SELF-ASSEMBLY OF HETEROARM STAR COPOLYMERS STUDIED BY LATTICE MONTE CARLO SIMULATION

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Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

Results of lattice Monte Carlo simulations on the self-assembly of heteroarm star copolymers in strongly selective solvents (athermal for A arms and considerably bad for B arms) are presented. The arms are modeled as the self-avoiding walks on a simple cubic lattice tethered to the point. A modified simulation algorithm and an improved recognition criterion of associated structures developed in our previous study are used. The paper is a continuation of our systematic study of heteroarm star copolymers and focuses on the effect of the ratio of numbers of soluble to insoluble arms and the distribution of A and B segments in short or long arms on the self-assembly. It confirms the predictable effect of the soluble-to-insoluble arm number ratio on the association behavior. Nevertheless, the comparison of results for different architectures with the same numbers of soluble and insoluble segments, but different lengths of soluble and insoluble arms shows a strong effect of the distribution of A and B segments in different arms.

Keywords: Heteroarm star copolymers; Lattice Monte Carlo simulations; Self-assembly; Polymeric micelles.

Heteroarm star copolymers (containing arms of different chemical nature tethered to a negligibly small crosslinked core) are interesting polymer materials which offer a number of potential applications[1–4]. Similarly to block copolymers, they self-assemble in solutions in selective solvents (solvent for one type of arms and at the same time precipitant for the other type of arms) and form polymer micelles but, in comparison with linear diblocks of the same overall composition, the association number is lower, the critical micelle concentration higher and segregation of the insoluble core-forming and soluble shell-forming arms is less strong, thanks to their unique architecture. The "hairy" heteroarm copolymers containing high numbers of

arms of both types can also form unimolecular micelles with collapsed insoluble and expanded soluble arms[5–8].

There exist a number of experimental papers devoted to the synthesis and physico-chemical studies of the rheological and associative behavior of star polymers, but the number of theoretical and computer studies is fairly limited. Moreover, the published studies focus mainly on homoarms. The behavior of homopolymer stars was first addressed by Daoud and Cotton[9]. They used a model based on the blob theory of de Gennes and were able to offer a fairly successful explanation of the behavior of homoarm stars[10]. The model was later improved by Birhstein and Zhulina[11]. At present, the computer-based Monte Carlo (MC) simulations are the main tool for studying the conformational behavior of heteroarm star copolymers in solvents differing in quality and selectivity[7,12,13]. Even though the MC and molecular dynamic simulations on polymer systems became recently very frequent, association of heteroarm star copolymers has been only little studied and their behavior has not yet been explained in all details because the simulations are very demanding from the computational point of view[14].

In our laboratory, we have been studying the behavior of solutions of heteroarm star copolymers, both experimentally and by computer simulations[5,15]. Recently, we published the first series of MC data on the self-assembly of star copolymers[16,17]. In the present paper, we discuss new results on this topic. We study mainly the effect of the ratio of numbers of soluble and insoluble arms and the effect of their lengths on the size and structure of associates.

COMPUTATIONS

The self-assembly of heteroarm star copolymers in selective solvents (good solvent for A and nonsolvent for B) has been studied using a new version of a configuration-bias dynamic lattice MC method described in our previous papers[16]. We study star copolymers formed by f arms of a segments of type A and g arms consisting of b segments of type B: $(A_a)_f(B_b)_g$. Star copolymers are modeled as self-avoiding walks tethered to the star centre. The method was optimized for studies of copolymer solutions. The algorithm allows for using independent parameters that reflect different solvent quality for different types of segments without a major decrease in the computational efficiency. The pair interactions are described by interaction parameters, $\varepsilon_{\alpha\beta}$, between nearest lattice points occupied by components α and β. For the calculation of probabilities of individual conformations, we use the parameter $z_{\alpha\beta} = \varepsilon_{\alpha\beta} - \varepsilon_{S\beta}$ (expressed in $k_B T$ energy units), which describes the en-

ergy difference between "α-β" and "S-β" neighbors (A, B or solvent S). The use of Z_i makes the simulation algorithm fast and efficient because the total energy difference between systems with either α or S in the i-th position can be expressed simply as $Z_i = \sum_m z_{\alpha\beta}^m$. Index m denotes different neighboring positions around the i-th lattice site. As usual, the interaction energy between neighboring (bonded) segments in the chain is zero. In our optimized variant, the energy difference parameter Z_i fulfils the role of E_i, i.e., it appears in the detailed balance condition[18] and the following mathematical treatment leads to analogous relations for the modified Rosenbluth weights and acceptance probabilities as those in classical configurational bias Monte Carlo (CBMC)[18] method with the only exception that Z_i is used instead of E_i. The optimized algorithm works similarly as the classical CBMC, but it is much faster, especially when copolymer systems are studied in selective solvents.

We use two types of MC moves: (i) a randomly chosen part of an arm of a randomly selected star copolymer is dissolved and reconstructed, and (ii) a randomly chosen star copolymer is totally dissolved and reconstructed from a random lattice site. During the k-th step of the chain reconstruction (or dissolution), the probability that the segment will be localized at lattice site j is given by

$$P_j = \frac{\exp(-Z_j/k_B T)}{\sum_j \exp(-Z_j/k_B T)} = \frac{p_j}{\omega_k}$$

$$\omega_k = \sum_j p_j, \quad p_j = \exp(-Z_j/k_B T)$$

where ω_k is the weight of segment k and the summation runs over all free positions around the $(k-1)$th segment. The total weight of a random star copolymer conformation (new or old) is the product of weights of all segments

$$W_{new(old)} = \prod_k \omega_k.$$

The acceptance criterion is exactly the same as that used in CBMC: new conformation is accepted with probability $p = \min(1, W_{new}/W_{old})$.

In our study, we use an improved recognition criterion that two copolymers belong to the same associate developed in our earlier study[16]. Accord-

ing to the most often used criterion[19–21], two copolymers associate when they create at the minimum one neighbor pair of insoluble segments B from different copolymers. The use of this criterion does not exclude "random clusters" formed as a result of random contacts (collisions) in the simulation box. The random clusters continuously form and disappear in the course of simulation in homopolymer solutions in good solvents, in which no self-assembly takes place. The new criterion distinguishes better between real associates and random clusters. A group of star copolymers is considered to be an associate only if there exist a higher number of contacts between insoluble blocks belonging to different star copolymer molecules than that in a random star homopolymer cluster formed by stars of the same architecture and lengths of arms (with the exception that all arms are soluble) under the same conditions. Although the used criterion is fairly simple (it is based on one parameter only), it corrects and improves the distribution of association numbers significantly in favor of the closed association scheme. It is also important that the use of the improved criterion almost does not slow down the simulation procedure.

In this work, we study heteroarm star copolymers which contain 6 arms (in most cases, of the same length) and differ in the numbers of soluble and insoluble arms. The simulations were performed on a simple cubic lattice (dimension $62 \times 62 \times 62$) with periodic boundary conditions. The interactions between the insoluble segments and the solvent, ε_{BS}, and between the insoluble and soluble segments, ε_{AB}, are repulsive, while all the other interactions are zero. The simulations mimic thus the behavior of heteroarms in a strong-selective solvent ($\varepsilon_{AB} = \varepsilon_{BS} = 0.45$). The system of homopolymers in an athermal solvent (all interactions parameters equal to zero), which was studied in our previous paper, is used as a reference system if necessary.

Calculated Characteristics

Critical micelle concentration, cmc, is an important characteristic of copolymer self-assembly. It is defined as the concentration at which micelles first appear in the solution. The cmc can be estimated as the intersection of two linear parts of the concentration dependence of the free copolymer on the overall copolymer concentration. Below cmc, the star copolymers do not associate and the concentration of free star copolymers equals that of the copolymer, while above the cmc, the former concentration remains constant and does not depend on the overall concentration. We express the relative concentrations by fractions of lattice points occupied by the segments of free (unimer) star copolymers and of all star copolymers (total

concentration), respectively. Even though the curves necessary for the estimation of cmc are not shown, all characteristics are always discussed with respect to cmc.

For characterizing the masses of aggregates, we use the weight distribution functions of association numbers, i.e., the weight fraction of associates with a given association number, A_S,

$$m_w(A_S) = \frac{A_S N(A_S)}{\sum\limits_{A_S} A_S N(A_S)} .$$

$N(A_S)$ is the number of associates consisting of A_S star copolymers and the summation gives the total number of polymer star copolymers in the solution.

For the characterization of sizes of associates, their shapes and structures, we calculate distribution functions of radii of gyration of all insoluble blocks in associates, $\rho_{GB}(R_{GB})$ and the distribution of gyration radii of insoluble blocks of one star copolymer involved in a given associate, $\rho_{gB}(R_{gB})$. Further we enumerate segment densities, $\rho_{dA}(r)$ and $\rho_{dB}(r)$, respectively, as functions of the distance r from the associate gravity centre, which are defined as the volume fractions of segments A and B at a given distance.

RESULTS AND DISCUSSION

In our recent papers, we started a systematic research of the self assembly of star copolymers. So far we have studied mainly symmetrical systems with the same number and length of soluble and insoluble arms. We focused mainly on the effect of the total number and length of arms. In this paper we investigate the role of the ratio of soluble to insoluble arms on the self-assembly of heteroarm star copolymers. Two sets of star copolymers containing always 6 arms of either the same or different length were studied. The star copolymers in the first set differ in the number of insoluble arms which ranges from 1 to 5.

The first series of figures (Figs 1–4) present the weight distribution of associates with particular association numbers for increasing numbers of insoluble arms B_{10} and decreasing numbers of arms A_{10} and for several concentrations. A comparison of individual figures indicates that the self-assembling behavior of star copolymers with the same length of all arms in strongly selective solvents can be divided into several categories with respect to the ratio of numbers of insoluble and soluble arms.

The star copolymers $(A_{10})_5(B_{10})$ with an excess of arms A_{10} are sufficiently soluble in the selective solvent and do not associate. The weight distribution functions of associates are shown in Fig. 1a. We can see the monotonically descending curves, the shape of which almost does not depend on the total concentration. The distribution is dominated by unimer and the populations of higher associates are negligible in the whole studied concentration range. It is evident that the solubility of star copolymers with 5 soluble arms (83.3% of soluble segments) prevents the self-assembly even though the solvent is very bad for the arm B_{10}. Figure 1b shows a snapshot of the simulation box, where we see only well-separated non-
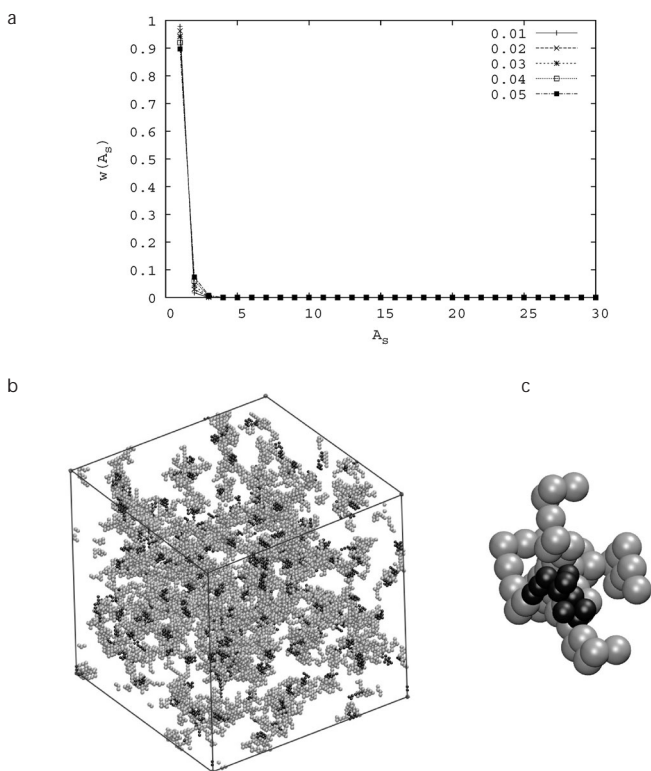
FIG. 1

Weight distribution function (a) of associates formed by star copolymers $(A_{10})_5(B_{10})$ in a strong-selective solvent (ε_{BS} = 0.45). A typical snapshot of the simulation box for a concentration (fraction of occupied lattice sites) 0.05 (b) and a snapshot of a typical star copolymer (c). Different curves correspond to different concentrations. The grey and black spheres depict the soluble and insoluble segments, respectively

associated star copolymers. Figure 1c zooms in a typical star copolymer conformation. It is evident that arms A_{10} are expanded, while the arm B_{10} is partially collapsed. The weight distributions of associates of star copolymers $(A_{10})_4(B_{10})_2$ with 4 soluble and 2 insoluble arms are depicted in Fig. 2a. The curves are basically similar to those in Fig. 1a, but at higher concentration, the populations of associates with fairly low association numbers are not negligible and increase with total concentration as a result of lower solubility of star copolymers containing 66.7% of soluble segments. The weight distribution does not show any token of local maxima, i.e., the fractions of associates decrease with association number A_S. Hence we can conclude that the association, which is strongly shifted in favor of unimer in all cases, does not obey the closed association model. A snapshot of the simulation box is depicted in Fig. 2b and a typical conformation in Fig. 2c. They are similar to snapshots in Fig. 1.

In Fig. 3, we depict the behavior of symmetrical heteroarm star copolymers $(A_{10})_3(B_{10})_3$ with 3 soluble and 3 insoluble arms. The weight distribution function (Fig. 3a) shows one relatively narrow peak with a maximum around $A_S = 15$. Neither the shape of the distribution nor the position of maximum depends appreciably on concentration. It is evident that the associative behavior obeys the closed association model quite well. The association number is fairly low compared with the corresponding diblock copolymer, which is in agreement with experimental observations[5,6,22–27]. A typical snapshot of the simulation box (Fig. 3b) shows associates coexisting with isolated star copolymers. The snapshot in Fig. 3c shows a typical associate formed by 15 star copolymers with fairly segregated arms A_{10} and B_{10}. As compared with the associates formed by corresponding diblocks, the core is less compact and the segregation of A and B segments is less strict.

The star copolymers with an excess of B_{10} arms are less soluble in comparison with the previous case as suggested not only by the formation of associates with quite high association numbers but also by a tendency to secondary association manifested by the formation of micellar clusters. Figure 4a for star copolymers $(A_{10})_2(B_{10})_4$ with 4 insoluble arms shows a high fraction of associates with association numbers below 20 together with non-negligible amounts of large aggregates. The simulations for systems with a low solubility are very time-consuming (and only little efficient) and the data are noisy. Nevertheless, they show all important features of the behavior. An inspection of the associate, which is shown in Fig. 4b, reveals that a relatively low number of soluble arms does not protect enough the collapsed B domain (micellar core) against interactions with the solvent. An attempt to hide the bare surface of the B domain and
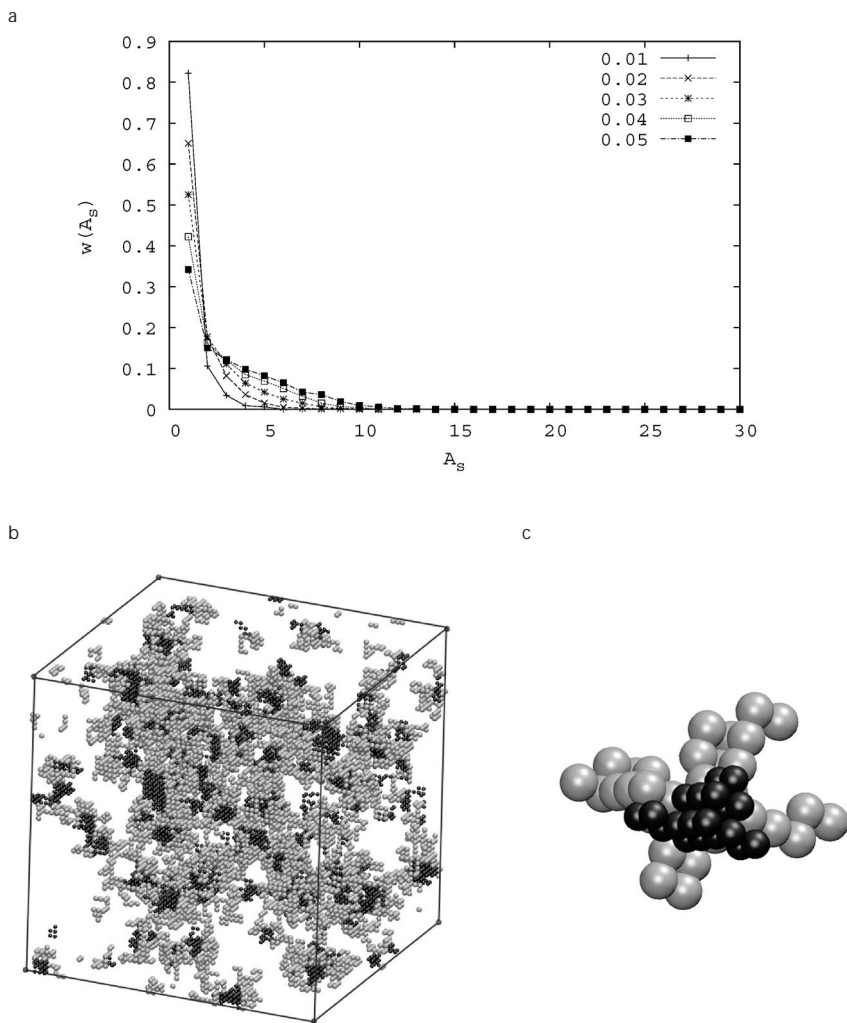
a

b

c

FIG. 2

Weight distribution function (a) of associates formed by star copolymers $(A_{10})_4(B_{10})_2$ in a strong-selective solvent, snapshots of the simulation box (b) and of one star copolymer (c). Other parameters are the same as in Fig. 1
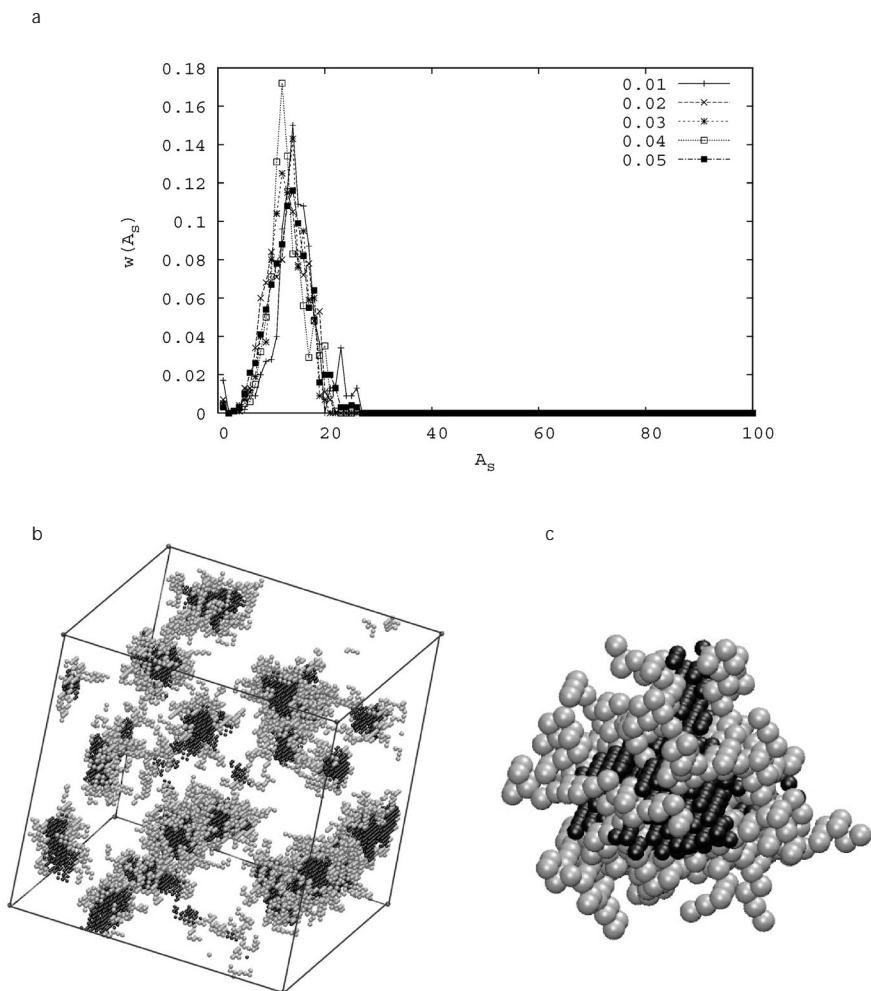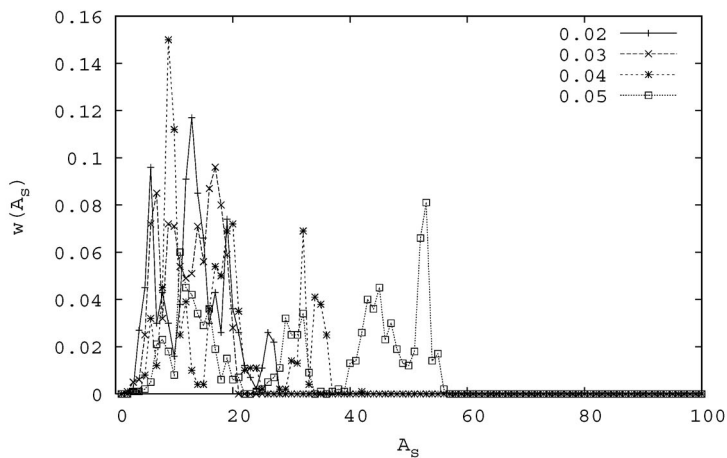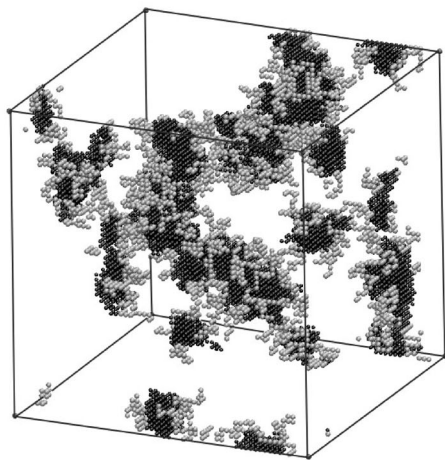
a

b

c

FIG. 3
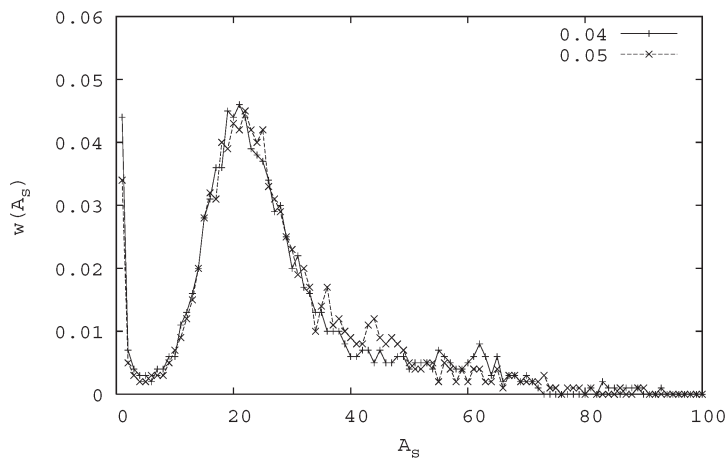Weight distribution function (a) of associates formed by star copolymers $(A_{10})_3(B_{10})_3$ in a strong-selective solvent and snapshots of the simulation box (b) and a typical associate formed by 15 star copolymers (c). Other parameters are the same as in Fig. 1

a

b

FIG. 4

Weight distribution function (a) of associates formed by star copolymers $(A_{10})_2(B_{10})_4$ in a strong-selective solvent and snapshots of the simulation box (b)

FIG. 5

Weight distribution function of associates formed by star copolymers $(A_{10})_2(B_{10})_4$ in a mild-selective solvent ($\varepsilon_{BS} = 0.33$) for two solutions with concentrations 0.04 and 0.05
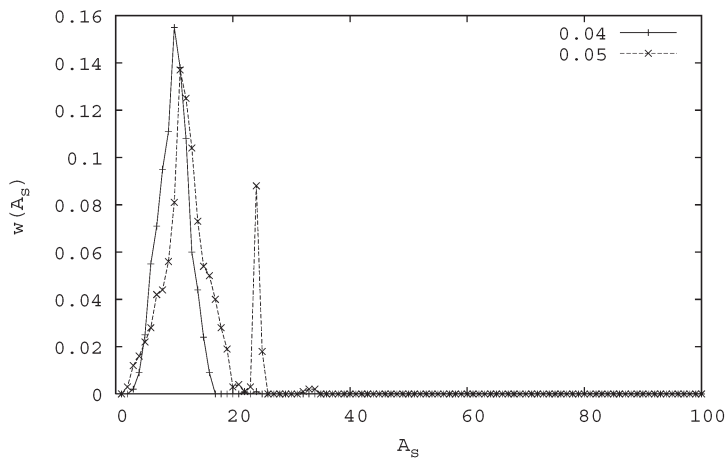

FIG. 6

Weight distribution function of associates formed by star copolymers $(A_{20})_2(B_{10})_4$ in a strong-selective solvent

to prevent contacts with the solvent results in the formation of micellar clusters. The results for the star copolymer with 1 soluble and 5 insoluble arms indicate that this star copolymer is practically insoluble in the selective solvent with $\varepsilon_{BS} = 0.45$. The distribution (not shown) suggests the formation of all possible associates. The fractions of associates differing in association numbers almost do not depend on A_S, which, in our opinion, suggests a strong tendency to macroscopic separation in real systems.

For star copolymers $(A_{10})_2(B_{10})_4$ with 2 soluble and 4 insoluble arms, we also studied the effect of more factors that influence their overall solubility. In the second series of simulations, we investigated how the solvent selectivity and the length of soluble arms affect the self-assembly process. Figure 5 shows the weight distribution of associates for a less selective solvent with $\varepsilon_{BS} = 0.33$ (the value for Θ-solvent is 0.27). Its shape indicates the coexistence of unimers with associates. The average association number is ca. 25, but the distribution of associates is quite broad and asymmetrical with a tail towards high A_S. Figures 6 and 7 present distribution function for star copolymers with two- and four-times longer soluble arms, i.e., for star copolymers $(A_{20})_2(B_{10})_4$ and $(A_{40})_2(B_{10})_4$, respectively, in a strong-selective solvent with $\varepsilon_{BS} = 0.45$. With increasing star copolymer sol-
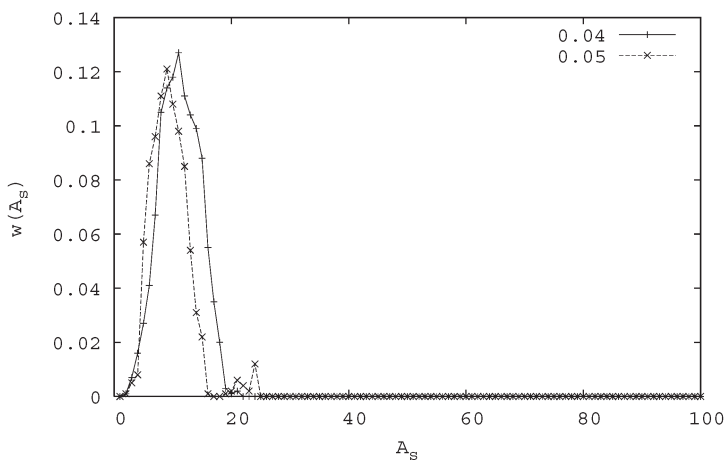

FIG. 7

Weight distribution function of associates formed by star copolymers $(A_{40})_2(B_{10})_4$ in a strong-selective solvent

ubility (i.e., with increasing length of A arms), the average association number, $\langle A_S \rangle$, decreases and the distribution becomes narrower. It is interesting to compare the curves in Figs 2a and 7 because in both cases, the star copolymers contain identical fractions of soluble segments (66.7%), but differ in their distribution $(A_{10})_4(B_{10})_2$ contains 4 short arms A_{10} and $(A_{40})_2(B_{10})_4$ contains 2 long A arms). The comparison shows a strong effect of the architecture on the self-assembly. The association of star copolymers with the same overall chemical composition but different distribution of A and B segments strongly differs: star copolymers with 4 soluble and 2 insoluble arms of the same length do not associate, while those with 4 short insoluble and 2 long soluble arms do associate in the same solvent.

CONCLUSIONS

The MC study confirmed a strong predictable effect of the ratio of soluble to insoluble arms on the associative behavior. The star copolymers with a considerable excess of soluble arms do not almost associate in strongly selective solvents, while those with a significant excess of insoluble arms do not dissolve. The star copolymers with more insoluble than soluble arms (though in comparable numbers) associate, but their solutions are not very stable because limited numbers of soluble arms do not allow for the protection of the insoluble core against unfavorable interactions with solvent. The shape of distribution functions suggests the formation of micellar aggregates.

The self-assembly obeying the closed association scheme was observed for star copolymers containing similar numbers of soluble and insoluble arms of the same length. The association number is fairly low as compared with corresponding diblock copolymers, the blocks are less segregated and the core-shell structure is less pronounced; however, the basic features of the closed association are obvious.

The simulations for systems with the same numbers of A and B segments, but different architectures (i.e., in star copolymers with a higher number of shorter A arms and a lower number of longer B arms and in star copolymers with a lower number of longer A arms and a higher number of shorter B arms) revealed a strong effect of the architecture on the self-assembly.

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