Conformational transition of telechelic star polymers

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ABSTRACT

We report dynamic Monte Carlo (DMC) simulation study of solution behavior of multi-arm telechelic star polymers, wherein the number of branching (f) increases with decreasing arm length (n); thus keeping the total number of monomer (N) in the molecule around a constant value. On deteriorating solvent quality, the conformational change occurs from an open to a compact globule structure. The terminal functional groups form aggregate as the solution is cooled progressively and the aggregation phenomenon drives the collapse transition. The transition temperature follows a non-monotonic trend with the functionality, in comparison with an equivalent series of star homopolymers. The non-monotonic behavior of telechelic star polymer is attributed to the interplay between enthalpic gain due to end-monomer aggregation and entropic loss due to loop formation. Structural analysis reveals that, aggregation of end group yields a structure resembles to "watermelons" (WM). Simulation results for the systems with varying N (keeping f or n constant and varying n or f) shows the similar mechanism to the constant N system. Further, we discuss results on highly branched telechelic star polymer with shorter arm length, where, we observe the formation of collapsed structures with single and double aggregates in isothermal and non-isothermal cooling respectively.

1. Introduction

Understanding self-assemble behavior of amphiphilic polymer is essential for fundamentals of polymer physics as well as vast applications in the field of nanoscience and nanotechnology. The rich variety of structures formed through self assembly may provide a unique avenue to prepare tailor-made materials for potential applications [1]. Telechelic star polymers are functionalized star molecules, which have active terminal units. Star polymers with functionalized end groups are amphiphilic copolymers that provide a unique opportunity to prepare nanoscale materials. The functionalized end groups form aggregate by mutual attraction (intra- and/or inter-molecular) to yield varieties of nanoscale structures. In a very dilute solution (much below the overlap concentration, e.g., single chain), aggregation yields globular structure with aggregate of terminal units. For many chain systems (concentration above the overlap concentration), a percolating network is formed due to intermolecular aggregate formation.

Advancement of synthetic chemistry enables to synthesize polymers with complex architectures, such as star, dendrimer [2–5].

A star polymer is a branched polymer, wherein numbers of polymers (branches) emanate from a central branch point. Anionic polymerization has been used to synthesize telechelic star poly(ethylene-co-propylene) with terminal self-complementary multiple hydrogen bonding sites [6]; amine functionalized telechelic star poly(-dimethylsiloxane) [7]; and three-arm polybutadienes with one, two, and three functional end capped with dimethylamine and corresponding zwitterionic species [8,9]. Reversible addition-fragmentation chain transfer (RAFT) has been employed to synthesize allyl-functionalized star polystyrene [10]; maleimide end-functionalized four-arm star poly(N-isopropylacrylamide) [11]. Group transfer polymerization technique has been successfully applied to synthesize ABA triblock copolymer consisting of relatively long poly(2-(dimethylamino) ethyl methacrylate) block with shorter block (terminal group) with poly(methyl methacrylate) [12].

In a good solvent condition, molecules exist in an expanded coil state conformation. On deteriorating solvent quality (e.g., lowering temperature) the conformation changes from an expanded coil to a compact globule structure. The functional terminal groups, in suitable solvent condition, self-assemble to form aggregates, which has been investigated by various experiments [12–16] and simulations [17–21]. Aqueous solution of an ABA triblock copolymer [12] exhibit two different types of self-assembly behavior: at low concentration, end-to-end linear association and star-like "hairy" loose aggregate; whereas, in higher concentration, microgel

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structure has been observed. Aggregation behavior also depends on solvent quality (viz., polymer–solvent interaction). It has been observed that dimethylamine-capped three-arm polybutadienes do not associate in cyclohexane solvent; however, the corresponding zwitterionic species associate strongly in this solvent [8,9]. Small angle X-ray scattering and rheological study revealed that they self assemble into different types of supramolecular structures suggesting the presence of both intra- and intermolecular association [22]. Existence of transient network formation via intermolecular self-assembly has been revealed, which depend on the molecular weight of the arm of the telechelic star polymer [23]. Molecular dynamics simulations have predicted that in a very dilute solution (viz., single chain system), the terminal monomers aggregate to yield a structure resembles to "watermelon" (WM) for a low-functionality (≤ 5) telechelic star polymer [18]. With increasing the degree of functionality (~ 10), formation of double watermelon (DWM) morphology has been observed [19]. Star copolymers with HPHP sequence (alternating copolymer) exhibit shifting of transition toward higher temperature as the arm length and number of arm increases [17]. The self-assemble properties of end-functionalized star polymer have been exploited to prepare protein-star polymer conjugate, which would have potential applications in nanotechnology and medicine [11]. Therefore, understanding the conformational behavior of telechelic star polymer is an important issue from the polymer science point of view.

In this paper, we describe simulation results on the effect of branching on collapse behavior of telechelic star polymers. We take telechelic star polymers with varying functionality (viz., number of arms) and arm length, keeping total number of units almost constant. We have also studied the collapse behavior of telechelic star polymers with varying total number of units (N) by keeping f (number of arms) fixed and varying n (branch length), and keeping n constant and varying f. The terminal units are functional groups, which form aggregate due to mutual attraction, in the presence of suitable solvent condition. We observe that with increasing branching number and decreasing arm length, the collapse behavior follows a non-monotonic trend with the degree of branching. We also present results on simulation of high functionality telechelic star polymer with shorter arm length, which produces some interesting results. Non-isothermal cooling results in the formation of single aggregate resemble to "watermelon" (WM) morphology whereas isothermal cooling produces double aggregates. We interpret this finding as the interplay between enthalpic gain due to end-unit aggregation and entropic loss due to loop formation.

We organize our paper as follows. In section 2, we report our model and simulation technique. We discuss our key results in the section 3 followed by the conclusions in the section 4.

2. Model and simulation technique

We employ dynamic Monte Carlo (DMC) simulation on a cubic lattice. We model a star molecule as a molecule containing f number of branches (or arms) originating from a common point (viz., the branch point). For a star polymer with f number of branches and each arm contains n number of repeat unit, the total number of unit becomes N ($f(n$-1$) + 1$). Polymer chain is represented by connecting the successive lattice sites on a simple cubic lattice of size 128^3. Larger size lattice has been used for longer arm length. The terminal element of each arm is designated as the functionalized units (viz., co-monomer). The occupied lattice sites are either a monomer (m), or a co-monomer unit (c). The vacant sites represent the solvent molecules (s). We employed single site bond fluctuation method [24,25] along with the periodic boundary

conditions to simulate the chain molecule in the lattice. A strict self avoiding walk model chain has been used to implement excluded volume interaction. One lattice site is occupied by only one unit and no bond cross with any other bonds. Special care has been taken for the movement of the branch point, so that the connectivity is not lost. Interaction between monomer (co-monomer) and solvent has been modeled by quasi-chemical approximation, incorporating exchange energy between monomer (commoner) and solvent. We employed the Metropolis sampling scheme to sample the new conformation with a probability, $p = \exp(-\Delta E/kT)$. The new conformation is accepted if $p \geq r$, where r is a random number, $0 \leq r \leq 1$, generated by using random number generator, MT19937 [26]. The change in energy in an MC move is modeled as:

$$\Delta E = \frac{1}{2}\sum_{\substack{i \neq j}} \Delta N_{ij} B_{ij},$$ where, $i,j \in \{m,c,s\}$ and ΔN_{ij} are the net change in

the number of contacts between i and j units; B_{ij} are the exchange energies (normalized by kT, k is the Boltzmann constant and T is the temperature in K) between i-j contacts respectively. We take $B_{ms} = B$, which is equivalent to the Flory's χ parameter and inversely proportional to temperature (viz. $B \sim 1/T$). The enhanced m-c and c-s interaction over the m-s interaction due to the functional c-units are given by: $B_{cs} = B_{mc} = \lambda B$, where, the stickiness parameter, $\lambda > 1$. For simulating telechelic star polymer, we set $\lambda = 20$ and for simulating star homopolymer we set $\lambda = 0$. For non-isothermal experiments, we equilibrate sample system at $B = 0$ (T $= \infty$, athermal state) and progressively cooled the system by increasing B in steps of 0.002. At each value of B, we equilibrate the sample for large number of Monte Carlo steps (MCS) and calculate structural and thermodynamic properties over an equal number of MCS. N number of attempted MC move is defined as one MCS. For isothermal experiments, we equilibrate the sample system at $B = 0$ and quench to $B = 0.1$ (viz. in the collapsed state). To monitor transition from coil to globule state, we calculate the mean square radius of gyration, mean square center-to-end distance and constant volume specific heat, C_v (form the fluctuation of the total energy of the system) and size of the aggregate from aggregate size distribution.

3. Results and discussions

We describe simulation results of telechelic star polymers ($\lambda = 20$) with varying number of branches ($f = 3, 6, 9, 12, 16$), with various combinations of arm length (n), such that the total number of units, N remain constant (in one case) and vary (in other case). For constant N systems, the value of N varies from 511 to 517, which is inevitable to have an integer value of the number of monomer per arm (viz., arm length). For variable N systems, N varies across a wide range of values (see Table 1 for details of simulation systems).

Table 1
Details of sample systems used in simulation. Bold numbers of n and N represents systems with constant N.

f	n	N	f	n	N
3	22	64	9	29	253
	43	127		**58**	**514**
	86	256	12	6	61
	171	**511**		12	133
6	12	67		23	265
	22	127		**44**	**517**
	44	259	16	5	65
	86	**511**		9	129
9	8	64		17	257
	15	127		**33**	**513**