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3D Cellular Automata of Polymer Structural Response to Solvent Quality

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Received: 10 June 2026 | **Revised:** 3 September 2026 | **Accepted:** 8 September 2026

Keywords: cellular automata | coil-globule transition | lattice polymer model | polymer collapse | reproducible simulation | solvent quality

ABSTRACT

A three-dimensional cellular automaton (3DCA) model is presented for describing the structural response of polymer systems to solvent quality. Polymer segments occupy a cubic lattice and evolve through local solvent-polymer exchange moves with fixed chain connectivity, excluded volume, bond-crossing rejection, nearest-neighbor interactions, and Metropolis-type acceptance. Solvent quality is controlled by the solvent-polymer interaction energy, while polymer-polymer cohesion is described by a separate contact energy. The model reproduces distinct poor-, θ -, and good-solvent regimes, including chain collapse, intermediate coil conformations, swelling, and aggregation. Radius-of-gyration scaling identifies the θ condition through a Flory exponent close to 0.50 and provides a basis for relating the lattice interaction energies to the Flory-Huggins parameter. Multichain simulations further show that chain topology strongly affects structural evolution: finite chains undergo pronounced restructuring associated with free chain ends, whereas periodically self-connected chains preserve fibrillar and system-spanning morphologies more effectively. The model therefore provides a minimal and transparent framework for linking local interaction rules to solvent-dependent mesoscale polymer structure, supported by an openly available simulation-to-figure workflow.

1 | Introduction

Cellular automata (CA) have long been used as a discrete alternative to molecular dynamics for modeling polymer systems, allowing polymer dynamics to be represented through local lattice update rules. Early studies demonstrated that essential polymer statistics, including correct scaling of the radius of gyration and diffusion behavior, can emerge from purely local lattice update rules without explicitly solving equations of motion [1]. Subsequent developments established CA as a scalable framework for flexible polymers by preserving chain connectivity under parallel updates and enabling simulations of gels, external fields, and transport phenomena such as reptation and electrophoresis [2, 3]. More physically detailed lattice formulations further incor-

porated excluded volume, effective long-range interactions, and emergent elasticity while maintaining computational simplicity [4–6].

A closely related lattice approach is the Bond Fluctuation Model (BFM) introduced by Carmesin and Kremer [7]. In the classical BFM, polymer monomers occupy excluded-volume lattice cells and undergo local Monte Carlo displacements subject to a restricted set of allowed bond vectors. This combination provides conformational flexibility while preventing monomer overlap and, in the standard formulation, bond crossing. The BFM has subsequently been adapted to highly parallel implementations, including GPU algorithms for large polymer systems [8]. A body-centered-cubic variant of the BFM was also developed

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specifically to improve parallel scalability in three dimensions [9]. The present work does not claim a computational-speed advantage over these optimized BFM implementations. Explicit solvent is not itself unique to the present approach, because explicit-solvent BFM simulations have previously been used to study single-chain behavior and identify the theta condition [10]. The distinctive feature of the present implementation is the combination of a minimal one-cell-per-segment representation, local solvent-polymer swaps, direct control through E_{sp} , CA-oriented local rules, and systematic comparison across solvent qualities. In contrast, the present 3DCA model represents each polymer segment by a single lattice cell and uses local solvent-polymer swaps rather than direct monomer displacements into vacant lattice positions. Bond connectivity is imposed through a fixed bond list with a maximum bonded distance, while solvent quality is represented explicitly through solvent-polymer contact energies. Thus, although both approaches are lattice-based Monte Carlo descriptions with fluctuating polymer conformations and excluded volume, the present model differs from the classical BFM in its move rule, bond representation, explicit solvent cells, and focus on solvent-dependent structural response. The scaling exponents obtained here are compared with the standard asymptotic polymer-scaling values rather than with a new BFM calculation. Likewise, the collapse and aggregation pathways reported below should be interpreted as pathways generated by the present local swap rule and are not assumed to be quantitatively equivalent to BFM kinetics. Recent explicit-solvent lattice Monte Carlo work has likewise examined polymer collapse over varying solvent quality, providing a particularly relevant precedent for the present solvent-response comparison [11].

Another important class of lattice-based polymer methods is numerical self-consistent-field (SCF) theory of the Scheutjens-Fleer type. SCF methods use a deterministic mean-field iteration to calculate ensemble-averaged polymer density profiles and have been applied extensively to brushes, adsorbed layers, and related inhomogeneous polymer assemblies [12]. Such methods are generally more efficient and more rigorously established for equilibrium mean-field structure and scaling calculations. In contrast, the present stochastic lattice model resolves individual polymer configurations, conformational fluctuations, and Monte Carlo pathways associated with fixed chain connectivity and the presence or absence of free chain ends. Its contribution should therefore be understood in terms of configuration-resolved structural evolution rather than superior efficiency for ensemble-averaged equilibrium calculations.

Reusable open-source implementations of lattice polymer models are also available. LeMonADE provides an open-source C++ implementation of the BFM [13], while PIMMS provides reusable high-performance lattice Monte Carlo tools for multi-component and heteropolymer systems [14]. Open publication of three-dimensional lattice simulation code has also accompanied peer-reviewed polymer studies [15, 16]. A recent lattice/BFM application to amphiphilic polymer networks in selective solvent further illustrates continuing activity in solvent-dependent lattice modeling [17]. These precedents provide general or specialized lattice-simulation capabilities; the present work instead emphasizes a minimal CA-oriented representation for controlled solvent-response experiments and an end-to-end reproducible simulation-to-figure workflow.

With the extension of CA models to three dimensions, their scope expanded beyond equilibrium chain statistics toward conformational transitions, folding, and collapse phenomena. Several studies demonstrated that polymer densification, self-organization, and kinetic scaling can be reproduced using probabilistic local permutations governed by interaction energies, providing a discrete alternative to molecular dynamics [18]. Related approaches applied CA to amphiphilic self-assembly, polymer crystallization, and biomimetic morphogenesis, showing that complex structures can arise from local interaction rules coupled to thermodynamic or transport constraints [19–23]. Reviews of this period emphasize the flexibility of CA models and their ability to bridge microscopic mechanisms and mesoscale structure formation [22].

A major application domain of cellular automata has been the modeling of degradation, erosion, and mass transport in polymer systems, particularly in pharmaceutical and bioengineering contexts. CA-based models successfully described diffusion–erosion transitions, swelling-controlled release, and autocatalytic degradation using local probabilistic rules, often achieving quantitative agreement with experiments while avoiding the solution of coupled differential equations [24–28]. These studies established CA as a powerful tool for describing coupled transport and structural evolution in multiphase polymer media.

More recently, CA methods have evolved toward hybrid and multiphysics implementations aimed at engineering applications. Cellular automata have been combined with finite-element methods for structural optimization, applied to damage and deformation of polymer composites, and extended to chemically and optically driven degradation processes [29–32]. In parallel, CA-based models have been developed for nanoscale self-assembly of block copolymers, where local interaction energies govern the formation of ordered morphologies during annealing [33].

At a conceptual level, cellular automata have also been generalized toward chemical reactivity and topological dynamics. Chemical Cellular Automata introduced explicit valence and bond-stability rules to describe bond formation and molecular stability using discrete local updates [34]. Related stochastic and reactive coarse-grained models, both on- and off-lattice, further blurred the boundary between CA and Monte Carlo approaches, enabling the study of polymerization, branching, and complex topologies within unified discrete frameworks [35].

Within CA-based polymer modeling, systematic comparisons of the same polymer representation across poor-, theta-like-, and good-solvent conditions using a single tunable solvent-polymer interaction parameter remain comparatively limited. In addition, end-to-end reproducible implementations linking simulation, quantitative analysis, and the published figures are still uncommon in this specific class of models.

The present work makes three contributions. First, a minimal three-dimensional CA implementation systematically reproduces poor-, theta-like-, and good-solvent structural responses. Second, these regimes are evaluated quantitatively through the radius of gyration R_g , the Flory exponent ν , the interchain-contact concentration c_{inter} , the transverse bundle radius R_{perp} , the axial order parameter S_z , the interchain radial distribution $RDF(r)$, and the largest connected-component fraction f_{LCC} .

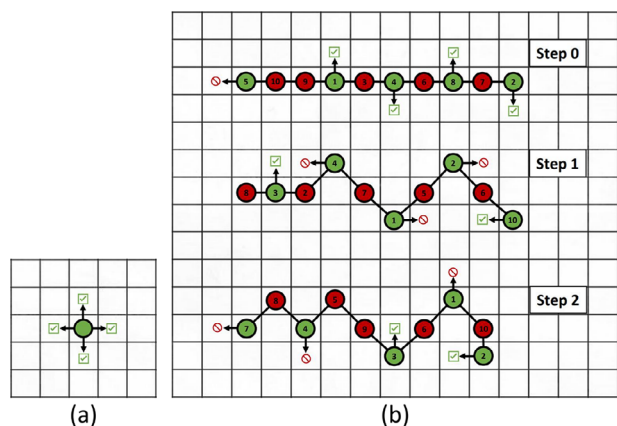


FIGURE 1 | Schematic illustration of the local Monte Carlo update of a polymer chain in a 2D projection of the lattice model. Empty lattice sites correspond to solvent cells (s-cells). Circles denote polymer cells (p-cells), and black lines denote chain bonds. (a) A selected p-cell can attempt a trial move only to one von Neumann neighboring cell: left, right, up, or down in the 2D projection. In the full 3D lattice, this corresponds to six directions: $\pm X$, $\pm Y$, and $\pm Z$. (b) Randomized order of trial moves within one Monte Carlo step. The numbers inside the p-cells indicate the randomly assigned order in which p-cells are checked. Green p-cells indicate cells whose trial move can be considered because their directly bonded neighboring p-cells have not moved earlier in the current step. Red p-cells indicate cells whose move is forbidden because one neighboring p-cell in the chain has already moved. Arrows show randomly selected local displacement directions. A green check mark means that the move satisfies the bond-length constraint and is then tested by the Metropolis criterion. For simplicity, all geometrically allowed moves in this scheme are accepted, that is, $P_{\text{acc}} = 1$. A red forbidden sign denotes a move rejected due to violation of the bond-length constraint (hard-wall-like potential), for example excessive bond stretching. Steps 1 and 2 show successive stages of chain updating. The assumption $P_{\text{acc}} = 1$ is used only for schematic illustration in Figure 1; all simulations reported in the Results use the Metropolis-type acceptance rule defined in Section 2. Geometrically admissible moves are additionally subjected to the bond-crossing test described in Section 2 before the Metropolis acceptance test.

Third, application of the same model to multichain systems reveals a strong influence of free chain ends and periodic self-connection on aggregation pathways and persistent morphology. The model contains no explicit interchain crosslinks and is therefore not intended to reproduce the gelation transition itself.

2 | Methodology

The model is a three-dimensional cellular-automaton lattice model evolved using local kinetic Monte Carlo solvent-polymer exchange rules with Metropolis-type acceptance.

2.1 | Lattice Model

We used a three-dimensional cubic lattice to model polymer systems. Local interactions and trial moves were defined using the von Neumann neighborhood (Figure 1a). Each lattice cell interacted only with its six face-sharing neighbors along the $\pm X$,

$\pm Y$, and $\pm Z$ directions. Diagonal neighbors were not considered. Periodic boundary conditions were applied in all directions.

2.2 | Polymer and Solvent Cells

Solvent cells (s-cells) were represented by the integer value 0. Polymer cells (p-cells) were assigned unique consecutive positive integer identifiers beginning with 1. These identifiers were used only to track individual polymer segments and define chain connectivity; their numerical values had no physical meaning. Every lattice site not occupied by a p-cell was an s-cell. All s-cells were equivalent and carried no additional local solvent-composition or concentration variable. Thus, the solvent was represented explicitly as lattice cells, while solvent quality was controlled by the contact energy E_{sp} rather than by a spatially varying solvent-concentration field. Unlike concentration-resolved Vanag-type lattice diffusion models [36], the present model does not propagate a separate solvent-concentration field.

2.3 | Bonded Interactions and Chain Connectivity

Bonded connectivity within each polymer chain was defined by a fixed bond list connecting consecutive p-cell identifiers; for example, the beginning of a chain was stored as the pairs (1, 2), (2, 3), and so on. For a chain closed through periodic self-connection, an additional bond connected its last segment to its first segment. The bond list and chain connectivity did not change during the simulation. The term “bonded” is used here solely to indicate chain connectivity that was not allowed to break during the simulation [2]. Bonded distances were constrained by the lattice geometry: neighboring bonded p-cells were allowed to remain within $r \leq \sqrt{3}$, the diagonal of the unit cube. Trial configurations exceeding this limit were penalized by a large bonded energy contribution, producing an effective hard-wall-like constraint [37]. This constraint suppresses unphysical chain stretching while preserving local conformational mobility.

Polymer cells can move only through local p-cell–s-cell swaps; p-cell–p-cell swaps are not allowed. Therefore, two polymer cells cannot occupy the same lattice site, and excluded volume is preserved at the level of polymer cells. The released implementation additionally applies an explicit geometric bond-crossing constraint. For every proposed p-cell move, the maximum bond-length condition $r \leq \sqrt{3}$ is evaluated first. Only geometrically admissible trial bonds are then tested for crossing. Under this bond-length restriction and minimum-image periodic boundary conditions, every bond vector has components -1 , 0 , or 1 , and two non-incident lattice bonds can intersect only at a common geometric midpoint. The algorithm therefore stores twice the midpoint coordinates of all bonds, which avoids floating-point half-integer coordinates, and compares the midpoint of each trial bond with the indexed midpoints of the existing non-incident bonds. A trial move that would create a coincident midpoint, and hence a bond crossing, is rejected before the Metropolis acceptance test. The crossing constraint is enabled by default; disabling it is retained only for explicit reproduction of trajectories generated with the legacy move rule. All production simulations reported in this work used bond-crossing rejection.

Nearest-neighbor contact interactions. Contact interactions were evaluated only between face-sharing nearest-neighbor lattice cells. A constant energy E_{pp} was assigned to every spatial p-cell-p-cell contact, including a bonded pair when its two segments occupied face-sharing lattice sites, and a constant energy E_{sp} was assigned to every p-cell-s-cell contact. Interactions between two s-cells were ignored. The bond-length constraint was evaluated separately from these spatial contact energies. For each trajectory, E_{sp} was held constant throughout the simulation; different solvent qualities were investigated in separate simulations. No change of E_{sp} or solvent-quality quench was applied within an individual trajectory. In the local energy calculation used for the Metropolis criterion, the contact energies were summed over the local neighborhoods of the two cells involved in a proposed swap, as described below.

2.4 | Trial Move

The system dynamics was implemented through local kinetic lattice Monte Carlo solvent-polymer swaps [11, 38]. At each Monte Carlo step, all p-cells were processed once in a random order (Figure 1b). For each p-cell, a local trial move was constructed by examining its six von Neumann neighbors and selecting s-cells. If no neighboring s-cell was available, the p-cell was skipped to avoid violating the excluded-volume constraint for p-cells [2]. Otherwise, one s-cell-neighbor was chosen at random as a trial target, and a swap between the p-cell and s-cell was proposed.

2.5 | Metropolis Acceptance

The bonded and non-bonded terms introduced above were combined in the local energy used for the Metropolis acceptance step. The proposed p-cell/s-cell swap was accepted or rejected according to the Metropolis criterion [38]. The acceptance probability was written as

$$P_{\text{acc}} = \min [1, e^{-(\beta \cdot \Delta E)}]$$

where β is the inverse temperature defined as $\beta = 1/(k_B T)$, with k_B the Boltzmann constant and T the temperature of the system. In the present simulations, β was set to 1, corresponding to reduced units with $k_B T = 1$. This Metropolis-type acceptance rule favors energetically favorable moves, whereas energetically unfavorable moves are accepted with a Boltzmann probability depending on ΔE .

For each proposed swap, the local energy was evaluated before and after the trial move, and the local energy difference was defined as

$$\Delta E = E_{\text{after}} - E_{\text{before}}$$

where E_{before} and E_{after} are the local energies before and after the proposed swap, respectively. Here, E denotes the local energy used in the Metropolis criterion. It was written as

$$E = E_{\text{nonbonded}}^p(i) + E_{\text{nonbonded}}^s(j) + E_{\text{bond}}^p(i)$$

where i is the selected p-cell and j is the selected s-cell. The first two terms describe nearest-neighbor non-bonded interactions around the two cells involved in the swap, while E_{bond}^p is the bonded connectivity term for the moved p-cell.

The non-bonded terms were evaluated as sums over the local von Neumann neighborhoods excluding the swap partner:

$$E_{\text{nonbonded}}^p(i) = \sum_{k \in N_j(i)} \epsilon_{p,t_k}$$

$$E_{\text{nonbonded}}^s(j) = \sum_{k \in N_i(j)} \epsilon_{s,t_k}$$

here, $N(i)$ is the full 6-neighbor von Neumann neighborhood of cell i , while $N_j(i) = N(i) \setminus \{j\}$ denotes the same neighborhood after excluding the swap partner j . Analogously, $N_i(j) = N(j) \setminus \{i\}$. Thus, although each lattice cell has 6 nearest neighbors in the full cubic lattice, only 5 neighbors were used for each of the 2 cells involved in the swap. The direct contact between the two swap partners was excluded because it remains a p-cell-s-cell contact before and after the exchange and therefore cancels in ΔE .

The symbol t_k denotes the type of neighboring cell k , either p-cell or s-cell. The contact energies were defined as $\epsilon_{p,p} = E_{pp}$, $\epsilon_{p,s} = \epsilon_{s,p} = E_{sp}$, and $\epsilon_{s,s} = 0$. Therefore, $E_{\text{nonbonded}}^p(i)$ contains the sum of all p-cell-p-cell and p-cell-s-cell contacts around the moved p-cell, whereas $E_{\text{nonbonded}}^s(j)$ contains only s-cell-p-cell contacts around the selected s-cell because s-cell-s-cell contacts were ignored.

The bonded constraint term was evaluated separately from the spatial nearest-neighbor contact interactions. It was computed only over the bonded chain neighbors of the moved p-cell, as defined by the fixed bond list, rather than over all von Neumann neighbors. We denote this bonded-neighbor set as $B(i)$. For a terminal p-cell of a finite chain, $B(i)$ contains one bonded neighbor; for an internal p-cell and for every p-cell in a periodically closed chain, it contains two bonded neighbors. A bonded pair may therefore contribute a spatial E_{pp} contact when its segments are face-sharing, while the separate bonded term enforces the maximum permitted separation and prevents bond breaking.

$$E_{\text{bond}}^p(i) = \sum_{k \in B(i)} U_{\text{bond}}(r_{ik})$$

with

$$U_{\text{bond}}(r_{ik}) = \begin{cases} 0, & r_{ik} \leq \sqrt{3} \\ 10^6, & r_{ik} > \sqrt{3} \end{cases}$$

where r_{ij} is the minimum-image lattice distance between the trial position of p-cell i and its bonded chain neighbor j . Allowed bonded distances contributed no bonded penalty, whereas forbidden bond stretching introduced a penalty of 10^6 in the same reduced energy units used for E_{pp} and E_{sp} , with $\beta = 1$. This practically infinite penalty implements an effective hard-wall-like constraint, although it is formally represented by a finite energy value. The trial coordinate was passed directly to the bonded-energy calculation without modifying the stored coordinate array. The stored lattice and coordinate array were updated only after a trial move had been accepted.

Update order. To reduce excessive chain distortions within a single Monte Carlo step, two directly bonded p-cells were not allowed to complete accepted moves during the same step. Successfully moved p-cells were recorded in a set, and a p-cell was skipped if one of its direct bonded neighbors was already present in that set. A rejected trial did not add the p-cell to the set; consequently, its bonded neighbor remained eligible for a later trial in the same step. When a move was accepted, the p-cell and selected s-cell values were exchanged in the lattice and the p-cell coordinate array was updated. After the randomized list of p-cells had been processed, the step counter was increased.

Because the eligibility of a trial move within a sweep depends on whether a bonded neighboring p-cell has already moved, strict detailed balance of the complete sweep-level update is not assumed here. The algorithm is therefore interpreted as a kinetic lattice Monte Carlo scheme with Metropolis-type local acceptance rather than as a rigorous equilibrium Monte Carlo sampler. The restriction is introduced to limit excessive local chain distortion during an update sweep.

Trajectory output and reproducibility. At a user-defined interval, a full copy of the lattice was saved, with s-cells encoded as 0 and p-cells represented by their positive segment identifiers. The resulting snapshots and their Monte Carlo step numbers constitute the trajectory used for subsequent analysis and visualization. Two separately controllable seeds were provided for reproducibility. The initialization seed (*init_seed*) determines the stochastic construction of randomly positioned multi-chain initial configurations; deterministic initial structures do not depend on this seed. The dynamics seed (*dynamics_seed*) initializes the pseudo-random generators that determine the randomized p-cell update order, trial-target selection, and Metropolis acceptance decisions throughout the complete trajectory. The trajectory metadata also records whether bond-crossing rejection was active, the number of geometrically admissible trial moves checked, the number rejected because of crossing, and the corresponding rejection fraction. The archived research record also contains the scripts used for simulation, analysis, and visualization, together with the software dependencies and figure-specific reproduction instructions.

3 | Results

3.1 | Polymer Response to Solvent Quality

Separate simulations at fixed E_{sp} define the poor-, θ -, and good-solvent conditions used as a common reference for the single-chain and multi-chain results discussed below.

3.2 | Single Linear Chain: Reference Case

Figure 2 illustrates the time evolution of a single linear polymer chain with length $L = 100$ cells under different solvent conditions. The initial configuration (Figure 2a) is an extended, straight chain spanning the simulation box. Single-chain simulations used a $50 \times 50 \times L$ lattice containing L polymer cells, corresponding to a polymer volume fraction $\varphi = 0.0004$ for all investigated chain lengths. This initial state is identical for all three independently

simulated solvent regimes (poor solvent, θ regime, and good solvent), allowing direct comparison of the subsequent structural response at fixed E_{sp} (Figure 2b–d).

In poor-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -0.3$; Figure 2b), the chain undergoes rapid collapse and evolves from an initially linear conformation into a compact globular structure. The collapse pathway is illustrated step by step in Figure 3, which shows that the process does not occur uniformly along the chain. Instead, the chain first begins to compact at its free ends, where small dense terminal clusters are formed. These compact end regions then progressively grow and approach each other, while the remaining central part of the chain continues to contract. This end-initiated collapse pathway is consistent with earlier cellular automaton simulations by Ostrovsky et al. [18], who showed that polymer collapse can be dominated by migration of the chain ends along the contour, with terminal aggregates accreting monomers and smaller clusters until they meet in the middle. This observation describes the kinetic pathway generated by the present local Monte Carlo move set and should not be interpreted as a direct prediction of physical polymer dynamics. A Monte Carlo step has no established mapping to physical time, and different move sets or the inclusion of hydrodynamic interactions may produce different collapse pathways. In particular, terminal p-cells have only one bonded neighbor, whereas internal p-cells have two, which may increase the mobility of chain ends and contribute to the observed end-initiated restructuring. Off-lattice dynamical studies have also reported distributed pearl-necklace-type collapse pathways and sensitivity of collapse kinetics to hydrodynamic interactions [39, 40]. As the simulation proceeds, the entire chain densifies and ultimately merges into a single compact globule. After 1 million Monte Carlo steps, the polymer forms a dense aggregate with strongly reduced spatial extension, as seen in Figure 2b. The final conformation is stable and exhibits only minimal large-scale fluctuations, indicating the dominance of attractive polymer-polymer interactions over solvent-polymer interactions.

At the θ condition ($E_{pp} = -2.0$, $E_{sp} = -0.75$; Figure 2c), the behavior is qualitatively different. The chain relaxes from the initial stretched configuration into a more disordered and partially compact structure, but does not collapse into a dense globule. The resulting conformation remains relatively open, with visible internal voids and moderate segment mobility. This intermediate morphology reflects a balance between polymer-polymer and solvent-polymer interactions.

In good-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -1.0$; Figure 2d), solvent-polymer interactions dominate. The chain does not collapse but instead adopts an expanded, irregular conformation. Although the initial straight geometry is lost, the final structure remains spatially extended and lacks the dense core characteristic of the poor-solvent case. The polymer explores the available volume more freely, consistent with swelling behavior expected in favorable solvent environments [6].

The three solvent regimes therefore lead to clearly distinct conformational states of the same initial chain. Poor-solvent conditions promote the formation of a compact globule, the θ -regime yields a moderately disordered coil, and good-solvent conditions result in a more extended structure. This

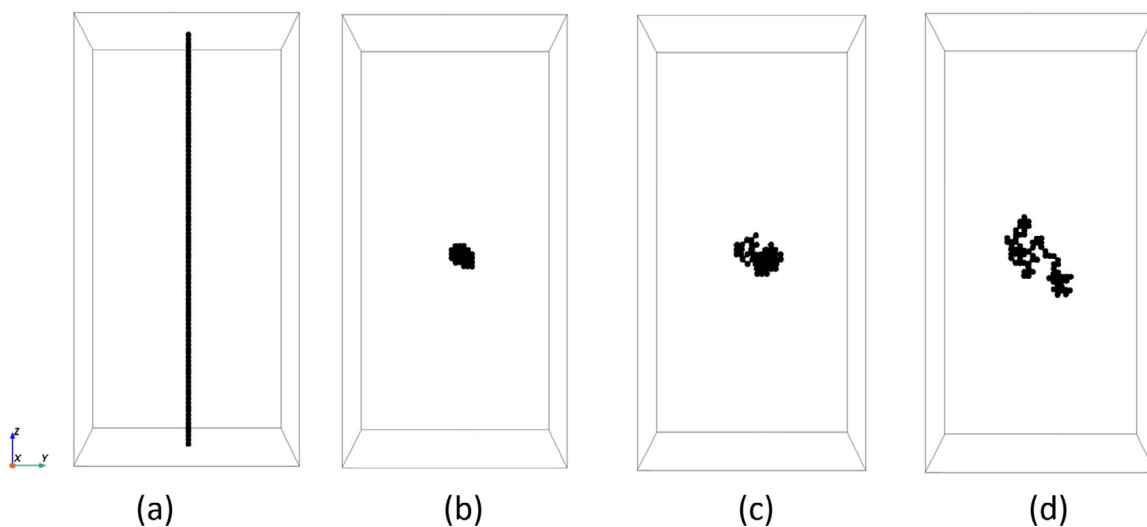


FIGURE 2 | Conformational evolution of a single linear polymer chain with length $L = 100$ cells. (a) Initial configuration. Final configurations after 1 million Monte Carlo steps: (b) poor solvent ($E_{pp} = -2.0$, $E_{sp} = -0.3$), (c) θ solvent ($E_{pp} = -2.0$, $E_{sp} = -0.75$), and (d) good solvent ($E_{pp} = -2.0$, $E_{sp} = -1.0$).

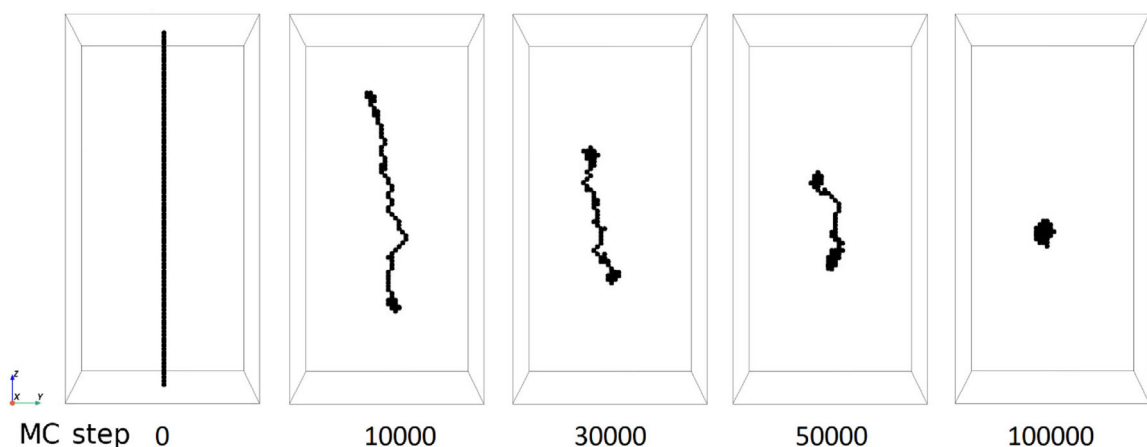


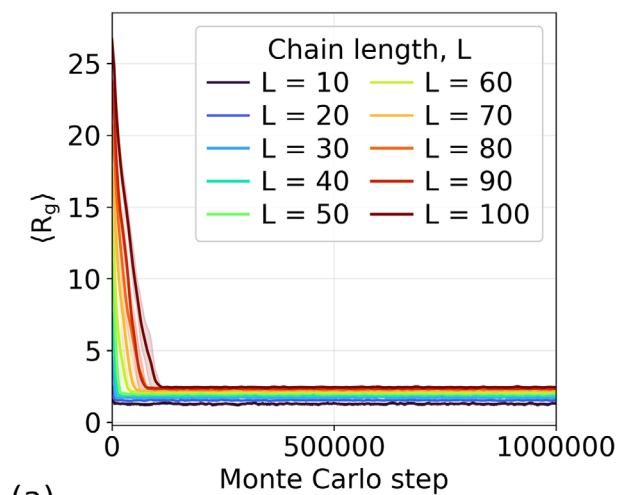
FIGURE 3 | Time-resolved collapse of a single linear polymer chain ($L = 100$ cells) under poor-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -0.3$). The initially extended chain progressively contracts during the simulation. Within the present local Monte Carlo trajectory, collapse starts from local compaction at the chain ends, followed by growth and coalescence of the terminal compact regions into a single dense globule. Snapshots are shown at 0, 10000, 30000, 50000, and 100000 Monte Carlo steps.

qualitative evolution provides the basis for the quantitative analysis of chain statistics discussed in the following subsection.

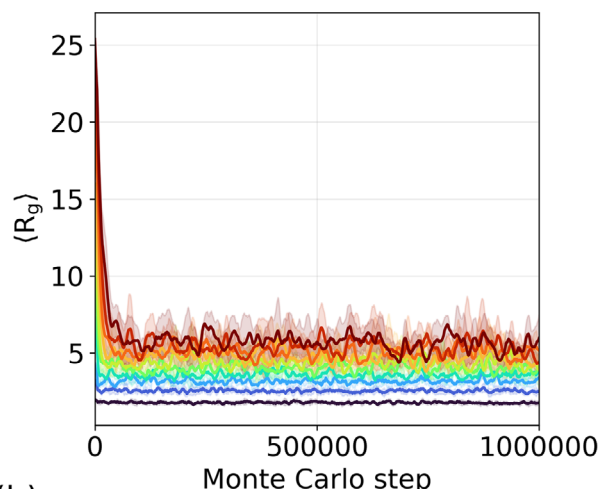
Figure 4 shows the time evolution of the radius of gyration $R_g(t)$ for polymer chains of different lengths under poor, θ , and good-solvent conditions. In all cases, the initially stretched chains relax toward stationary Monte Carlo regimes determined by the chosen interaction parameters E_{pp} and E_{sp} . In the poor-solvent regime (Figure 4a), R_g decreases sharply and quickly reaches a low, nearly constant value, indicating collapse into compact globules [11]. In the θ regime (Figure 4b), R_g fluctuates around intermediate values, reflecting a stationary balance between compaction and expansion. In good-solvent conditions (Figure 4c), the chains retain significantly larger R_g values and exhibit stronger fluctuations, consistent with expanded coil-like

conformations [6]. For all solvent qualities, longer chains display larger stationary R_g values, as expected.

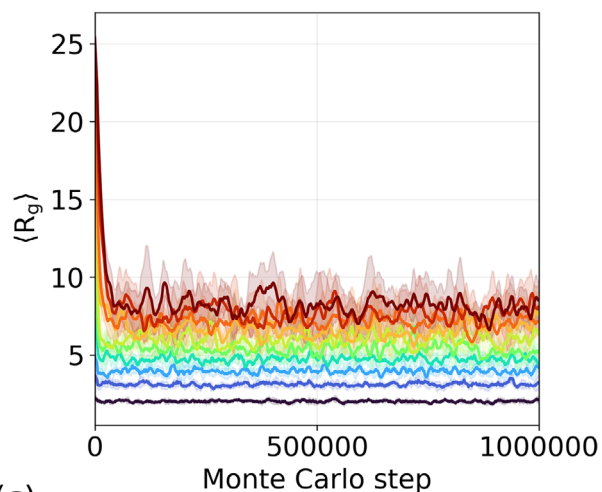
The conformational scaling of polymer chains was analyzed by plotting the average radius of gyration after relaxation as a function of chain length in logarithmic coordinates (Figure 5), following the relation $\log\langle R_g \rangle = \nu \cdot \log L + \text{const}$ [1–3, 6, 18]. The slope of this dependence yields the Flory exponent ν , which characterizes the post-relaxation chain statistics resulting from the balance between polymer-polymer and solvent-polymer interactions. In polymer theory, $\nu = 0.5$ corresponds to the θ condition, where the chain behaves as an ideal random coil, while $\nu \approx 0.588$ represents the universal value for polymers in a good solvent under three-dimensional conditions. Smaller exponents, down to the limiting case $\nu = 1/3$, correspond to poor-solvent environments and signify a collapsed, globular polymer



(a)

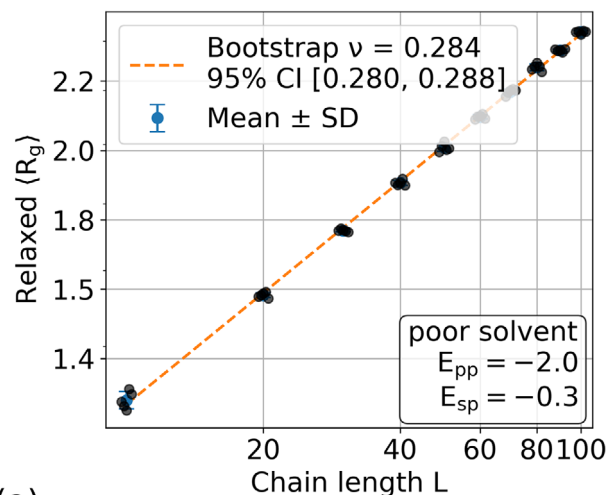


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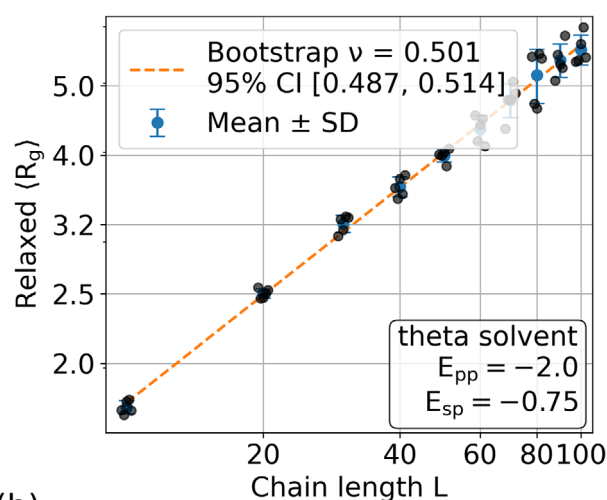


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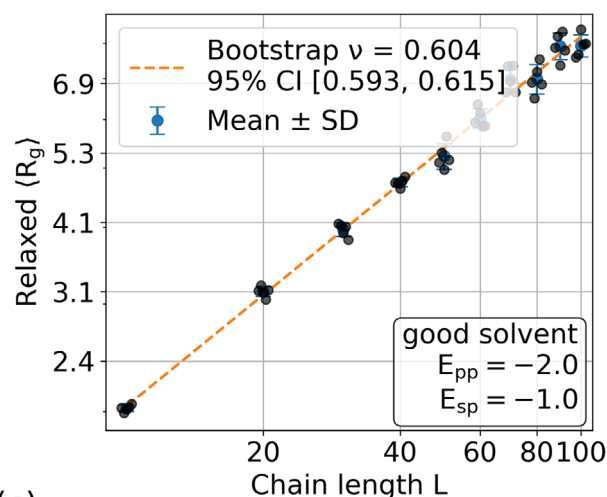
FIGURE 4 | Time evolution of the radius of gyration $R_g(t)$ for polymer chains of different lengths L under three solvent-polymer interaction energies E_{sp} . The curves show values averaged over five independent simulations, and the shaded regions indicate the standard deviation around the mean. Panel (a) shows the poor-solvent environment ($E_{sp} = -0.3$), panel (b) shows the θ solvent ($E_{sp} = -0.75$), and panel (c) shows the good-solvent environment ($E_{sp} = -1.0$). The polymer-polymer interaction energy was fixed at $E_{pp} = -2.0$.



(a)



(b)



(c)

FIGURE 5 | Bootstrap analysis of the scaling of the relaxed radius of gyration $\langle R_g \rangle$ on chain length L . For each chain length, black points show the post-relaxation mean from each of five independent simulations, calculated over the last 20% of saved frames. Blue points and error bars show the mean $\pm$ standard deviation across the five independent simulations. Dashed lines show the power-law scaling based on the bootstrap-mean Flory exponent; the corresponding 95% confidence interval is reported in each panel. Bootstrap resampling was performed

state [18, 41]. The universal good-solvent exponent $\nu \approx 0.588$ originates from the renormalization-group theory applied to the self-avoiding walk (SAW) model of polymer statistics in three dimensions [42]. In our simulations, the extracted ν values provide a quantitative benchmark for assessing whether the post-relaxation chain statistics are approximately consistent with the expected finite-chain scaling regimes.

To quantify the uncertainty of the Flory exponent without treating correlated trajectory frames as independent observations, the bootstrap resampling unit was one independent simulation. For every solvent condition and chain length, the unsmoothed radius of gyration was recalculated from the saved lattice snapshots using the stored polymer-segment identifiers and minimum-image chain unwrapping. One post-relaxation mean R_g was then obtained from the last 20% of each of five independent trajectories. Within every chain length, these five replicate-level means were resampled with replacement, and $\log\langle R_g \rangle = \nu \cdot \log L + \text{const}$ was refitted for each of 10000 bootstrap samples (bootstrap seed 20260827). The 2.5th and 97.5th percentiles of the resulting ν distribution define the reported 95% bootstrap confidence interval. These intervals quantify uncertainty arising from replicate-to-replicate variability under the present finite-chain sampling and fitting protocol; they do not account for potential systematic deviations associated with finite-chain or finite-size effects, lattice discretization, or model form. Repeating the complete analysis using the last 30% of each trajectory served as a sensitivity test for the post-relaxation averaging window.

The replicate-level bootstrap estimates quantitatively support the three assigned solvent regimes (Figure 5). In poor solvent, $\nu = 0.284$ with a 95% confidence interval of [0.280, 0.288]. This interval does not include the asymptotic collapsed-globule value 1/3, indicating that replicate-to-replicate variability alone does not account for the observed offset within the present finite-chain analysis. The deviation is consistent with finite-chain, finite-size, and lattice-discretization effects over the range $L = 10\text{--}100$. In good solvent, $\nu = 0.604$ with a 95% confidence interval of [0.593, 0.615]; the asymptotic three-dimensional self-avoiding-walk value $\nu \approx 0.588$ lies just below this replicate-level bootstrap interval. Because this interval quantifies replicate-to-replicate statistical variability but does not account for potential systematic deviations associated with finite chain length, finite size, lattice discretization, or model form, the small offset from the asymptotic value is not interpreted as evidence against the expected good-solvent scaling regime. We therefore interpret the calculated exponents as finite-chain estimates consistent with the expected solvent-dependent scaling regimes rather than as exact determinations of their asymptotic limits.

For the θ condition, the bootstrap estimate was $\nu = 0.501$ with a 95% confidence interval of [0.487, 0.514], which includes the

ideal-chain value $\nu = 0.5$. We therefore identify $E_{pp} = -2.0$ and $E_{sp} = -0.75$ as the operational θ state of the model. The results were insensitive to the post-relaxation averaging window: using the last 30% instead of the last 20% gave $\nu = 0.282$ for poor solvent, 0.498 for the θ condition, and 0.604 for good solvent, with confidence intervals strongly overlapping those of the primary analysis.

To relate the observed $\nu \approx 0.50$ to the thermodynamic Flory-Huggins parameter χ , we use the standard lattice exchange-energy formulation [43]. In the Flory-Huggins model, the mixing free energy contains an entropic contribution and an enthalpic contact term $\chi \cdot \phi \cdot (1 - \phi)$, where ϕ is the polymer volume fraction, $1 - \phi$ is the solvent volume fraction, and χ quantifies the energetic preference of solvent-polymer contacts relative to polymer-polymer and solvent-solvent contacts. The present Flory-Huggins mapping should therefore be interpreted in the dilute single-chain limit represented by $\phi = 0.0004$. Thus, larger χ values correspond to less favorable solvent-polymer mixing and poorer solvent conditions. In Flory-Huggins theory, χ is derived from the exchange energy $\Delta w = w_{12} - 0.5 \cdot (w_{11} + w_{22})$ via $\chi = z \cdot \Delta w / (k_B \cdot T)$ [43, 44]. Here z is the lattice coordination number, k_B is the Boltzmann constant, T is the absolute temperature, and w_{ij} are the contact energies between components i and j . Identifying w_{12} with the solvent-polymer energy E_{sp} , w_{11} with the polymer-polymer energy E_{pp} , and using $w_{22} = E_{ss} = 0$ as the reference solvent-solvent energy, we obtain $\chi \approx \beta \cdot z \cdot (E_{sp} - 0.5 \cdot E_{pp})$, with $\beta = 1 / (k_B \cdot T)$. In our simulations, β was set to 1, corresponding to reduced energy units with $k_B \cdot T = 1$, consistent with the Metropolis acceptance factor $e^{(-\Delta E)}$.

A key feature of our algorithm is that each Monte Carlo move consists of exchanging two neighboring lattice sites, and the corresponding energy change ΔE is computed from the local environments of both sites involved in the swap. The direct polymer-solvent contact between the two swap partners is excluded because it remains unchanged by the exchange, whereas contacts to the remaining neighboring cells contribute according to the local polymer and solvent populations. Consequently, the local energy change cannot be identified directly with a mean-field contact count based on the geometric coordination number $z = 6$. We therefore treat the coordination factor used below as an effective parameter of the present update and energy-counting scheme rather than as the geometric coordination number of the cubic lattice.

Because the Flory-Huggins expression for χ is defined per lattice site, whereas our local update involves an exchange of two neighboring cells, we introduce an effective coordination parameter z_{eff} for mapping the interaction energies of the present update scheme onto the Flory-Huggins expression. Importantly, z_{eff} is not identified from the geometric coordination number of the cubic lattice. Instead, it is inferred from the θ state independently identified by conformational scaling. For $E_{pp} = -2.0$ and $E_{sp} = -0.75$, the simulations give $\nu \approx 0.50$, while $E_{sp} - 0.5 \cdot E_{pp} = 0.25$. Using $\chi_\theta \approx 0.5$ and $\beta = 1$ therefore gives $z_{\text{eff}} \approx 2$.

To test the consistency of this mapping at a substantially different interaction-energy pair, we next set $E_{pp} = -4.0$ and selected $E_{sp} = -1.75$, thereby preserving the same exchange-energy difference $E_{sp} - 0.5 \cdot E_{pp} = 0.25$. The scaling analysis again

at the independent-simulation level with 10000 samples. (a) Poor solvent ($E_{sp} = -0.3$), $\nu = 0.284$, 95% CI [0.280, 0.288]. (b) θ solvent ($E_{sp} = -0.75$), $\nu = 0.501$, 95% CI [0.487, 0.514]. (c) Good solvent ($E_{sp} = -1.0$), $\nu = 0.604$, 95% CI [0.593, 0.615]. The polymer-polymer interaction energy was fixed at $E_{pp} = -2.0$.

gives $\nu \approx 0.50$ (see [Supporting Information](#)), showing that both parameter pairs produce the same θ -like conformational scaling when the exchange-energy difference is preserved. Because the second parameter pair was selected according to the exchange-energy condition obtained from the first θ point, this calculation is not an independent determination of z_{eff} . Rather, it provides a numerical consistency test of the proposed Flory-Huggins mapping at different absolute values of E_{pp} and E_{sp} .

A methodological distinction is important. In the present model, the θ state is identified directly from the post-relaxation conformational scaling criterion $\nu \approx 0.50$. The Flory-Huggins relation is then used to provide a thermodynamic interpretation of this independently identified θ point and to infer the corresponding effective parameter z_{eff} . The second parameter pair described above tests the reproducibility of the resulting exchange-energy condition but does not constitute a second independent determination of z_{eff} . The value of z_{eff} should therefore be regarded as an effective parameter associated with the local update rule and energy calculation rather than as the geometric coordination number of the cubic lattice. Any modification of the move rules, neighborhood definition, or local energy calculation would require re-evaluation of this mapping.

3.3 | Cylindrical Assemblies

Many polymer gels contain bundle-like, fibrillar, or junction-zone-type structural motifs, which have been directly observed in experimental structural studies of various polymer hydrogels [45–50]. These morphologies reflect the competition between polymer-polymer association, which promotes lateral aggregation and compaction, and solvent-polymer interactions, which promote hydration, swelling, and dispersion. Similar solvent-dependent polymer-rich morphologies were also observed in our previous all-atom simulations [51]. Therefore, we next consider cylindrical assemblies as a minimal model of fibrillar or bundle-like polymer domains, allowing us to test how free chain ends and periodic chain continuity affect the stability of such structures under different solvent qualities.

3.3.1 | Finite Chains

Figure 6 shows the evolution of a cylindrical assembly of initially aligned polymer chains without additional geometric or topological constraints. The initial configuration (Figure 6a) consists of parallel finite chains arranged in a bundle with a radius of 3 lattice cells. The cylindrical systems were simulated in a $20 \times 20 \times 20$ lattice and contained 29 chains of length 20, corresponding to 580 polymer cells and a polymer volume fraction $\phi = 0.0725$. In poor-solvent conditions (Figure 6b), the cylindrical geometry is not preserved. The chains collapse into a compact aggregate, and the initial alignment is lost. At the θ condition (Figure 6c), the bundle disorders and spreads within the simulation box. No stable cylindrical structure remains. In good solvent (Figure 6d), the dispersion is stronger, and the chains separate into an extended, disordered configuration. Thus, for finite chains without constraints, the imposed cylindrical arrangement does not remain stable and relaxes toward solvent-dependent conformations.

3.3.2 | Infinite Chains

In the previous subsection, the cylindrical assembly composed of finite chains did not remain stable. Instead of preserving the fibrillar morphology, the system relaxed toward solvent-controlled conformations, and in poor solvent collapsed into a single compact aggregate. Within the present local Monte Carlo update scheme, this behavior is associated with the presence of free chain ends, which exhibit fewer bonded-neighbor constraints and participate in end-initiated restructuring.

To suppress this effect and isolate the role of lateral interactions within the cylindrical bundle, we consider here a modified configuration in which each chain is closed through periodic boundary conditions along the axial direction. This periodic self-connection eliminates chain ends and effectively mimics an infinite fibril. The initial configuration (Figure 6e) again consists of aligned chains forming a cylindrical assembly with a radius of 3 lattice cells. However, due to axial periodic closure, the bonded connectivity of each chain is continuous across the simulation boundaries. In poor-solvent conditions (Figure 6f), the cylindrical morphology is preserved to a much greater extent than in the finite-chain case. The bundle remains compact and aligned along the axial direction, without collapsing into a single globule. At the θ condition (Figure 6g), the structure undergoes internal rearrangements and transverse fluctuations, yet the overall cylindrical organization remains recognizable. In good solvent (Figure 6h), lateral cohesion decreases further, and the chains exhibit significant transverse motion. Nevertheless, axial continuity imposed by periodic closure maintains the global columnar organization.

Having compared the finite and periodically closed cylindrical morphologies visually in Figure 6, we next quantified their structural evolution using three complementary descriptors: the normalized interchain-contact concentration cinter (interchain contacts per polymer cell), the transverse bundle radius $R_{\perp}$, and the axial orientational order parameter S_z . Each descriptor was evaluated for every saved frame and then averaged over five independent simulations for each solvent condition.

$$c_{\text{inter}} = \frac{N_{\text{inter}}}{N_p}$$

here, N_{inter} is the number of distinct non-bonded nearest-neighbor contacts between polymer cells belonging to different chains, with each contacting pair counted once, and N_p is the total number of polymer cells. Accordingly, larger c_{inter} indicates a greater concentration of interchain contacts and therefore stronger lateral association within the assembly.

$$R_{\perp} = \sqrt{\frac{1}{N_p} \sum_{i=1}^{N_p} [(\Delta x_i)^2 + (\Delta y_i)^2]}$$

here, Δx_i and Δy_i are the minimum-image displacements of polymer cell i from the periodic circular center of the assembly in the transverse XY plane. Smaller $R_{\perp}$ indicates a narrower, more compact bundle, whereas larger values indicate lateral swelling

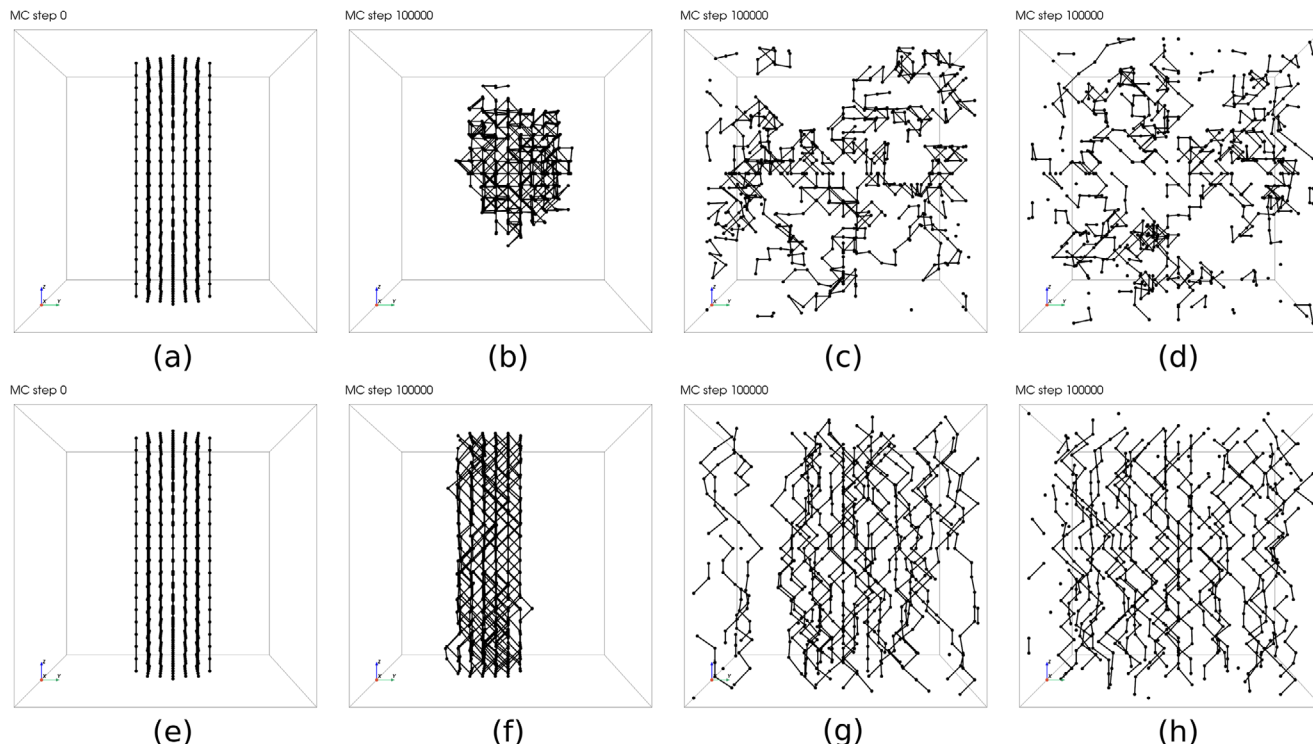


FIGURE 6 | Conformational evolution of cylindrical assemblies of aligned polymer chains with a radius of 3 lattice cells and a chain length of 20. (a–d) Finite chains without periodic self-connection: (a) initial configuration; final configurations after 100000 Monte Carlo steps under (b) poor-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -0.3$), (c) θ -solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -0.75$), and (d) good-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -1.0$). (e–h) Corresponding configurations under the same conditions as in (a–d), respectively, for chains closed through axial periodic boundary conditions (effectively infinite chains).

or dispersion.

$$S_z = \frac{1}{N_b} \sum_{j=1}^{N_b} \frac{3(\cos \theta_j)^2 - 1}{2}; \quad \cos(\theta_j) = \frac{|\Delta z_j|}{|\mathbf{d}_j|}$$

here, N_b is the number of bonded backbone links, $\mathbf{d}_j$ is the minimum-image bond vector, and θ_j is the angle between that bond and the Z axis. The limiting values are $S_z = 1$ for perfectly axial alignment, $S_z \approx 0$ for an isotropic bond distribution, and $S_z = -0.5$ for bonds oriented perpendicular to Z.

The time evolution of all three descriptors is shown in Figure 7; solid curves represent finite chains, dashed curves represent periodically closed chains, and shaded bands indicate ± 1 standard deviation across the five independent simulations.

As shown in Figure 7a, the interchain-contact concentration decreases as the solvent quality improves, consistent with progressive loss of lateral cohesion. Periodically closed chains retain more interchain contacts than finite chains under every condition: the final cinter values are 2.172 ± 0.035 versus 1.684 ± 0.033 in poor solvent ($E_{sp} = -0.3$), 0.258 ± 0.047 versus 0.189 ± 0.040 at the θ condition ($E_{sp} = -0.75$), and 0.071 ± 0.019 versus 0.059 ± 0.018 in good solvent ($E_{sp} = -1.0$), for periodically closed and finite chains, respectively. This higher contact concentration indicates that axial periodic continuity helps preserve lateral interchain association.

The geometric and orientational descriptors provide complementary information (Figure 7b,c). In poor solvent, the final $R_\perp$ is 3.35 ± 0.14 for finite chains and 2.27 ± 0.02 for periodically closed chains. The finite assembly loses its initial axial order ($S_z = 0.011 \pm 0.013$), whereas periodic closure retains partial axial alignment ($S_z = 0.323 \pm 0.022$). At the θ condition, both assemblies swell laterally, but only the periodically closed chains retain appreciable axial order ($S_z = 0.284 \pm 0.014$). In good solvent, the transverse radii converge to 7.76 ± 0.09 and 7.71 ± 0.18 for finite and periodically closed chains, respectively, indicating extensive lateral dispersion; nevertheless, periodic closure retains measurable axial order ($S_z = 0.243 \pm 0.014$), whereas the finite assembly remains isotropic. Together, the three descriptors quantitatively confirm that free chain ends facilitate lateral and orientational relaxation, while periodic chain continuity preserves interchain contacts and partial axial organization.

3.4 | Disordered Assemblies

In the previous section, cylindrical assemblies were used as a minimal model of fibrillar or bundle-like polymer domains. However, in real gels such fibrils and polymer-rich domains usually do not remain isolated; they further form disordered, entangled, or porous networks that define the material structure at larger length scales [45–50]. Therefore, in this section we consider randomly placed chains as a minimal model of disordered polymer assemblies with network-like morphologies [51].

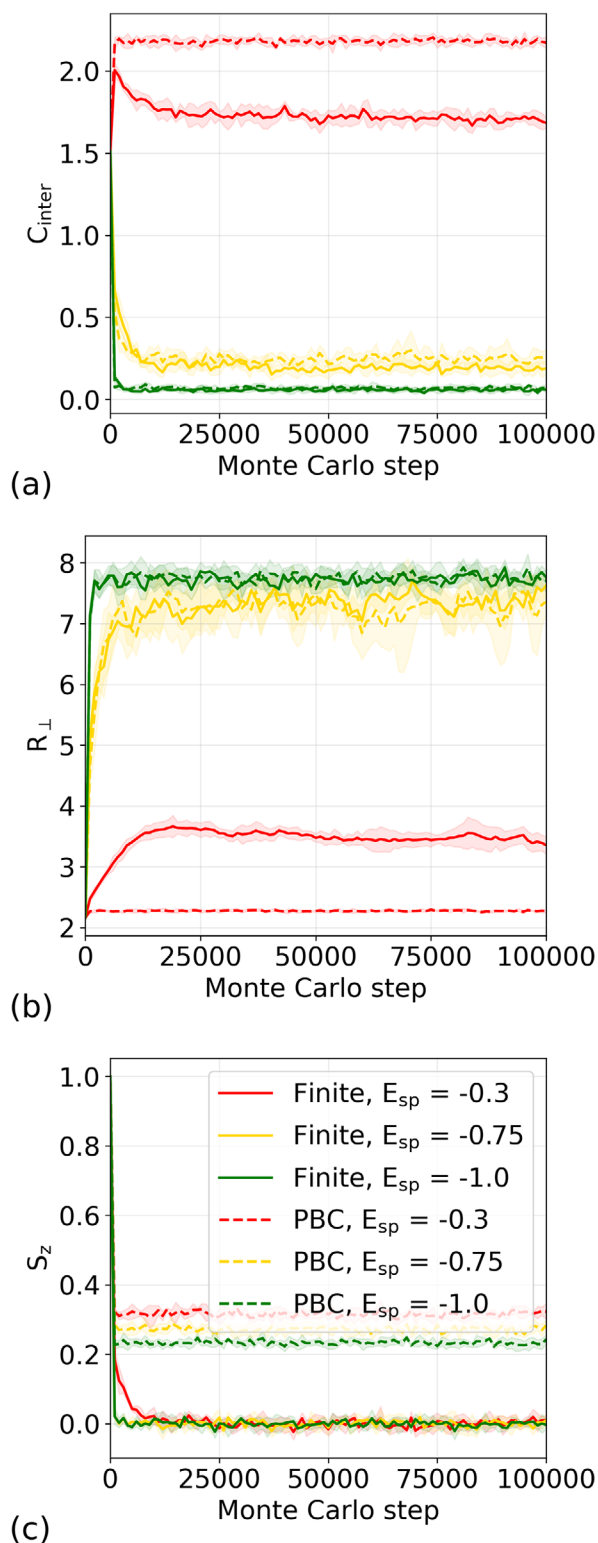


FIGURE 7 | Quantitative evolution of cylindrical assemblies composed of finite chains (solid lines) and chains closed through axial periodic boundary conditions (dashed lines), averaged over five independent simulations; shaded regions indicate ± 1 standard deviation. (a) Normalized interchain-contact concentration c_{inter} (contacts per polymer cell). (b) Transverse bundle radius $R_{\perp}$. (c) Axial orientational order parameter S_z . Conditions: $E_{pp} = -2.0$ and $E_{sp} = -0.3, -0.75$, or -1.0 ; 100000 Monte Carlo steps.

3.4.1 | Finite Chains

Figure 8 shows the evolution of a system composed of 30 randomly positioned finite polymer chains with a length of 20 lattice cells, without periodic self-connection. In the initial configuration (Figure 8a), the chains are distributed throughout the simulation box, with 10 chains initially aligned along each of the X, Y, and Z directions. The disordered systems were simulated in a $20 \times 20 \times 20$ lattice and contained 30 chains of length 20, corresponding to 600 polymer cells and a polymer volume fraction $\phi = 0.075$. In poor-solvent conditions (Figure 8b), the system undergoes rapid aggregation. The chains collapse into a compact cluster, forming a dense globular structure. The initial orientational distribution is lost, and most chains participate in a single aggregate. At the θ condition (Figure 8c), the system remains partially aggregated. Several chains form transient clusters, while others remain more extended. The resulting configuration is heterogeneous, with both compact and dispersed regions. In good-solvent conditions (Figure 8d), aggregation is significantly reduced. The chains are more uniformly distributed throughout the simulation box and adopt extended conformations. Although occasional contacts between chains occur, no persistent global cluster is formed. Overall, the solvent quality governs the balance between inter-chain aggregation and spatial dispersion in systems composed of finite, randomly oriented chains.

3.4.2 | Infinite Chains

Figure 8 shows the evolution of a system composed of 30 randomly positioned polymer chains closed through periodic boundary conditions, effectively eliminating chain ends. As in the finite case, 10 chains are initially aligned along each of the X, Y, and Z directions, and the chain length is 20 lattice cells. However, due to periodic self-connection, each chain remains bonded across the simulation boundaries and has no free chain ends. In poor-solvent conditions (Figure 8f), aggregation occurs, but the resulting morphology differs from that observed for finite chains. Instead of collapsing into a single compact globule, the system forms an extended, interconnected network spanning the simulation box. Within the present Monte Carlo scheme, the absence of free chain ends suppresses the end-associated restructuring observed for finite chains and favors a spatially extended structure. At the θ condition (Figure 8g), the network becomes less compact and exhibits increased fluctuations, while maintaining overall connectivity. The system remains spatially extended, without forming a dense central cluster. In good-solvent conditions (Figure 8h), lateral aggregation is further reduced. The chains display significant transverse motion, yet global connectivity persists due to periodic closure. The resulting configuration is highly fluctuating but remains system-spanning. Thus, in randomly oriented systems, periodic self-connection qualitatively changes the aggregation pathway by preventing complete globular collapse and favoring extended network-like conformations under poor and intermediate solvent conditions.

To complement the visual comparison in Figure 8, we quantified the organization of the disordered assemblies using two descriptors that capture different structural levels: the shell-volume-corrected interchain radial distribution function $RDF(r)$, which describes the radial population of polymer-cell pairs belonging

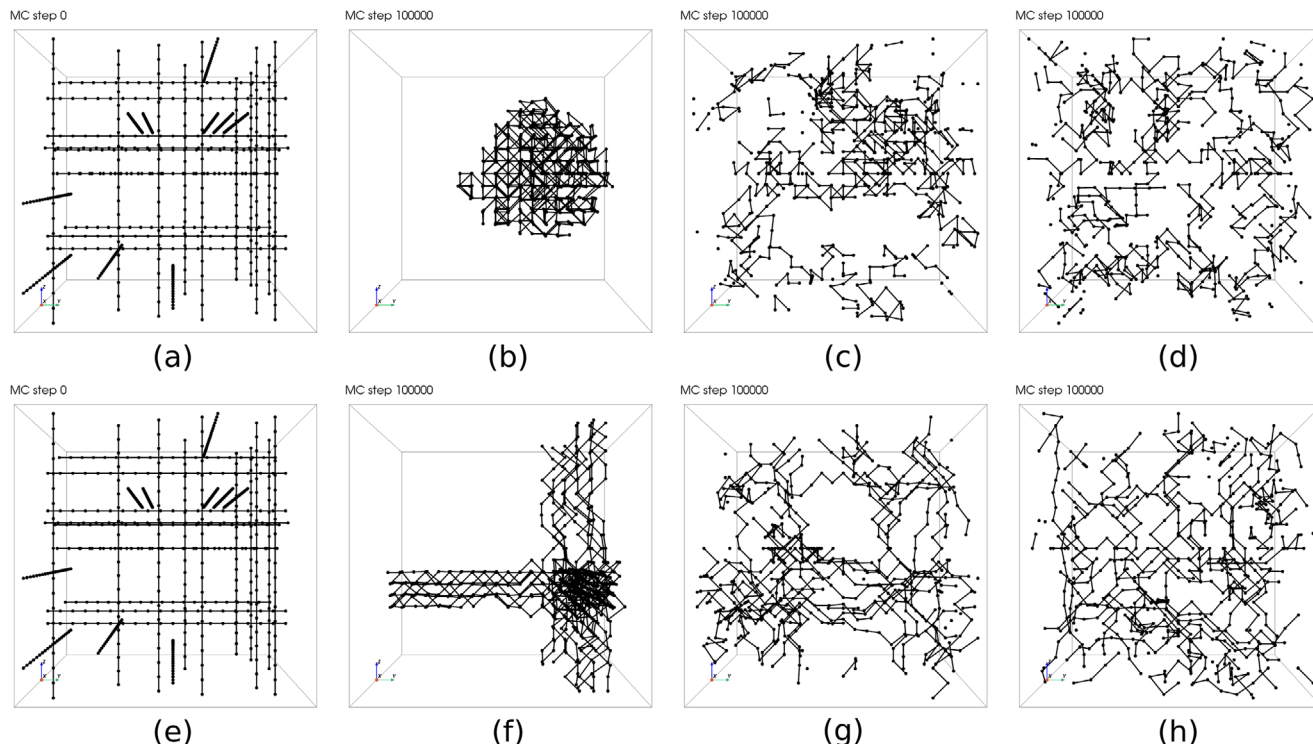


FIGURE 8 | Conformational evolution of 30 randomly positioned polymer chains of length 20 lattice cells, with 10 chains initially aligned along each of the X, Y, and Z directions. (a–d) Finite chains without periodic self-connection: (a) initial configuration; final configurations after 100000 Monte Carlo steps under (b) poor-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -0.3$), (c) θ -solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -0.75$), and (d) good-solvent conditions ($E_{pp} = -2.0$, $E_{sp} = -1.0$). (e–h) Corresponding configurations under the same conditions as in (a–d), respectively, for chains closed through periodic boundary conditions (effectively infinite chains).

to different chains, and the largest chain-contact component fraction f_{LCC} , which measures system-scale connectivity. Both quantities were first averaged over the last 20% of saved frames within each trajectory and then averaged over five independent simulations for every solvent condition. Interchain distances were evaluated with the minimum-image convention, and every unique interchain pair was counted once.

$$RDF(r_k) = 100\% \times \frac{N_k / \Delta V_k}{\sum_{i=1}^{n_{bins}} [N_i / \Delta V_i]}, \quad \Delta V_k = \frac{4\pi}{3} (r_{k+1}^3 - r_k^3)$$

here, N_k is the mean number of unique interchain polymer-cell pairs in radial bin k , and ΔV_k is the corresponding spherical-shell volume. Division by ΔV_k corrects for the increasing shell volume with distance. The denominator is the sum of the shell-volume-corrected populations over all bins; consequently, the plotted values satisfy $\sum_k RDF(r_k) = 100\%$. Thus, $RDF(\%)$ reports the relative radial population after shell-volume correction and is not expected to approach unity at large r .

$$f_{LCC} = \frac{N_{chains}^{largest}}{N_{chains}}$$

For this analysis, each polymer chain is a node in a contact graph, and an edge connects two chains when at least one non-bonded nearest-neighbor contact exists between them. $N_{chains}^{largest}$ is the number of chains in the largest connected component and N_{chains} is the total number of chains. Thus, $f_{LCC} = 1$ means that all

chains belong to one system-spanning contact network, whereas smaller values indicate fragmentation into separate clusters.

The two descriptors are summarized in Figure 9. Solid and dashed RDF (%) curves denote finite and periodically closed chains, respectively; shaded bands and error bars indicate ± 1 standard deviation across the five independent simulations.

As shown in Figure 9a, poor-solvent conditions concentrate the shell-volume-corrected radial population at short separations, producing the largest peaks near the first accessible lattice shells and a rapid decrease toward longer distances. Finite and periodically closed chains share the same peak positions because the allowed separations are fixed by the cubic lattice, while their different peak amplitudes reflect topology-dependent packing. The oscillatory profile arises from the discrete geometry of the cubic lattice, for which only specific intercell distances $r = \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2}$ can occur. Consequently, some radial intervals contain few or no geometrically accessible lattice separations, producing the pronounced downward dips between the allowed-distance peaks. Under θ - and good-solvent conditions, the short-range peaks are lower and the normalized population is distributed over a broader range of separations, consistent with more spatially extended assemblies. The peak amplitudes also reflect the unequal degeneracy of the accessible lattice distances. Because each curve is normalized to 100%, its ordinate is a percentage contribution to the complete shell-corrected radial distribution rather than a conventional $g(r)$ value approaching unity.

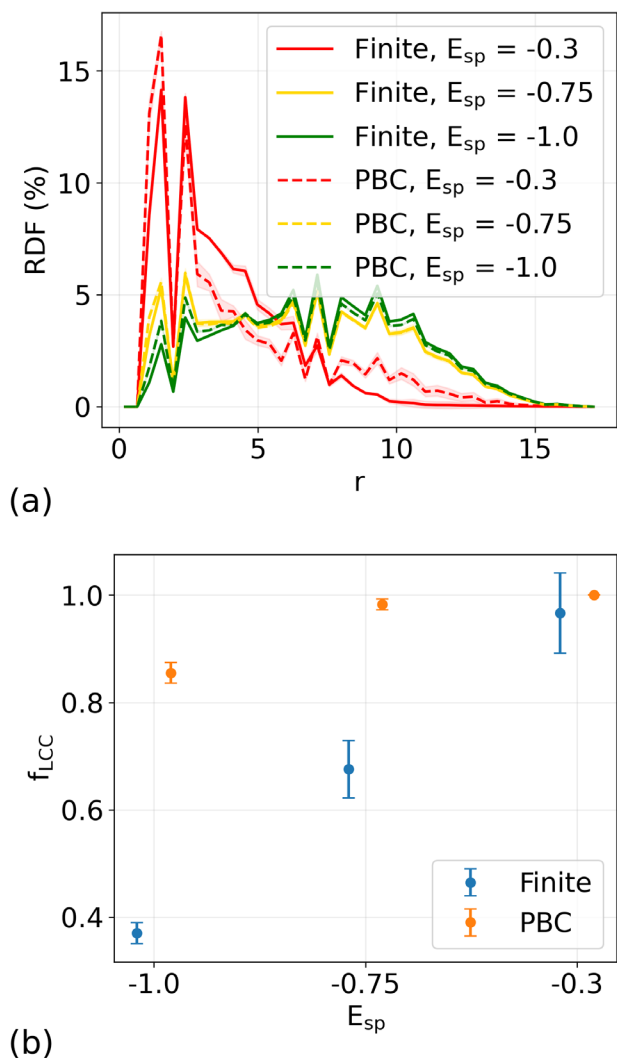


FIGURE 9 | Quantitative characterization of disordered assemblies composed of finite chains and chains closed through periodic boundary conditions (PBC), averaged over five independent simulations. (a) Shell-volume-corrected interchain radial distribution, RDF (%), calculated over the last 20% of saved frames and normalized so that the sum over all radial bins equals 100%; solid curves represent finite chains, dashed curves represent periodically closed chains, and shaded regions indicate ± 1 standard deviation. (b) Largest chain-contact component fraction f_{LCC} ; error bars indicate ± 1 standard deviation. Conditions: $E_{pp} = -2.0$ and $E_{sp} = -0.3, -0.75, \text{ or } -1.0$; 100000 Monte Carlo steps.

The connectivity analysis reveals a complementary distinction (Figure 9b). In poor solvent, both finite and periodically closed systems remain nearly fully connected ($f_{LCC} = 0.967 \pm 0.075$ for finite chains and 1.000 ± 0.000 for periodically closed chains). At the θ condition, the largest component contains 0.676 ± 0.054 of the finite chains but 0.983 ± 0.010 of the periodically closed chains. In good solvent, the finite system becomes strongly fragmented ($f_{LCC} = 0.370 \pm 0.019$), whereas the periodically closed system remains largely connected (0.855 ± 0.019). Thus, periodic self-connection preserves system-scale network connectivity even when local interchain correlations weaken. Together, the RDF and connected-component analyses quantitatively support the visual interpretation of Figure 8: finite chains favor compact aggregation followed by fragmentation as solvent quality

improves, whereas periodic chain continuity favors extended, persistent networks.

4 | Conclusions

In this work, we developed and analyzed a three-dimensional cellular automaton model of polymer systems with an explicit solvent-polymer interaction parameter E_{sp} . The model was designed as a minimal framework for solvent-responsive polymer assemblies, preserving chain connectivity and local update rules while testing whether classical polymer behavior can emerge from discrete local interactions.

Across all studied geometries, from a single chain to multi-chain systems, separate simulations at fixed E_{sp} reproduced the three canonical solvent regimes. Poor solvent conditions led to compact globules or dense aggregates, the θ regime produced moderately compact fluctuating coils, and good solvent conditions resulted in swelling and spatial dispersion. These structural responses emerged from local polymer-polymer and solvent-polymer contacts combined with Metropolis-type local acceptance, rather than from imposed target morphologies.

The model approximately reproduced the expected finite-chain scaling trends. Analysis of the radius of gyration gave the Flory exponent ν and identified the θ state at $\nu \approx 0.50$. Mapping this independently identified θ state onto the Flory-Huggins relation gives an effective coordination parameter $z_{eff} \approx 2$, while a second interaction-energy pair preserving the same exchange-energy difference reproduces the same θ -like scaling as a consistency test.

In multi-chain systems, chain connectivity and the presence or absence of free chain ends were as important as interaction energy. Finite chains without additional constraints lost their imposed organization through an end-associated Monte Carlo restructuring pathway, whereas periodic self-connection suppressed this pathway and favored extended fibrillar or network-like structures. These observations concern the kinetic pathways of the present local update rule and are not claimed to represent physical-time polymer dynamics. In randomly oriented systems under poor-solvent conditions, periodically self-connected chains formed extended connected networks, whereas finite chains formed compact clusters. Thus, solvent quality controls lateral cohesion, while chain connectivity and the presence or absence of free ends strongly influence the structural pathway and final morphology.

Overall, the results show that a three-dimensional cellular automaton based on simple local update rules can capture essential features of solvent-dependent polymer behavior, including collapse, swelling, aggregation, preservation of fibrillar morphologies, and distinct conformational regimes associated with solvent quality. The model contains no separate solvent-concentration diffusion field, continuous coordinates, or force calculations; the relevant physics is encoded in local exchanges and energy differences. Its minimal structure makes it a transparent platform for further extensions, including temperature control through β , time-dependent interaction parameters, heterogeneous interactions, multiple solvent species, different p-cell types, and explicit solvent mass transport through con-

centration fields or Vanag-type diffusion. The present model therefore provides a minimal and transparent computational testbed for linking local solvent-polymer interaction rules to solvent-dependent mesoscale structure and for developing further cellular-automaton models of responsive polymer systems.

General-purpose lattice simulation frameworks provide broader or higher-performance capabilities; the purpose of the present implementation is not performance superiority, but a minimal and transparent CA representation suited to controlled solvent-response experiments. The accompanying openly available simulation-to-figure workflow is intended to facilitate direct reproduction, modification, and extension of the model.

Author Contributions

Vasilii Korotenko: conceptualization, methodology, software, data curation, formal analysis, visualization, investigation, writing – original draft, writing – review and editing. **Irina Smirnova:** supervision, funding acquisition, project administration, resources, writing – original draft, writing – review and editing, conceptualization. **Pavel Gurikov:** writing – original draft, writing – review and editing, supervision, conceptualization, methodology, funding acquisition, project administration, resources.

Acknowledgements

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – SFB 1615 – 503850735 – subproject B01.

Open access funding enabled and organized by Projekt DEAL.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The Python simulation, analysis, and visualization scripts, simulation data, random seeds, software dependencies, and step-by-step instructions required to reproduce the results and figures reported in this work are openly available in the TUHH TORE repository at <https://doi.org/10.15480/882.16813>.

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