Coarse grained simulation of the aggregation and structure control of polyethylene nanocrystals

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Received 20 December 2020, revised 11 March 2021
Accepted for publication 15 April 2021
Published 25 May 2021

Abstract
Polyethylene (PE) telechelics with carboxylate functional groups at both ends have been shown to assemble into hexagonal nanocrystal platelets with a height defined by their chain length in basic CsOH-solution. In this coarse grained (CG) simulation study we show how properties of the functional groups alter the aggregation and crystallization behavior of those telechelics. Systematic variation of the parameters of the CG model showed that important factors which control nanoparticle stability and structure are the PE chain length and the hydrophilicity and the steric demand of the head groups. To characterize the aggregation process we analyzed the number and size of the obtained aggregates as well as intramolecular order and intermolecular alignment of the polymer chains. By comparison of CG and atomistic simulation data, it could be shown that atomistic simulations representing different chemical systems can be emulated with specific, different CG parameter sets. Thus, the results from the (generic) CG simulation models can be used to explain the effect of different head groups and different counterions on the aggregation of PE telechelics and the order of the obtained nanocrystals.

Keywords: polyethylene, telechelics, nanocrystals, molecular dynamics, aggregation, coarse grained model

1. Introduction

Controlling the shape, size and surface properties of nanoparticles is one of the key challenges in modern materials chemistry. While it is well established to rely on the crystallization process to control the shape and physical properties of inorganic nanoparticles, only rather recently the formation of a crystalline core has been used to generate anisotropic polymer nanoparticles [1–7]. In particular, precise functionalized polyethylene (PE) which is substituted with hydrophilic functional groups (FGs) placed at regular distances along the PE chain can form crystalline layers. The height of the layer therein is strongly correlated to the spacing between the FGs along the chains [8, 9]. Later studies found that those precise polymers can also form hexagonal nanocrystal platelets in aqueous solution. As is the case in the crystalline layered materials, the respective height of the platelets is strongly correlated to the distance between FGs along the chain [4]. More recent studies revealed that this behavior even occurs in precise PE telechelics, that is relatively short PE chains of a precise chain length with FGs as end groups at both chain termini, for example linear PE chains containing 48 carbon atoms with carboxylate groups at both ends. Note though, that for relatively short telechelics (21 methylene units) no nanocrystal formation was observed—in contrast to precise polymers with a sim-
ilar FG distance along the PE chain that do form nanocrystals [6, 10].

Molecular dynamics (MD) simulations provide a valuable tool to study physico-chemical properties and processes at very high spatial and temporal resolution levels of various soft matter systems and processes. Here, we employ MD simulations as a way to gain insight into assemblies of polymer chains into aggregates and their crystallization behavior.

Layered crystal structures of precisely functionalized PE have been investigated by classical atomistic simulations. It was found that the lamella structures where the polymer bends at the FGs is energetically more stable than a more elongated polymer backbone with fewer or no bends at the FG sites [11]. This structure was also found by x-ray diffraction experiments [9]. Further experimental and computational efforts were made to understand the parameters governing the formation of crystalline platelets from PE telechelics. Systems with carboxylate terminated telechelics in combination with multiple different counterions as well as sodium sulfonate with carboxylate terminated telechelics in combination with multiple different counterions as well as sodium sulfonate with carboxylate telechelics were investigated experimentally in combination with atomistic MD simulations [12]. In experiment no nanocrystals were found for short chain telechelics. Long chain telechelics formed nanocrystals with carboxylate FGs and caesium counter ions and with sulfonate FGs and sodium counter ions. For the carboxylate FGs, also sodium and potassium were tested as counterions, but in both cases no nanocrystals were observed, but dynamic light scattering experiments showed that larger structures occurred. With the sodium sulfonate FGs on the long telechelics, smaller and less well defined nanocrystals were found compared to the caesium carboxyate system. The atomistic simulations, in which small hexagonal nanocrystals containing 91 telechelics were set up, showed that caesium carboxylate FGs on the short telechelics lead to a dissociation of the nanocrystal into smaller noncrystalline aggregates. With the long telechelics, smaller, more strongly coordinating counterions lead to an increased ordering of the nanocrystals in the simulations. By exchanging the carboxylate FG with the larger, less coordinating sulfonate group, the order of the nanocrystal was reduced compared to the carboxylate simulation with the same counterion (sodium). Thus, atomistic simulations confirmed the nanoparticle structure made up by a crystalline core of regularly arranged stretched hydrocarbon chains with FGs on the platelet surfaces. The atomistic simulations also linked the steric demand of the FGs and the degree of dissociation of the counter ions to the order of the nanocrystal which, in turn, could be connected to the experimentally observed size and (colloidal) stability of the particle.

Yet, atomistic models are limited due to their comparatively high resolution. This makes them computationally quite costly, which discourages their use in studies on larger spatial and temporal scales. To overcome these limitations, coarse grained (CG) simulation models, where atoms are grouped together, can be employed when studies of longer time- and length-scales are desired [13–20]. For the present system, atomistic models exhibit the right chemical accuracy to investigate structural and interfacial properties of preassembled nanoparticles, however they are not well suited to simulate how such particles form. To simulate the aggregation and crystallization of PE telechelics, we used the monatomic water model (mW) by Molinero [21] and TraPPE-UA [22–24] to model water and the polymer chains. To study the qualitative effects of the FGs and their solvation properties, different combinations of parameters were modeled. The systems were then analyzed for their aggregation behavior and the formation of ordered nanoparticles as a function of hydrophilicity and spatial demand of the FGs. In a second step, the relationship between the stability of preassembled nanocrystals and the FG parameters was studied. Finally, comparison of CG and atomistic simulation data allowed to establish a relationship between the CG models and the different chemical systems studied experimentally and by atomistic simulations.

2. Computational Methods

2.1. Simulations

MD simulations were carried out using the LAMMPS simulation package [25]. Water was modeled using the mW water model, a united-atom representation using short-ranged three-body interactions to generate the tetrahedral structure of water [21]. It is often used to study liquid and crystalline water phases and solutions. Interactions between alkane groups (methylene units) were modeled using the TraPPE-UA force-field. For the interaction of water and alkane groups a potential from the LAMMPS moltemplate package was used [25, 26] (see caption of table 1). We tested properties of alkane-water systems obtained with this potential, e.g. the alkane-water surface tension compared to atomistic simulations in analogy to reference [27]. The mapping scheme of the telechelics including the one-bead representation of the FGs is shown in figure 1 and described in the caption.

Table 1. List of CG parameter sets. $\epsilon$ values for FG–FG interactions is 2.0 kcal mol$^{-1}$, for FG–CH$_2$ a value of 0.119 15 kcal mol$^{-1}$ was used. CH$_2$–CH$_2$ $\sigma$ is 3.95 Å, CH$_2$–mW $\sigma$ is 3.558 Å and CH$_2$–mW $\epsilon$ is 0.119 15 kcal mol$^{-1}$.

| Parameter set | FG–FG $\sigma$ | FG-water $\epsilon$ | FG-water $\sigma$ | FG-CH$_2$ $\sigma$ |
|---------------|----------------|---------------------|-------------------|-------------------|
| lowH-small    | 2.88           | 0.41583             | 2.88              | 3.558             |
| lowH-medAd    | 3.95           | 0.41583             | 2.88              | 3.558             |
| lowH-medium   | 3.95           | 0.41583             | 3.558             | 3.95              |
| lowH-3.95     | 5.925          | 0.41583             | 4.4475            | 4.9375            |
| intermH-small | 2.88           | 0.83166             | 2.88              | 3.558             |
| intermH-medAd | 3.95           | 0.83166             | 2.88              | 3.558             |
| intermH-medium| 3.95           | 0.83166             | 3.558             | 3.95              |
| intermH-longAd| 4.95           | 0.83166             | 3.558             | 4.45              |
| highH-small   | 2.88           | 1.24749             | 2.88              | 3.558             |
| highH-medAd   | 3.95           | 1.24749             | 2.88              | 3.558             |
| highH-medium  | 3.95           | 1.24749             | 3.558             | 3.95              |
| highH-3.95    | 5.925          | 1.24749             | 4.4475            | 4.9375            |

Time integration was performed using a variation of the velocity-Verlet integrator with a timestep of 5 fs [28, 29]. NpT simulations were carried out with a Nosé–Hoover chain thermostat [30, 31], the relaxation time for temperature being
Figure 1. (A) Chemical composition of the telechelics superimposed onto the CG mapping scheme. CH$_2$ are represented as 1 bead, with the position of the carbon atom. The FGs are represented by a single bead. For comparison to atomistic structures the mapping is as indicated. COOX: the carboxylate carbon and oxygen atoms are mapped into 1 bead together with the counterion X (X in the atomistic data being Cs, K, or Na), the bead is located at the position of the C atom. SO$_3$Na: the sulfonate carbon and oxygen atoms are mapped into 1 bead together with the counterion Na, the bead is located at the position of the S atom. The orange arrows display example vectors used for order parameter calculations. (B) Particle generated with a simulation using FGs with intermediate hydrophilicity and of a medium size starting from a previously assembled nanoparticle. Visualization of different descriptors used to characterize the nanoparticle structure: pink arrows (elongated for visibility) on top of the blue highlighted molecule on the left indicate typical vectors for the calculation of the internal order parameter. Yellow arrows (elongated for visibility) on top of the purple highlighted molecules on the right indicate typical vectors for the calculation of the local nematic order parameter. The green highlighted molecule in the center illustrates the end-to-end distance.

100 fs, for the pressure 1000 fs. The temperature was set to 300 K and the pressure to 101.325 kPa (1 atm). Periodic boundary conditions were used in all directions and the center of mass movement was removed.

Initial structures of the systems with telechelics randomly distributed in solution were generated with the EMC-builder created by in’t Veld [32] which relies on a short Monte Carlo simulation. As the EMC builder does not support the mW model, water was represented with the SPC/E model and the telechelics as dihydroxy-alkanes using the TraPPE-UA force-field [22–24]. To convert the generated structures to the CG level of representation (i.e. the mW model and TraPPE-UA with generic FGs), all hydrogen atoms were removed from the EMC-built structure, i.e. the water oxygen became the mW beads, and the positions of the hydroxy oxygen atoms were used as positions for our generic FGs.

Table 1 shows the Lennard-Jones parameters that were used in the different models throughout this study. The pattern for the naming of the parameter sets is as follows: FG hydrophilicity (i.e. the $\epsilon$ parameter of the FG-water interaction) is described by the categories low (labeled as lowH), intermediate (intermH) and high (highH). FG size (i.e. the $\sigma$ parameter of the FG interactions) is described with the labels small, medium, large, and very large (vlarge). FG–FG and FG-water $\sigma$ values are adjusted to scale proportionally. In addition, for some parameter sets (denoted by the labels medAd and largeAd) the scaling of the $\sigma$ values was adapted such that the FG–FG $\sigma$ scales comparably stronger than the FG-water $\sigma$. The FG-water interaction parameters were chosen based on a few initial tests. We started with FGs of comparatively low hydrophilicity (lowH) (somewhat more hydrophilic than a methyl group would be). The particles that were formed in initial simulations with this model appeared to be overly ordered compared to atomistic reference data, thus we gradually increased the interaction strength of the FGs with water. Here we show the results obtained with a representative selection of the investigated parameters in the range where we observed nanoparticle formation in general agreement with observations from experiments and atomistic simulations. Three-body interaction terms between the FGs and water (i.e. terms that could account for the water structure around the FGs due to hydrogen bonds) were not taken into account for the CG model at the present stage. Also, no explicit electrostatic interactions are present in the simulation. This is in line with the mW model where water molecules are represented by single, chargeless beads. In this type of coarse-grained models electrostatic interactions—including the effects of dielectric screening—are represented by (typically comparatively short ranged) effective interactions between the CG beads. A short discussion of modeling choices such as the representation of electrostatics interactions and the representation of counterions, etc can be found at the end of the results section where we compare the CG simulations to atomistic data.

Simulations were started from initial structures with randomly distributed polymer chains in solution as well as from preassembled nanoparticles. Detailed information about the
Table 2. List of simulations starting from a random distribution of telechelics in water. The parameter sets listed in the parameters column are presented in table 1. Systems are characterized by the type of telechelics (count of superatoms, i.e. CG beads, per chain; CSAC), number of telechelics, number of water molecules, the resulting concentration of telechelics in solution and the simulated time.

| Simulation | Parameters | CSAC | No. Chains | No. Water | c (mol%) | sim len (ns) |
|------------|------------|------|------------|-----------|---------|-------------|
| 1          | lowH-small | 23   | 130        | 28519     | 0.4538  | 350         |
| 2          | lowH-medAd | 23   | 130        | 28519     | 0.4538  | 450         |
| 3          | lowH-medium | 23   | 130       | 28519     | 0.4538  | 150         |
| 4          | intermH-medAd | 23   | 130     | 28519     | 0.4538  | 200         |
| 5          | intermH-medium | 23   | 130     | 28519     | 0.4538  | 400         |
| 6          | highH-small | 23   | 130       | 28519     | 0.4538  | 150         |
| 7          | highH-medAd | 23   | 130       | 28519     | 0.4538  | 200         |
| 8          | highH-medium | 23   | 130      | 28519     | 0.4538  | 400         |
| 9          | lowH-medium | 23   | 127      | 517398    | 0.02454 | 250         |
| 10         | lowH-medium | 23   | 127      | 258699    | 0.04907 | 400         |
| 11         | highH-medium | 23   | 127      | 258699    | 0.04907 | 400         |
| 12         | lowH-small | 48   | 132       | 41000     | 0.3209  | 600         |
| 13         | lowH-medAd | 48   | 132       | 41000     | 0.3209  | 600         |
| 14         | lowH-medium | 48   | 132      | 41000     | 0.3209  | 1200        |
| 15         | intermH-medium | 48   | 132   | 41000     | 0.3209  | 300         |
| 16         | highH-small | 48   | 132      | 41000     | 0.3209  | 300         |
| 17         | highH-medAd | 48   | 132      | 41000     | 0.3209  | 300         |
| 18         | highH-medium | 48   | 132     | 41000     | 0.3209  | 300         |
| 19         | lowH-medium | 48   | 127      | 258699    | 0.04907 | 300         |
| 20         | highH-medium | 48   | 127     | 258699    | 0.04907 | 600         |

aStructure obtained from simulation 2 after 250 ns was used as nanoparticle structure to test nanoparticle stability (see table 3).
bStructure obtained from simulation 12 after 450 ns was used as nanoparticle structure (see table 3).
cStructure obtained from simulation 13 after 450 ns was used as alternative nanoparticle structure for simulation 31 (see table 3) for cross-validation.

simulated systems (used parameter set, number and types of polymer chains, number of water molecules, initial structure, simulation length) can be found in the respective results sections in tables 2–4. Note that due to the intrinsic speedup of CG simulations [33, 34], the presented simulation times do not directly translate to real times. For example, the diffusion of the mW model at 298 K is about three times faster than that observed in experiment [35]. Visualization of simulation structures was performed using VMD [36].

2.2. Analysis of aggregation count

The polymer chains were assigned to aggregates with the distance based algorithm built-in to LAMMPS (compute aggregate/atom). If any two CG-beads are within 4.5 Å of each other the respective chains were considered to belong to the same aggregate. Aggregate IDs were modified in post-processing in such a way that the numbering remains stable with simulation time whenever possible and adopts small values.

2.3. Analysis of order parameters

The ordering of the polymer chains is described by order parameters which rely on alignment evaluation through vector comparison. The vectors have been defined analogous to earlier approaches to describe the crystallinity of alkanes [37, 38] (see figure 1(A)). Here, unit vectors are defined from the vectors connecting the centers of the alkane C–C bonds. To compute local order parameters the position of the segments is determined as the midpoint between two neighboring bond centers. Vectors are determined between all bonds within the CG-telechelic molecules.

The local order parameter uses the equation for the local nematic order [39] (equation (1)) and describes the intermolecular alignment of pairs of short chain segments based on their distance (see figure 1(B), yellow arrows on the right side).

\[
Q_a(r) = \frac{\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (\delta(a_i,a_j))(1 - \delta(m_i,m_j)) \delta(r - |r_i - r_j|)P_2(\vec{u}_i \ast \vec{u}_j)}{\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (\delta(a_i,a_j))(1 - \delta(m_i,m_j))\delta(r - |r_i - r_j|)} .
\]

with: \[ P_2(x) = \frac{3}{2} x^2 - \frac{1}{2} \]

\[ 0 \leq Q_a(r) \leq 1 \]
### Table 3. List of simulations starting from preassembled nanoparticles (for starting structures see information in table 2). Used parameter sets are shown in parameters, count of superatoms (CG beads) per chain (CSAC), number of telechelic chains, number of water molecules/beads, the concentration of telechelics in solution (c) and the simulated time.

| Simulation | Parameters   | CSAC | No. Chains | No. Water | c (mol%) | sim len (ns) |
|------------|--------------|------|------------|-----------|----------|--------------|
| 21         | lowH-small   | 23   | 130        | 28519     | 0.4538   | 150          |
| 22         | lowH-medAd   | 23   | 130        | 28519     | 0.4538   | 450\(^a\)    |
| 23         | lowH-medium  | 23   | 130        | 28519     | 0.4538   | 150          |
| 24         | lowH-vlarge  | 23   | 130        | 28519     | 0.4538   | 150          |
| 25         | intermH-small| 23   | 130        | 28519     | 0.4538   | 150          |
| 26         | intermH-medium| 23   | 130    | 28519    | 0.4538 | 150          |
| 27         | highH-small  | 23   | 130        | 28519     | 0.4538   | 150          |
| 28         | highH-medAd  | 23   | 130        | 28519     | 0.4538   | 200          |
| 29         | highH-medium | 23   | 130        | 28519     | 0.4538   | 150          |
| 30         | highH-vlarge | 23   | 130        | 28519     | 0.4538   | 150          |
| 31         | lowH-small   | 48   | 132        | 41000     | 0.3209   | 150\(^b\)    |
| 32         | lowH-medAd   | 48   | 132        | 41000     | 0.3209   | 150          |
| 33         | lowH-medium  | 48   | 132        | 41000     | 0.3209   | 150          |
| 34         | intermH-small| 48   | 132        | 41000     | 0.3209   | 150          |
| 35         | intermH-medium| 48   | 132    | 41000    | 0.3209 | 150          |
| 36         | highH-small  | 48   | 132        | 41000     | 0.3209   | 150          |
| 37         | highH-medAd  | 48   | 132        | 41000     | 0.3209   | 150          |
| 38         | highH-medium | 48   | 132        | 41000     | 0.3209   | 150          |

\(^a\)Simulation was continued, because starting structure for the nanoparticle was generated from this simulation.

\(^b\)Simulation started from the alternative structure generated from simulation 13 (see table 2).

### Table 4. List of simulations starting from a perfect hexagonal crystal as set up for atomistic atomistic simulations [12]. Used parameter sets are shown in parameters (see table 1), count of superatoms (CG beads) per chain (CSAC), number of telechelic chains, number of water molecules/beads and the concentration of telechelics in solution (c). Because in experiment the number of methylene groups for the sodium sulfonate telechelics is larger by 2, atomistic and CG simulations of these systems contain PE chains with two more CH\(_2\) units (i.e. simulations 41 and 42).

| Simulation | Parameters   | CSAC | No. Chains | No. Water | c (mol%) | sim len (ns) |
|------------|--------------|------|------------|-----------|----------|--------------|
| 39         | lowH-medAd   | 48   | 91         | 42521     | 0.2136   | 200          |
| 40         | intermH-medAd| 48   | 91         | 42521     | 0.2136   | 200          |
| 41         | intermH-medium| 50   | 91         | 42521     | 0.2136   | 100          |
| 42         | intermH-largeAd| 50   | 91         | 42521     | 0.2136   | 100          |
| 43         | highH-medAd  | 48   | 91         | 42521     | 0.2136   | 100          |
| 44         | highH-medium | 48   | 91         | 42521     | 0.2136   | 100          |
| 45         | highH-vlarge | 48   | 91         | 42521     | 0.2136   | 100          |

Here, \(P_2\) is the second Legendre polynomial, \(\vec{u}_i\) and \(\vec{u}_j\) are the unit vectors describing the orientation of the segments \(i\) and \(j\), respectively. \(N\) is the number of vectors in the system and can be calculated by multiplying the number of segments per molecule (i.e. number of beads per molecule minus 2) with the number of telechelics in the system. \(r_i\) and \(r_j\) are the positions of the segments \(i\) and \(j\). \(m_i\) and \(m_j\) are indices for the respective molecules those segments belong to while \(ai\) and \(aj\) are indices for the aggregates the molecules belong to. In this form the equation uses three Kronecker deltas. \(\delta(r - |r_i - r_j|)\) yields 1 when the distance between both segments equals \(r\), \(\delta(m_i m_j)\) assumes 1 when \(m_i\) equals \(m_j\), \(\delta(ai aj)\) takes on a value of 1 if the regarded molecules belong to the same aggregate. This way our calculation only considers segment pairs that are not part of the same molecule and thus yields a distance dependent description of the intermolecular alignment. For an aggregate-wise calculation only vector pairs that belong to the same aggregate are considered. As last step, the obtained order parameters are averaged, either over aggregates of similar sizes (see figure 5(c)) or over the whole system.

The internal order parameter complements the local order parameter and the end-to-end distances in describing the ordering of the chains. Here, we evaluate only segment pairs within the same molecule (see figure 1(B), pink arrows on the left side) to show how well aligned a molecule is with itself (equation (2)).
Figure 2. Overview of general aggregation behavior for telechelics of two chain lengths and systematic variation of FG parameters (left panel: 132 chains of fC48; right panel: 130 chains of fC23). FG hydrophilicity increases from left to right, FG size increases from top to bottom.

\[
Q_m = \frac{\sum_{i=1}^{N-1} \sum_{j=r+1}^{N} \delta(m,m_j) P_2(\mathbf{u}_i \cdot \mathbf{u}_j)}{\sum_{i=1}^{N-1} \sum_{j=r+1}^{N} \delta(m,m_j)}.
\]  

This is a modification of equation (1) which drops \( \delta(r - |r_i - r_j|) \), thus removing the dependency of \( r \), and because it is an intramolecular parameter also eliminating the need for the \( \delta(a_{ij}) \) Kronecker delta, because per definition a molecule as a whole is part of an aggregate. The remaining \( \delta(m,m_j) \) now introduces a dependency with the molecule identity \( m \). The values are averaged for the whole molecule, meaning that every chain is characterized by a single internal order parameter at each time frame. Note that the end-to-end distance alone can only certify this self-alignment when it assumes high values and the molecule is stretched out. As for the local order, the internal order parameter is averaged either over aggregates of similar sizes (see figure 5(b)) or over the whole system.

3. Results

To investigate the influence of the properties of FGs on aggregation and crystallization of PE telechelics, the spatial demand of the FG and the FG-water interaction strength were varied for two chain lengths and different system setups. Features of the resulting aggregates that were analyzed are among others: aggregate size distribution, end-to-end distances and internal (intramolecular) order, (intermolecular) local nematic order, i.e. alignment of neighboring chains and radial distribution functions (RDFs). Figure 1 shows—along with the mapping scheme of the CG model—an example of a nanoparticle that illustrates typical chain conformations as well as the mentioned structural properties that were analyzed. The simulated telechelic chains contain 21 CG methylene beads and 2 FGs (in the following denoted as fC23, following the naming convention of the experimental system) or 46 CG methylene beads and 2 FGs (denoted fC48). Regarding the CG model it should be noted that it centers around the mW water model where the structural properties of water are reproduced without explicit electrostatic interactions [21, 40, 41]. Thus, we decided for this study to treat the interactions of the FGs also entirely based on LJ potentials, i.e. FGs were simulated without explicit charges and no compensating counterions are included in the simulation. Instead, the effect of different counterions (e.g. caesium vs potassium or sodium) is accounted for by varying the LJ parameters of the FGs. Thus steric and electrostatic effects due to differences in the ion coordination (potassium or caesium as cations or sulfonate as anions, see reference [12]) are effectively accounted for by the properties of the FGs. A detailed comparison of different CG model parameters to data from all-atom simulations is made at the end of the results section.

3.1. Aggregation and particle formation

In a first step, we simulated the aggregation process starting from a random distribution of telechelics of both chain lengths. We systematically varied the hydrophilicity of the FGs (via the \( \epsilon \) parameters of the FG-water interactions) as well as their size (via the \( \sigma \) parameters of the Lennard Jones potentials). For details regarding the model parameters and the nomenclature for the different models see table 1 and the computational methods section. The performed simulations including system composition and simulation lengths are listed in table 2. A qualitative impression of the behavior of the different systems can be gained from snapshots of the respective final structures shown in figure 2. We see that the FG parameters have a drastic effect on the morphology of the resulting aggregates. Depending on the model parameters we observe a tendency of the telechelics to spontaneously form nanocrystals that exhibit a hexagonal arrangement of the aligned telechelics—corresponding quite well to the hexagonal PE nanoparticles found experimentally. Large particles are preferentially found for simulations with smaller FGs of relatively low \( H \) and appear to be stabilized by increasing chain length. Figure 3 further illustrates the aggregation process in the different simulations by monitoring the time evolution of the number of aggregates. In general, a higher hydrophilicity of the FG leads to slower aggregation and smaller aggre-
Figure 3. Time evolution of the number of aggregates during different simulations. Results for short chained telechelics (fC23) are marked by circles, for long chained telechelics (fC48) by diamonds. Line colors denote the different FG-water interaction strengths. Low hydrophilicity: light blue lines; intermediate hydrophilicity: dark blue lines; high hydrophilicity: dark red lines. Panel (a): parameter sets with a small FG size. Panel (b): parameter sets with adapted medium FG size (medAd). Panel (c): parameter sets with a medium FG size. Panel (d): parameter sets with very large FG size (vlarge).

gates. Small aggregates tend to exhibit disordered spherical structures with FGs exposed to the aqueous medium. Different parameters for the FGs do not seem to have a strong effect on the appearance of those structures. Once the aggregates get larger the chains start to align, the extent of this process and the resulting shape are strongly dependent on the FG parameters. For polymers with FGs of low H and moderate size (FG–FG σ not larger than the CH2–CH2 σ, see caption of table 1) nanocrystals are formed rapidly. A FG that is significantly larger than the methylene groups leads to a reduced alignment of the chains, i.e. the aggregates fray at the FG rich surfaces. Moreover, the tendency of the chains to tilt in the particles seems to increase. A similar behavior has been observed for aggregates of bola-surfactants, in which a tilt allows the surfactants to pack closer to each other [42]. Also with higher hydrophilicity of the FGs, the obtained nanoparticles tend to be more frayed and show a tilt of the chains. With very strong FG-water interactions, aggregates start to stick to each other by solvent separated FG contacts. For a given FG hydrophilicity (i.e. ε of the FG-water interaction) and a given FG size (i.e. σ of the FG–FG interaction) we further notice that the σ value of the FG-water interaction has an effect on the order of the particles (see for example the more ordered particles when using the medAd parameter sets compared to the ones labeled medium.

In the following, the structural analyses are first shown in depth for one simulation, where the system is decomposed at each timestep based on the aggregate size. Subsequently, the different parameter sets are compared based on system wide averages of the structural properties. An example of the performed analyses is displayed for Simulation 19 (table 2) which employs low H and a medium sized FG with a relatively low concentration of long chain fC48 molecules. This system was chosen, because the aggregation process went through a wide range of different aggregate sizes, which existed for longer time periods. Therefore, this system is ideally suited to analyze aggregate properties based on their size. A rough distribution of aggregate sizes during the course of the simulation is displayed in figure 4, along with snapshots of structures of the different aggregate groups at the time they were analyzed. Distributions of end-to-end distances, local (intermolecular) and internal (intra-chain) order parameters are shown in figure 5 for the different aggregate sizes. The two figures clearly show the stretching of the polymer chains once the particles have reached a certain size. The data also show that the stretching that can be seen both in the end-to-end distance and in the internal order parameter is accompanied by an increased alignment of the chains that is visualized through the local nematic order parameter of the particles. Further examples of this detailed analysis of individual simulations are shown in the SI (https://stacks.iop.org/JPCM/33/264001/mmedia).

Regarding the end-to-end distances, the following needs to be considered: a fully extended fC23-molecule is about 29 Å long. The maximum of the end-to-end distance in the small, disordered spherical aggregates depends on the aggregate’s size. The smallest aggregates exhibit values of about 16 Å while the largest ones yield about 23 Å. Larger aggregates usually form nanocrystals with end-to-end distances close to the extended chain length i.e. maxima at 28 Å, often accompanied by a second maximum at about 26 Å.

In the case of fC48, a fully extended chain would be about 60 Å long. The dependence of the position of the maxima in the end-to-end distance distribution for those longer chains depends more strongly on the aggregates size than it does for the short chains. In very small aggregates, the maximum lies at about 20 Å, growing with aggregate size to about 45 Å for disordered aggregates (figure 5(a)). Larger
aggregates show alignment of the chains and thus yield maxima at about 58 Å, sometimes accompanied by a second local maximum at shorter distances of about 56 Å. In these nanocrystals, the amount of back-bent chains also increases and thus, dependent on FG size, yield small local maxima at about 5 to 10 Å, which correspond to chains containing a hair-pin style loop.

An internal order parameter was defined (equation (2)) because end-to-end distance alone is not a good measure of internal chain alignment, except if it assumes values close to the maximum chain-length. This order parameter assumes values of 0.6 to 1 for molecules where the different segments in the chain are well aligned, which includes in addition to stretched chains also ordered back-bent ones. Thus, well-ordered particles yield order parameter distributions close to 1 (figure 5(b)). For disordered aggregates distributions between $-0.05$ and 0.25 are obtained, which correspond to mostly random coils, although there might also be chains with kinks that yield similarly small values. Due to strong correlation of neighboring bonds the alkane chains are not perfectly random coils, which would yield a distribution centered around 0. The remaining obtained values between 0.25 and 0.6 likely stem from molecules with kinks in them, which predominantly occur close to the particles’ rims.

To determine the alignment of different chains the (intermolecular) local nematic order parameter \cite{37–39} is computed (see equation (1)). In this case, the alignment of the vectors is only evaluated if the chain segments do not belong to the same molecule. For all systems, the decline of local order with distance is heavily dependent on the aggregate’s size, i.e. a steeper decline with increasing distance is observed for smaller aggregates (figure 5(c)). As expected, larger nanocrystals show good alignment, with order parameter values of about 0.8 and more at short distances and only a minor decay for longer distances. Smaller aggregates at best show small order parameter values of 0.2 to 0.4 at contact distance and occasionally a recognizable second maximum for the second coordination shell.

Having gained a better understanding of how the end-to-end distances and local and internal order parameters structurally characterize the nanoparticles we now use these properties to compare the different parameter sets and the different telechelic chain lengths. Instead of dissecting the system into differently sized aggregates we here compute averages over the entire system, shown in figure 6.

For the short (fC23) chains the end-to-end distance decreases with increasing FG hydrophilicity (see figure 6(a)), confirming the above observation that increasing FG hydrophilicity stabilizes smaller aggregates with solvated...
Figure 5. Analyses of structural properties of aggregates depending on aggregate size, i.e. number of telechelics in an aggregate (chain count CC) evaluated at every simulation timestep (for the simulation shown in figure 4). Properties are averaged over all aggregates in the specified size range. (a) End-to-end distance (b) internal (intramolecular) order (c) local (intermolecular) order. To enhance visibility, results for different aggregate sizes are displayed by a vertical offset and the area under the curves is colored according to the color bar shown in figure 4.

FGs. Figure 6(b) shows that less hydrophilic FGs usually lead to higher short ranged local order and also to a slower decline with increasing distance, i.e. these simulations exhibit aggregates with a longer-aligned alignment of the chains. The internal order of the molecules, displayed in figure 6(c), agrees very well with the previous observations. In addition, this property also shows, that a system with high local (intermolecular) order and an end-to-end distance distribution with a narrow peak close to the chains’ maximum extension does not solely contain well ordered chains, for example the simulations with small FGs with low H yield some chains that are rather coil like, as can also be seen in the obtained structures (figure 2).

The analyses for the long (fC48) chains (figures 6(d)–(f)) overall showed similar behavior, however some differences have to be mentioned. Most importantly, the long telechelics can form back-bent chains with a hair-pin style loop in addition to extended chains, which can be seen in the end-to-end distance distributions (figure 6(d)) in the form of small peaks at distances close to the FG–FG contact distance (5 to 10 Å). Yet the more dominant species are clearly the extended telechelics. Note also at this point that these aggregation simulations do not necessarily yield fully equilibrated nanoparticle structures since the simulations are carried out at substantial supersaturation. While we do observe stretching and aligning of chains upon aggregate growth and the healing of defects with increasing simulation time, it cannot be ruled out that the ratio of extended chains to hairpin structures does not correspond to an equilibrium ensemble. These back-bent chains lead to another distinct difference in the distribution of the internal order parameter (figure 6(e)): here a significant increase of order parameter values between 0.6 and 0.8 is observed, which correlates with the increased occurrence of small end-to-end distances (figure 6(d)). For the long chains the local (intermolecular) order (figure 6(e)) does not decline as strongly with increasing hydrophilicity as it does with the short telechelics (figure 6(b)). This is due to the fact that they have in general a stronger tendency to form larger nanoparticles with a high degree of alignment of longer chain segments (see figure 2).

In summary, it could be shown, that the hydrophilicity of the FGs and the length of the telechelics are major factors for the formation of nanocrystals, but regarding the order of the crystals also the spatial demand of the FGs is important.

3.2. Particle stability

To further test the influence of FG hydrophilicity and FG size, the stability and the structure of preassembled nanoparticles was investigated. To this end, for the short and the long chain system each, a well defined and ordered nanoparticle that had formed during the previous simulations was selected as starting structure (see captions of tables 2 and 3). From these preassembled nanoparticles we initiated simulations with different parameter sets (see table 3) and monitored again the structural stability, the end-to-end distances of the chains, the internal (intramolecular) and the (intermolecular) local nematic order parameters. Figure 7 shows snapshots of the final structures of these simulations. It was found that a higher hydrophilicity of the FGs leads to a loss in order. For the short chains, very hydrophilic and larger FGs (see figure 7, top panel bottom row) even can lead to disassembly of the particle into smaller frayed aggregates. For the long chain telechelics, no disassembly was observed—even with a combination of high hydrophilicity and very large size of the FGs. The effect of increasing the size of FGs mainly was a reduc-
Figure 6. Analyses of short (fC23, left graphs, (a)–(c)) and long (fC48, right graphs, (d)–(f)) chain telechelics. End-to-end distance and internal (intramolecular) order parameter distributions were averaged over all molecules in the system and over the last 50 ns of the respective simulations. Local (intermolecular) order parameter distributions were computed for the final structure (averaged over the last 1.5 ps) of the simulation. The end-to-end distance distributions are displayed with an offset for different parameter sets. (a) fC23 end-to-end distance distribution (b) fC23 local nematic order (c) fC23 internal order parameter distribution (d) fC48 end-to-end distance distribution (e) fC48 local nematic order (f) fC48 internal order parameter distribution.

tion of the particle order and an increased fraying at the particle rims.

The end-to-end distance behaves similarly for both short (fC23, figure 8(a)) and long telechelics (fC48, figure 8(c)). FGs with lower hydrophilicity overall favor chains that are well stretched out or back-bent into hair-pin conformations. Increasing the FG hydrophilicity results in broadening of the end-to-end distance distributions and in a shift of the maximum of the distribution towards shorter distances.

But the actual loss of order upon breaking up of the nanoparticle can best be seen in the (intermolecular) local nematic order of the fC23 systems. Figure 8(b) shows only very limited short ranged order for the two systems where full particle disassembly was observed (short chains (fC23), high hydrophilicity (highH) and medium or very large (vlarge) FG sizes). As no particle separation was found for the long telechelics (fC48), no such drastic reduction of local order was observed for those (see figure 8(d)). Even with the most extreme tested parameter set (high hydrophilicity and a very large FG (highH-vlarge), gray line figure 8(d) a significant short ranged order and also some mid ranged (10 to 20 Å) order remained. The dependence of the degree of ordering at the particle surface on the model parameters will be used in the next section for a comparison of the (generic)
CG simulations with atomistic simulations and experimental observations.

The disassembly of the short telechelic (fC23) nanocrystals into disordered aggregates shows that the ordered nanoparticle is not stable if the effective size of the head groups is large and the head groups are very well solvated. This could be an explanation why in experiments the short telechelics with carboxylate FGs and caesium counter ions do not form nanoparticles, but instead form a milky dispersion [10].

### 3.3. Comparison to all-atom simulations

In this section, we compare CG simulations made with different parameter sets with data from previously made atomistic simulations of varying chemical systems (exchanging the FGs and the counterions) [12]. A first scan of the results described in the previous section (simulations started from nanoparticles that had been obtained from CG simulations) was carried out to identify promising CG parameter sets that showed a good overall agreement with the atomistic behavior. Those parameter sets (shown in table 4) were then used to initiate CG simulations from a starting structure corresponding to the one of the atomistic simulations (a hexagonal nanocrystal containing 91 perfectly aligned telechelics). For these CG simulations we carried out a structural comparison to the atomistic reference data—with the aim to identify, which CG models, i.e. which FG parameters, best correspond to certain chemical systems. But before we go through this comparison, we illustrate in figure 9 the remarkably good overall structural agreement between atomistic and CG simulations. The upper panels of figure 9 show the endpoints of atomistic simulations of preassembled nanoparticles. One sees that for short chains (C23COOCs) the ordered nanoparticles disassemble in the atomistic simulations. For the long chains, the order at the rims of the particles strongly depends on the chemical nature of the head groups (carboxylate of sulfonate) or the types of counter ions (Na or Cs). The lower panels of figure 9 shows the endpoints of the respective CG simulations with those model parameters that yielded the best overall agreement to the different atomistic systems. In the following we show how these CG models were identified with the help of different structural properties. RDFs between FGs (FG–FG RDFs) and between FGs and water (FG-water/FG-OW RDFs) are suitable to describe the order and the fraying at the FG rich planes of the particles and the hydration of the FGs (figure 10). These data are complemented by the end-to-end distance distributions which capture the stretching of the chains and the order/disorder at the particle rims (figure 11). The upper panels of figures 10(a)–(c) show RDFs of atomistic simulations with carboxylate head groups and caesium and potassium counter ions (COOCs/COOK) compared to the corresponding RDFs from three CG models. The lower panels show atomistic data for carboxylate head groups (COONa, figure 10(d)) and sulfonate head groups (SO3Na, figure 10(e)) with sodium counter ions compared to two different CG parameter sets. For the atomistic systems, the carboxylate carbon atoms and the sulfonate sulfur atoms were used as centers to compute FG–FG RDFs as well as RDFs between FGs and water molecules (for water the water’s oxygen atoms were used as centers), allowing for a direct comparison to the CG data.

Judging from the FG–FG and FG-water RDFs (figure 10(d)), the CG parameter set with an intermediate hydrophilicity and an adapted medium FG size (intermH-medAd) shows a good correspondence to the structures found with carboxylate head groups and sodium counter ions. Also the end-to-end distance (figure 11(b)), shows similar results compared to the atomistic data.

The case of carboxylate head groups with caesium or potassium counter ions is not as clear. For a CG model with very hydrophilic FGs and an intermediate size (highH-medAd) the RDF peak positions are reproduced very well (figure 10(a)), while for CG models with the same degree of hydrophilicity but other FG–FG interactions (figures 10(b) and (c)) the distances of the FGs are not reproduced, i.e. the fraying at the nanoparticle rims is too large compared to the atomistic reference structure. Note though, that for the highH-medAd model (figure 10(a)) the FG–FG RDFs of the CG model are somewhat overstructured which is also visible in the end-to-end distance distributions shown in figure 11(a). It was not possible to identify a parameter set without this slight overstructuring while at the same time obtain a good solvation structure of the FGs. This is possibly due to the approximations made in the CG representation of the headgroups and counter ions in an effective FG bead.

The lower graph of figure 10(a) shows that the atomistic FG-water RDFs are very well reproduced by the CG highH-medAd parameter set. Increasing the σ parameter of the FG-water interaction (highH-medium or highH-vlarge, figures 10(b) and (c)) leads to deviations in the position of the first peak of the FG-water RDFs. For these two models, the alignment of the chains is reduced and because of that, local and internal order and end-to-end distance (figure 11(a)) fit
Figure 8. Analyses of short (fC23, left graphs) and long (fC48, right graphs) chain telechelics, started from preassembled nanoparticles. End-to-end distances distributions were averaged over all chains in the system and over the last 50 ns of the respective simulations. Local (intermolecular) order parameter distributions were computed for the final structure (averaged over the last 1.5 ps) of the simulation. The end-to-end distance distributions are displayed with an offset for different parameter sets. (a) fC23 end-to-end distance distribution (b) fC23 local nematic order (c) fC48 end-to-end distance distribution (d) fC48 local nematic order.

Figure 9. Comparison of atomistic and coarse grained simulation structures. Upper panels: snapshots of different chemical systems (varying chain length, functional group, counter ion type) after 100 ns of atomistic simulations started from an ordered crystal. Reprinted with permission from [12]. Copyright (2019) American Chemical Society. Lower panels: final snapshots from CG simulations with different models representing varying FG hydrophilicity and size (see tables 1 and 4).
the atomistic data more closely. Moreover, it should be noted that the highH-medium CG model caused the disassembly of a nanoparticle of short chain telechelics, which was not observed for the highH-medAd model. Because of this better agreement in the general assembly behavior, the structures obtained with this model were shown alongside the atomistic simulations of short and long chain telechelics with carboxylate head groups and Cs counterions in figure 9.

It should be noted at this point, that our very generic CG models do not contain any directed forces (implemented in the form of three-body potentials) between FGs and water. Such interactions are highly dependent on the geometry and the polarities of the FGs and would have reduced the generic character of the model. This explains why the local water structure around the FGs (FG-OW RDFs) is reproduced only moderately well. The obtained particle structures nonetheless are still quite similar to the ones from atomistic simulations, i.e. one might conclude that the directed nature of the hydrogen bonds is probably not the most important contribution to the particle structure. If one wanted to model specific FGs more accurately, one could improve the respective CG parameter set by switching to multibody potentials for the FG-mW interaction to reproduce the local water structure around the FGs [33, 43].

The parameter set with intermediate hydrophilicity and a medium FG size (intermH-medium) shows a FG-water RDF which is in good agreement with the atomistic simulations of telechelics with sulfonate head groups and sodium counter ions (figure 10(e)), but the FG–FG RDFs first peak occurs at a smaller distance than in the atomistic model. The order of the aggregates is also too high compared to the atomistic data. Increasing the FG–FG σ (parameter set intermH-largeAd, table 1) improved the agreement significantly. This model reproduces the FG–FG RDFs as well as the end-to-end distance (figure 11(c)) and the

![Figure 10](image-url)
Figure 11. End-to-end distance distributions of atomistic and CG simulations (displayed with an offset for different simulations): (a) CG parameter sets highH-medAd (blue), highH-medium (orange), and highH-vlarge (green), atomistic systems with carboxylate head groups with caesium counterions (red) and potassium counterions (purple). (b) CG parameter sets lowH-medAd (blue) and intermH-medAd (orange) and atomistic systems with carboxylate head groups and sodium counterions (green). (c) CG parameter sets intermH-medium (blue) and intermH-largeAd (orange) and atomistic systems with sulfonate head groups and sodium counterions (green).

In summary, we could show that a simple CG model could very well capture the atomistic behavior of the sodium carboxylate and sulfonate systems for all analyzed properties. Here, parameter sets of the CG model could be identified where we are confident that they are very well suited to study the formation and the structure of these telechelic nanocrystals (intramolecular) internal and (intermolecular) local nematic order better.

In this study we have used a CG model to simulate the aggregation of PE telechelics into nanocrystal platelets. The nanoparticles, in particular the ones obtained with CG model parameters that induced a high degree of order, showed a tendency to form hexagonal shapes on their own accord, in good agreement with experimental findings.

By systematic variation of the CG model parameters we could show that important factors which control nanoparticle stability and structure are the PE chain length and the hydrophilicity and the steric demand of the head groups. Particle size distributions, end-to-end distances and internal order of the chains, as well as intermolecular alignment in the particles were used to characterize the aggregation. Increasing hydrophilicity and/or steric demand of the FGs of the PE telechelics slows down the aggregation process and also reduces the alignment in the resulting particles. These trends could be confirmed by a second set of simulations started from preassembled nanoparticles. The correspondence of general system properties such as solvation/partitioning behavior or chain/segment length with the formation and stability of characteristic morphologies is quite reminiscent of amphiphilic block copolymers [44–48]. For such systems it is well known that one can draw up phase diagrams that are—in their general topology—indeed of the specific chemistry of the system. Consequently, one can study structure formation in an increased FG–FG repulsion, which cannot be easily captured by the model. Regarding this limitation, and judging the agreement of both structural data and the propensity to form nanoparticles, a CG model with a high hydrophilicity and a medium size of the FG (highH-medium) appears to be the better approximation for the caesium and potassium carboxylate system (compared to the highH-medAd).

In the atomistic simulations, electrostatic interactions dominate the behavior in the nanoparticle water interphase, with FG–FG repulsion, the attraction between the FGs and the respective counterions, and the dielectric screening by explicit (dipolar) water. In summary, the effective repulsion between the FGs depends on the strength of the coordination of the counterions to the FG-rich plane. This is nicely shown in the atomistic data (figure 9), where the stronger coordination of the sodium ions to the carboxylate plane reduces the repulsion of the carboxylate head groups and leads to a particle that is much more ordered than the one obtained with caesium counterions. We could show that we could emulate that behavior (almost surprisingly) well with effective interactions using different sets of FG sizes and hydrophilicities. A different approach would be a model that uses explicit counterions and an ion–ion repulsion term. One example for such a model that can be incorporated with the mW model was presented by Demille et al [40]. It should be noted though, that an explicit ion representation needs a careful parametrization at different ion concentrations, since multibody effects will lead to transferability problems of the CG model that are very difficult to solve without the use of density/concentration dependent potentials.

4. Conclusions

In this study we have used a CG model to simulate the aggregation of PE telechelics into nanocrystal platelets. The nanoparticles, in particular the ones obtained with CG model parameters that induced a high degree of order, showed a tendency to form hexagonal shapes on their own accord, in good agreement with experimental findings.

By systematic variation of the CG model parameters we could show that important factors which control nanoparticle stability and structure are the PE chain length and the hydrophilicity and the steric demand of the head groups. Particle size distributions, end-to-end distances and internal order of the chains, as well as intermolecular alignment in the particles were used to characterize the aggregation. Increasing hydrophilicity and/or steric demand of the FGs of the PE telechelics slows down the aggregation process and also reduces the alignment in the resulting particles. These trends could be confirmed by a second set of simulations started from preassembled nanoparticles. The correspondence of general system properties such as solvation/partitioning behavior or chain/segment length with the formation and stability of characteristic morphologies is quite reminiscent of amphiphilic block copolymers [44–48]. For such systems it is well known that one can draw up phase diagrams that are—in their general topology—indeed of the specific chemistry of the system. Consequently, one can study structure formation in
such systems very well with rather generic simulation models with tunable model parameters. Subsequently one can then adjust the parameters such that they correspond to a specific system or a reference simulation with a higher resolution model.

By comparison of CG and atomistic simulation data, it could be shown that atomistic simulations representing different chemical systems can be emulated with specific, different CG parameter sets. For telechelics with carboxylate and sulfonate head groups and sodium counterions, parameter sets of the CG model could be identified that closely reproduced all analyzed properties of the atomistic system. For the case of the caesium and potassium counterions, the weak coordinating nature of the caesium and potassium ions is probably the reason for the problems to simultaneously exactly reproduce all reference data. Nevertheless, also here a CG parameter set (with a high hydrophilicity and a medium size of the FG) could be identified that yielded a good representation of the structural properties and the general aggregation behavior of this system. Thus, the results from the (generic) CG simulation models can be used to explain the effect of different head groups and different counterions on the aggregation of PE telechelics and the order of the obtained nanocrystals.

Our simulations predict that decreasing PE chain length, and increasing hydrophilicity or steric demand of the FGs leads to less ordered and presumably also smaller nanoparticles. They also show, that undesired stacking of aggregates can occur once the functional group is too hydrophobic, which prohibits formation of well defined nanocrystals. It is to be noted though, that the number of telechelics in the shown simulations is significantly smaller than the amounts needed to get experimental sized nanocrystals (scaled by a factor of about 0.1, as a hexagonal nanocrystal of 20 nm is composed out of approximately 1000 telechelics). This means our simulations can only capture part of the experimental behavior, and simulations at realistic telechelic concentrations and of systems that allow to understand for example nanoparticle size control are still to be conducted. The CG models identified here, that correspond well to specific atomistic/experimental systems, will be used in the future to tackle exactly these open questions. The speed up of the CG model compared to atomistic simulations will allow to increase the size of the system, thus increasing the number of chains or lowering the concentration in future studies.

Acknowledgment

The authors are grateful to Christina Rank for discussions regarding the atomistic simulations and experimental findings, and Michael King and Christoph Gobisch for assistance in technical matters and highly valuable discussions. We also thank Kevin Sawade for carefully reading the manuscript. Financial support by the DFG (SFB1214) is gratefully acknowledged. The authors acknowledge support by the state of Baden-Württemberg through bwHPC.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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