $(40r_c)^3$ ,  $(60r_c)^3$ , and  $(100r_c)^3$  systems, respectively. The polymer concentration percentage defined by the number of polymer beads divided by the number of total beads in the system was set to 10.6%. The concentration was chosen as a likely one to result in finite size aggregates and experimentally typical. Initial simulation configurations were constructed by random distribution of the polymers in dilute solvent. 7  $\times$  10<sup>5</sup>, 1.3  $\times$  10<sup>6</sup>, and 2  $\times$  10<sup>6</sup> simulation steps were employed for the  $(40r_c)^3$ ,  $(60r_c)^3$ , and  $(100r_c)^3$  systems, respectively. Equilibration was checked against structural time evolution of the assemblies: the simulation duration is well sufficient for reaching structural equilibrium within the given system sizes. All DPD simulations were performed with the LAMMPS package [87]. Visualizations employ VMD [88]. Data analysis is based on the last 50 and 10 frames of the simulations for the  $(40r_c)^3$  and  $(60r_c)^3$  simulation systems, respectively. Each frame is 1000 DPD steps apart.

Average contact number between beads *i* and *j* is measured by calculating the cumulative radial distribution function, until a contact cutoff distance  $R_{\text{cutoff}}$ . For example, for the contact number between branch and middle beads  $N_{BA}$ , the value is obtained as

$$N_{BA} = \int_{0}^{R_{\text{cutoff}}} g_{BA}(r) dr = \int_{0}^{R_{\text{cutoff}}} \frac{\langle \rho_A(r) \rangle}{\langle \rho_A(r) \rangle_{\text{local}}} dr$$
(10)

Here,  $g_{BA}$  is the standard 3D radial distribution function, defined by the global average density and local, distance *r* dependent density, of beads *A* around beads *B*.  $N_{BB}$  and  $N_{BS}$  are calculated analogously. As the contact cutoff,  $R_{\text{cutoff}} = 1$  was used for all bead pair combinations to cover the first maximum of the radial distribution function.

The polymer conformations were analyzed based on middle block bending. For this, two vectors with origin at the center of the middle block and each ending on the last bead of the middle block at opposite ends, were defined. The distribution of the angle between the vectors  $\theta$  is used as the polymer conformations measure. The angle  $\theta$  varies between  $[0, \pi]$  radians with angles close to zero implying loop conformations and angles close to  $\pi$  bridge conformations.

# 3. Results

We first examined the assembly morphologies of the H-shape polymers. Fig. 2 shows the morphological phase diagram resulting from selfassembly of the polymers as a function of the middle block length  $L_{\rm MB}$ and interaction parameter between beads *A* and *B*,  $a_{\rm AB}$ . The presented aggregates are the cross-sections of the formed structures. For comparison, Supplementary Information Fig. S1 shows the corresponding full simulations systems, excluding the solvent. Six main regions in the assembly phase diagram emerge with varying these parameters. In the limited aggregate formation region, no well-defined aggregates form. In the mixed aggregate formation region, well-defined polymer assemblies with the *A* and *B* components readily mixing inside the assemblies form. The components can also partially segregate to form domains in otherwise mixed assemblies. This is referred to as domain forming mixed aggregates. Additionally, the domains can also involve a secondary



**Fig. 2.** Phase diagram showing the different aggregate morphologies obtained from H-shaped block copolymer architecture as a function of middle block length  $L_{MB}$  and interaction parameter  $a_{AB}$ . Six main regions of the phase diagram are identified: mixed, domain forming mixed, ordered domain, onion-like and vesicle-like aggregates, as well as, a region where only limited aggregate formation is observed.

length scale in their structural order. This is referred to as ordered domain aggregates. More complex morphologies involving secondary length scales in their order include for example onion-like aggregates and vesicles. These regions are all identified in Fig. 2.

Before discussing the assembly regions more in detail, it is important to note that the observed particle sizes and assembly morphologies here are subject to the simulation system size and the periodic boundary conditions. Supplementary Information Figs. S2 and S3 show a comparison of the assemblies formed in the same 10.6% polymer concentration but in different sized simulations boxes. Assemblies formed over the examined  $a_{AB}$  range in  $(40r_c)^3$  and  $(60r_c)^3$  boxes are presented for  $L_{\rm MB} = 15$  polymers (Fig. S2). For  $L_{\rm MB} = 20$ , additionally  $(100r_{\rm c})^3$  system size was examined (Fig. S3). The simulation system size may affect the size and structural characteristics of the particle. For example, the planar assembly morphologies corresponding to ordered domains or vesicles in Fig. 2 may convert to lamellar assemblies in significantly larger systems. However, the data also shows that the tendencies of polymer mixing, domain segregation, or formation of layers persist between the different system sizes. Furthermore, the observed transitions between the different assembly morphologies classified in Fig. 2 occur in the same ten unit interval of  $a_{AB}$  indicating relative stability of the phase boundaries. In further analysis, we take into account the system size dependencies focusing the analysis and conclusions on the local features in the assemblies.

Let us next discuss more in detail the assembling structures. First, poor or limited aggregate formation occurred at low middle block length  $L_{\rm MB} = 5$  and high interaction parameter  $70 \le a_{\rm AB}$ . This refers to the relatively high overall solubility of the chains as they are amphiphilic and the degree of polymerization of the solvophobic block is low. In this region, the highly solvophobic middle block is not protected by the slightly solvophobic branch blocks due to high immiscibility between beads *A* and *B* but also due to the short middle block inhibiting the formation of domains that would limit both A - B and B - S contacts simultaneously. The B - S interaction becomes more favorable than the A - B interactions and the polymers remain freely soluble. The region of

mixed aggregates refers to the formation of polymer assemblies with uniformly mixed internal composition. This morphology is present at short middle block length  $L_{\rm MB} \leq 10$  and low interaction parameter  $L_{\rm MB} \leq 60$  where the compatibility between the blocks compensate the unfavorable effect of short middle block length  $L_{\rm MB}$ .

Domain forming mixed aggregates are assemblies where the blocks of the H-shaped polymer phase separate and form several individual *A* and *B* rich domains. These aggregates form at long middle block lengths  $L_{\rm MB} = 15$  and  $L_{\rm MB} = 20$  with low interaction parameters  $a_{\rm AB} \le 40$  where the connectivity between beads causes the domain formation. Middle block lengths of  $6 \le L_{\rm MB} \le 10$  and high interaction parameter  $40 \le a_{\rm AB}$ also lead to formation of domain forming mixed aggregates but now mainly due to the high block incompatibility. In this region, the long middle block length  $L_{\rm MB}$  compensates the unfavorable effect of the blocks incompatibility (high  $a_{\rm AB}$ ) and promotes polymer aggregation. Notably, for each interaction parameter  $a_{\rm AB}$  value, a minimum middle block length  $L_{\rm MB}$  exists for cohesive aggregate formation. A larger interaction parameter  $a_{\rm AB}$  value results in longer middle blocks being required to overcome the incompatibility between the blocks and for the formation of the microdomains.

Increasing both the middle block length  $L_{\rm MB} \ge 15$  and interaction parameter  $a_{\rm AB} \ge 50$  enables self-assembly of structures with also longer range order in the form of ordered domain aggregates. Such longer range order can emerge at macroscale also as vesicles and onion-like assemblies, as well as lamellar and layered, larger scale assemblies. This widens further the possible assembly morphology space of H-shaped block-copolymers.

To elucidate the mechanisms influencing the assembly transitions of Fig. 2, further analysis of the assemblies was carried out. To characterize the phase (domain) separation and internal structure of the aggregates, Fig. 3 presents the average contact number of beads *B* with each other and the other two bead species *A* and *S* plotted as function of interaction parameter  $a_{AB}$  for all studied middle block lengths  $L_{MB}$ . The average contact number is referred to as  $N_{BA}$ ,  $N_{BB}$ , and  $N_{BS}$ , where  $N_{BA}$  is the average number of contacts that a bead *B* has with any beads *A* and so

on. The calculation is over all the polymers in the simulation, i.e. counts for both intra and intermolecular contacts.

Fig. 3a shows that increasing the interaction parameter  $a_{AB}$  decreases middle block - branch block contacts  $N_{BA}$ . This phenomena rises due to the increasing incompatibility of the two bead species in the DPD model and is the driving force of domain formation inside the aggregates. At a constant  $a_{AB}$ , increasing  $L_{MB}$  also decreases  $N_{BA}$ , which illustrates the importance of  $L_{\rm MB}$  in the internal phase separation and overall structure of the aggregate. Fig. 3b reveals that for long middle block length  $L_{\rm MB} \ge$ 6, the number of middle block - middle block contacts increases when increasing the interaction parameter  $a_{AB}$  while for middle block length  $L_{\rm MB}=$  5,  $N_{\rm BB}$  decreases. The increase in  $N_{\rm BB}$  is a measure of the phase separation inside the aggregates corresponding to formation of B and A rich domains, see Fig. 2. The increase in phase separation at constant  $L_{MB}$  with increasing  $a_{AB}$  is also demonstrated by the snapshots in Fig. 3d. A mixed aggregate is obtained at  $L_{\rm MB} = 10$  and  $a_{\rm AB} = 30$  while the internal structure transitions into a domain forming mixed aggregate as the interaction parameter is increased to  $a_{AB} = 80$ . Due to the high immiscibility of the polymer blocks, middle block B and branch block A rich domains form. Fig. 3d also shows how the internal structure of the aggregate transitions as the middle block length  $L_{MB}$  is increased while the interaction parameter  $a_{AB}$  is kept constant. As seen in Fig. 3d, domain forming mixed aggregate formed with middle block length  $L_{\rm MB}$ = 10 while  $L_{\text{MB}} = 20$  leads to formation of a lamellar layer which curves into a vesicle with interaction parameter  $a_{AB} = 70$ . The longer middle block lengths  $L_{\rm MB}$  allow the domains to merge together to form continuous phases inside the aggregate. This can be understood via the preferential middle block self-interactions inside the domain becoming proportionally stronger when the middle block length increases.

The phase separation inside the aggregate was also quantitatively characterized by an order parameter presented in Fig. S4 of the supporting information. As discussed previously, the aggregation is limited by a large  $a_{AB}$  that corresponds to poor miscibility of the A and B bead types and the short  $L_{\rm MB} \leq 7$  that corresponds to an increase in the solvophobic B bead content of the polymer. The limited aggregate formation region at  $L_{\rm MB} = 5$  and interaction parameter  $a_{\rm AB} = 70-80$  (see Fig. 2) shows as a sharp increase in contact number  $N_{BS}$  due to the increasing solvation of the polymers. Solvated polymers are also present, however to a much lesser extent in systems with middle block length  $L_{MB} = 6-7$  and high interaction parameter as seen from the increased contact number N<sub>BS</sub> and simulation snapshots in Fig. 3c. Polymers with middle block length  $L_{MB} \ge 10$  are able to self-assemble into aggregates such that middle block - solvent contact  $N_{BS}$  is minimal even at high interaction parameter while also decreasing  $N_{BA}$  contact.

To quantitatively determine the conformations of the polymers in the simulated systems and the resulting diverse assembly morphologies, an angle distribution measuring the middle block bending was calculated. The angle  $\theta$  is defined as the angle between two vectors pointing from the center of the middle block to the two ends of the middle block. Angles close to 0 imply curved conformations, while angles close to  $\pi$ imply extended conformations. The data is collected into Figs. 4 and 5. The results show that the conformation of polymers in the mixed aggregates with low interaction parameter  $a_{AB}$  resemble a normal distribution with expected value of  $\sim \pi/2$  radians. This indicates that in mixed aggregates the polymers adopt a wide range of conformations without clear favor toward any specific conformation. On the other hand, the shift in the middle block bending angle distributions to the left at high interaction parameter  $a_{AB}$  and  $L_{MB} \ge 7$  in Figs. 4c and 5 imply that polymers in microphase separated aggregates adopt increasingly curved conformations. However at short middle block lengths  $L_{\rm MB} \leq 6$ , the relatively large branches sterically prevent the folding of the middle block therefore limiting the possibility of curved conformations. Another way to consider this is that a short middle block is a rigid backbone for branches of this size whereas longer middle blocks are more flexible.

(c)

(a)

(b)

10

2

30

14

12

1(

 $N_{\rm BB}$ 

40

50

a<sub>AB</sub>

60

70

80

 $V_{BA}$ 



Fig. 3. Average contact number between a) branch and middle beads  $N_{BA}$ , b) middle and middle beads  $N_{\rm BB}$ , and c) solvent and middle beads  $N_{\rm BS}$  in the simulated systems as a function of interaction between the branch and the middle beads  $a_{AB}$ . The standard deviation of the data points is negligible and is thus omitted from the figures. The simulation snaphots present assembly structure visualizations at  $a_{AB} = 80$  for the systems. The legend provided for panel c) is valid for all panels a)-c). d) Snapshot visualizations of the corresponding morphological changes occurring in the aggregates.

In Fig. 4, the middle block bending angle distributions for polymers



**Fig. 4.** Middle block angle distribution for different interaction parameter  $a_{AB}$  values for polymers with middle block length a)  $L_{MB} = 5$ , b)  $L_{MB} = 6$ , and c)  $L_{MB} = 7$ . The legend provided for panel a) is valid for all panels a–c. The presented angle probability density is normalized to integrate to unity over the range  $[0,\pi]$ .

with short middle block lengths  $L_{\rm MB} = 5-7$  are presented along with a conformational change occurring in the polymers as the interaction parameter  $a_{\rm AB}$  is increased. The angle distribution in Fig. 4a show that polymers with  $L_{\rm MB} = 5$  are too rigid to adopt conformations that would correspond to the formation of domain forming mixed aggregates at all examined interaction parameter  $a_{\rm AB}$  values. However, an increasing interaction parameter  $a_{\rm AB}$  shifts the main peak of Fig. 4a slightly to the right, which indicates that stretched conformations become more favorable. This matches with the system reducing contact between the incompatible blocks, see Fig. 3. An increasing  $a_{\rm AB}$  promotes the loop conformation, however due to the rigidity of the chains, the extended conformations remain preferential.

Polymers with  $L_{\rm MB} = 6$  show limited transition in the angle distribution as the interaction parameter  $a_{\rm AB}$  is increased.  $L_{\rm MB} = 6$  represents a critical middle block length where the polymer chains are flexible enough to form microphase separated aggregates at high  $a_{\rm AB}$  values. This corroborates the finding of the phase diagram (see Fig. 2) where  $L_{\rm MB} = 6$  is the critical middle block length for domain forming mixed aggregate formation. However, it should be mentioned that segregation

within the aggregates and aggregate structure formation is still partially limited by the relatively low middle block length  $L_{\text{MB}}$  (see simulation snapshots in Fig. 3c).

In contrary to short middle block lengths, middle block length  $L_{\rm MB} =$  7 is long enough for polymers to readily adopt curved conformations at large interaction parameter  $a_{\rm AB}$  values, see transition of angle distribution peak to the left in Fig. 4c. This results in domain forming mixed aggregates as  $L_{\rm MB} =$  7 enables more readily curved conformations as  $a_{\rm AB}$  is increased reflecting their higher flexibility. This results in polymer self-assembly into domain forming mixed aggregates almost for the entire studied interaction parameter  $a_{\rm AB}$  range. However, at  $a_{\rm AB} = 30$  mixed aggregates are formed.

Fig. 5 presents an analogous comparison of backbone angle distribution for the polymers with long middle block lengths  $L_{\rm MB} \ge 10$ . Characteristic to this  $L_{\rm MB}$  range, the assemblies change from mixed and domain forming mixed assemblies to a variety of structures with ordered domains including also onion-like and vesicles with increasing  $a_{\rm AB}$ , see Fig. 2. The distributions presented in Fig. 5 reflect this by their smooth broadening with increasing  $L_{\rm MB}$ . The snapshots show the assembly structures at the  $a_{\rm AB}$  extremes.

Most notable structural assembly change for the polymers with middle block lengths  $L_{\rm MB} = 10-20$  is the emergence of two main type of polymer conformations: loop and bridge. The former refers to the polymer folding onto itself with the branches in one lump whereas the bridge conformation is extended and forms spanning networks in the assemblies. Fig. 5d shows a range of conformations between loop and bridge adopted by  $L_{\rm MB} = 10$  polymers. Polymers with middle block length  $L_{\rm MB} \ge 15$  and large interaction parameter  $a_{\rm AB}$  self-assemble into membranous structures (ordered and onion-like aggregates or vesicles and lamellae). Analysis of the polymer conformations reveals that polymers adopt the bridge and loop conformations such that small differences in the resulting overall assembly curvature dictate the precise assembly form. As shown in Fig. 5b, the angle distributions of the aggregates with  $L_{\rm MB} = 15$  are broader than those of  $L_{\rm MB} = 10$ . This corresponds to formation of larger domains and increased order. The broadening is enhanced at  $L_{\text{MB}} = 20$ . Notably, in Fig. 5c a bimodal angle distribution corresponding to the identified loop and bridge conformations emerges and relates directly to the formed structures.

Lastly, Fig. 5e presents the cross-section of the vesicle formed at  $L_{\rm MB}$ = 20 and  $a_{AB}$  = 70, along with the polymers adopting the loop and bridge conformations that were identified as the main conformations. The vesicle contains all the polymers in the system and thus is, at least in terms of diameter, but also the distribution of the loop and bridge conformations, influenced by the simulation system size. However, variation of the simulation parameters (Supplementary Information Figs. S2 and S3) shows that the bilayer formation is stable over a range of interaction parameters. The bilayer also readily curves onto itself to form a vesicle-like aggregate. Fig. 6 summarizes the vesicle assembly via a time series of simulation snapshots. At the beginning of the simulation, the polymer is randomly distributed in the solvent (Fig. 6a). The snapshots show that first, the polymer molecules assemble into smaller coreshell micelles (Fig. 6b). These small micelles assemble into connected worm-like micelles (Fig. 6c) which evolves further into bicelles (Fig. 6d). The bicelles stretch in the plane direction and start curving onto themselves (Fig. 6e). Finally, the assembly process is completed by the assembly closing to form a spherical vesicle (Fig. 6f). Such blockcopolymer vesicles have been reported experimentally, e.g. by Refs. 89, 90 The vesicle forms via a mechanism consistent with those suggested by both simulations [91,92] and high temporal resolution X-ray scattering experiments [93].

The assembly response here is subject to polymer concentration in the simulation system. Furthermore, it is worth pointing out that a prior computational study [94] raises attention to such vesicle-like assemblies having kinetically trapped character. However, the persistence of local membrane curvature preference over varied system sizes, see SI, points toward vesicle-like assemblies, instead of e.g. lamellar or bicontinuous



**Fig. 5.** Middle block angle distribution for different interaction parameter  $a_{AB}$  values for polymers with middle block length a)  $L_{MB} = 10$  b)  $L_{MB} = 15$ , and c)  $L_{MB} = 20$ . The legend provided for panel a) is valid for panels a–c. Panels d) and e) present examples of the bridge and loop conformations in the aggregates for d)  $L_{MB} = 10$  and e)  $L_{MB} = 20$ . The presented angle probability density is normalized to integrate to unity over the range  $[0,\pi]$ .

network under these conditions. We emphasize that the simulation setup is insufficient to rule out other membrane formation based morphologies.

#### 4. Discussion and conclusions

We examined via mesoscale DPD simulations the assembly of Hshaped polymers as function of the middle block length  $L_{\rm MB}$  and the miscibility of the branch blocks *A* and middle blocks *B* captured by the interaction parameter  $a_{\rm AB}$ . The findings of the simulations show that the assembly structures adopted by the H-shaped polymers vary significantly as the function of the examined parameters. The two main phenomena present in the simulations of the current work are aggregate formation and compositional phase separation within the aggregates. Phase separation inside block copolymer aggregates is driven by chemical incompatibility between the copolymer blocks, while the internal morphology of the phase separated aggregate depends mainly on the block composition and polymer architecture [95]. In the current system, the copolymer block incompatibility is captured by the  $a_{\rm AB}$ variation and block composition was altered by the middle block length  $L_{\rm MB}$ .

The presented findings show that aggregate formation is mainly dependent on  $L_{\rm MB}$ , which affects the ratio between the highly solvophobic B beads and slightly solvophobic solvent selective A beads. This is very much in agreement with literature as increasing the solvophobic/solvophilic ratio quite expectedly promotes aggregation and decreases cmc [96,97]. However, our findings also show that at short middle block lengths, sufficient immiscibility between the branch and middle blocks captured by a large interaction parameter  $a_{\rm AB}$  value may also limit aggregation as the solvophobic blocks are not protected from the solvent medium by the incompatible but significantly less solvophobic branch blocks. At most extreme, this leads to the observed

limited aggregate formation range. The findings point toward the existence of a minimum compatibility between the middle and branch blocks for each middle block length  $L_{\rm MB}$  for the formation of cohesive aggregates. Polymers with long middle blocks may counter this by folding onto themselves, reducing the solvophobic block exposure to solvent medium.

Interestingly, Moultos et al. [55] have showed for H-shaped polymers that their cmc does not depend monotonically on solvophobic/solvophilic ratio unlike for linear AB copolymers [98]. Instead, the cmc is influenced by the symmetry of the H-shaped polymer. They also concluded that H-shaped polymers with a large hydrophobic/hydrophilic fraction aggregated into nearly monodisperse spherical micelles while those with low hydrophobic/hydrophilic fraction did not aggregate under same conditions [55]. While the findings address different aspects of H-shaped polymer aggregation, the previously reported non-linearity and complex responses in terms of aggregation are consistent with our findings.

Besides the already discussed limited aggregate formation in polymer systems with short  $L_{\text{MB}}$  and large  $a_{\text{AB}}$ , we observed phase separation inside aggregates locally to domains at large interaction parameter  $a_{\text{AB}}$ , and finally the formation of morphologies with dual length scale and longer range order, such as aggregates with ordered domains or onionlike layering but also vesicle-like assemblies. These more ordered assemblies emerged for polymers with sufficiently long middle block and high immiscibility between the middle and branch blocks.

For aggregate formation to be favorable when the middle and branch blocks are incompatible, i.e. at interaction parameter  $a_{AB} \ge 60$ , the middle block has to be long enough to allow for phase separation inside the aggregate such that the middle block and branch contacts can be minimized, see Fig. 3a. Analysis of the polymer conformations revealed that for phase separation and domain formation at short middle block lengths  $L_{MB} \le 7$ , the polymer chains adopt curved conformations, see



**Fig. 6.** Sequential simulations snapshots showing the self-assembly of a vesicle in the  $L_{\rm MB} = 20$  system with  $a_{\rm AB} = 70$ . The snapshots show the simulation system at a) the initial state (0 steps), b)  $3.00 \times 10^3$  steps, c)  $1.00 \times 10^4$  steps, d)  $5.00 \times 10^4$  steps, e)  $1 \times 10^5$  steps and f)  $1 \times 10^6$  steps. Bead colors match Fig. 1. Solvent beads are omitted for clarity.

Fig. 4. At small middle block-to-branch ratios, such curved conformation cannot be adopted which leads to the high steric effect of the branches keeping the polymers with very short middle blocks soluble, see Fig. 4a. In these systems, energy is minimized by the middle blocks having solvent contacts, see Fig. 3c. Correspondingly, a low interaction parameter  $a_{AB}$  enables aggregate formation even at short middle block length due to the compatibility of the blocks. The aggregates formed are mixed aggregates.

In the middle section of the phase diagram of Fig. 2, domain forming mixed aggregates form. These aggregates have several middle block rich microdomains. In polymers with middle block length  $6 \le L_{\rm MB} \le 10$ , increasing the interaction parameter  $a_{\rm AB}$  allows for phase separation to take place inside the aggregate and domains form. The polymer middle block is long enough in this range to allow for the flexibility of the chain. This leads to both elongated and curved conformations, see Figs. 4 and 5. The free energy of the system is minimized by increasing middle block - middle block contacts (Fig. 3b) while decreasing middle block - branch contacts (Fig. 3a). The values of  $N_{\rm BB}$ ,  $N_{\rm BA}$ , and  $N_{\rm BS}$  are controlled by the interaction parameters capturing the polymer miscibilities, as well as the middle block length  $L_{\rm MB}$ . The latter signifies the connectivity between the segments. Notably, at long middle block lengths  $L_{\rm MB} \ge 15$  phase separation may occur even at low interaction parameter  $a_{\rm AB}$ .

Previously, Huang et al. [71] have reported that increasing complexity of polymer architecture (linear vs Y vs H or  $\pi$ ) decreases assembly stability and also that the greater entropy loss associated with the disorder-to-order transition for architectures such as H makes it more difficult for them to undergo a microphase separation. Our findings of the limited aggregation range and shifts in assembly phases in terms of  $a_{AB}$  with  $L_{MB}$  changes are consistent with their findings.

Finally, assemblies with longer range order and multiple structural

length scales form in the upper right corner of the phase diagram of Fig. 2. The incompatibility of the middle and branch blocks is still the driving force of the phase separation as shown by the increasing  $N_{\rm BB}$  in Fig. 3b and decreasing  $N_{BA}$  in Fig. 3a. The long middle blocks with  $L_{MB} \ge$ 15 allow the segregated microdomains to blend to form two continuous phases. The outcome is middle block and branch block rich stripes, layers, or continuous shells which give rise to formation of morphologies with longer range order such as onion-like aggregates, ordered aggregates and multi-, and single-walled vesicles (see Fig. S2 in supplementary information). In a prior study, Parent et al. [99] examined both experimentally and computationally the formation and structural evolution dynamics of assemblies from a solution of amphiphilic polymer dendrons. Their findings show similar single- and multi-walled vesicles as the current work. Comparison of the assembly responses shows that the vesicular assembly response rises from the relative solvophobicity and proportional sizes of the polymer blocks or branches but also from the polymer architecture posed constraints on shielding the more solvophobic regions.

The assemblies with longer range order in this H-shaped polymer system rise from a competition between the phase separation tendencies of the polymer blocks and the molecular level steric constraints posed by the architecture. Additional contribution to assembly order transitions rises from variation in the distribution of molecule conformations corresponding to loop folding and the bridge-like conformations. Notably, these bridge and loop conformations that we observed here have been reported also by Huang et al. [71] as the main conformations of H-shaped molecules. Let us next consider the effects of the observed polymer conformations changes to the self-assembling structures. The loop conformations result in a clearly conical effective packing shape. This promotes curved interfaces, such as finite size domains. The stretched and bridge-like conformations are more dumbbell-like in their shape. Closest surfactant analogy is bolaform, which is known to give rise to micelles but also nanotubules and vesicle-like assemblies [100]. It also readily adopts spiraling and other more complex curved assemblies [100]. Here, as the heads are polymeric, additional packing conformational freedom is obtained by the flexibility and length of the polymer branches. We observed that while a small  $L_{\rm MB}$  confines the polymers to a relatively rigid shape, the polymers readily adopted both loop and bridge conformations at a large enough  $L_{\rm MB}$ . As these conformations differ in resulting local curvature, this means, that in this range, small changes in the free energy landscape change the molecular level packing curvature and the resulting assembly. Our previous work shows that such changes can readily be induced, for example, by substrate [101, 102] or confinement of the polymeric head groups [103]. To our knowledge, the sensitivity of H-shaped polymer assemblies has not been mapped in this sense, but both block-copolymer and bolaform self-assembly reviews point toward a rich response range and tunability [100,104,105]

In conclusion, we investigated how the length of the middle block and compatibility between the two copolymer blocks affects selfassembly of H-shaped polymers using dissipative particle dynamics. The work demonstrated that both factors influence strongly polymer aggregation and internal phase separation. Assembly morphologies that rose in the modelling include, e.g. multicompartment, onion-like layered, and vesicle morphologies. The findings revealed the guidelines governing the assemblies internal structure which enables tuning the H-shaped polymer systems toward desired applications. In particular, the observed multicompartment, ordered layered, and vesicle morphologies are especially interesting due to their uses as encapsulating agents, confined reactions platforms, and selective solubilization [105,106].

# CRediT authorship contribution statement

Adam L. Harmat: Visualization, Investigation, Formal analysis, Writing – original draft, preparation. Sousa Javan Nikkhah: Methodology, Conceptualization, Writing – review & editing. Maria Sammalkorpi: Conceptualization, Supervision, Funding acquisition, Resources, Writing – review & editing.

# 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 data

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