

## SELF-ASSOCIATION OF COPOLYMERS WITH VARIOUS COMPOSITION PROFILES

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*Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.*

In this paper, we present Monte Carlo study of the self-assembly of linear copolymers consisting of two types of segments (well soluble A and insoluble B segments) in selective solvents. We used simple lattice model: chains were represented by self-avoiding random walks and quality of solvent for both types of segments was controlled by pair interaction parameters. We analyzed how the association behavior depends on the composition profile, i.e., on the sequence of segments A and B along the chain. The size and structure of associates formed by chains with different composition profiles were compared with those of diblock copolymers with the same content of A and B segments. It was shown that even small changes in the sequence of segments within the chains lead to significant differences in the association behavior. In addition to composition profiles, we also shown how the association behavior depends on the quality of solvent and copolymer concentration.

**Keywords:** Monte Carlo calculations; Amphiphilic polymers; Micelles; Diblock copolymers; Solvent effects.

The self-assembly of linear copolymers has been studied by many scientists by experimental, theoretical and simulation techniques for many years and has been described in thousands of papers and books. Here we mention just a few of them<sup>1–9</sup>. These studies are mainly concerned with the solutions of linear diblock or triblock copolymers. On the other hand, multiblock copolymer chains, in which two types of blocks regularly alternate along the backbone but their length varies with their position in the chain, were studied only a little. If the length of one block smoothly increases from one

polymer end to the other while the length of the second block decreases we call them gradient copolymers. Gradient copolymers were first studied by Pakula and Matyjaszewski in 1996 by means of computer simulations<sup>10</sup>. Their study was presented as a strictly academic problem, because by that time nobody believed that it would be possible to synthesize copolymers with such well-defined composition. The first experimental works describing the synthesis and characterization<sup>11–24</sup> and works focusing on solution behavior<sup>17,25–29</sup> of gradient copolymers appeared in the last few years. A few papers focused on computer modeling and simulations of such copolymers have also been published<sup>20,30,31</sup>.

In this paper, we present Monte Carlo study of the self-assembly of linear copolymer chains consisting of two types of blocks in selective solvents. Our study is motivated also by experimental observations of some unexpected behavior of samples of polystyrene-grad-poly(acrylic acid) copolymers which were synthesized by the group of Laurent Billon at University of Pau and studied by scattering techniques in our lab. These polymers contain a weak acid group and their aggregation tendency changes upon a change in pH. The experimental results have not been published yet and the presented simulations are expected to help interpreting the experiments. We study the influence of the distribution and length of individual blocks on the size and structure of associates. For this purpose we use linear chains with the same total number of segments of both, soluble and insoluble blocks. The simplest composition profile is linear diblock copolymer, other composition profiles are obtained by gradual intermixing of both types of segments. In such a way, we construct a series of copolymers with increasing length and decreasing steepness of the composition gradient of the middle part and shortening the soluble and insoluble end-parts.

## METHOD AND MODEL

As a simulation technique we use dynamic Monte Carlo method on a simple cubic lattice<sup>32,33</sup>. Copolymer chains are modeled as self-avoiding random walks (SAWs). Lattice sites which are not occupied by the segments are occupied by the solvent molecules. The quality of solvent is determined by the pair interaction parameters. We use a simple set of pair interaction parameters between the nearest neighbour lattice sites only.

Dynamic Monte Carlo methods are based on the generation of new conformations of the simulated system by small changes of the previous conformations. To do this, we use a modified configurational bias Monte Carlo algorithm<sup>34</sup> with two types of Monte Carlo moves:

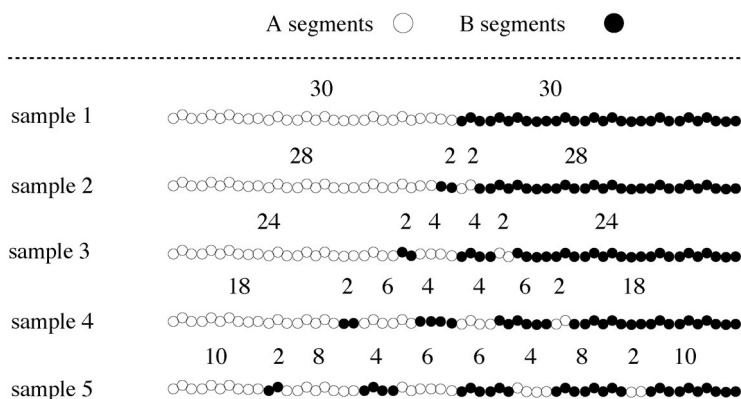
- a randomly chosen part of a randomly chosen chain is deleted and generated again,
- a randomly chosen chain is completely deleted and rebuilt from a randomly chosen lattice point.

New conformations are accepted or rejected according to the modified Metropolis criterion<sup>35</sup>. A high number of statistically independent conformations is then used for determination of various mean values and distribution functions of measurable quantities.

For the purpose of analysis of individual conformations it is necessary to define and identify the associates. We use the following criterion: A cluster of copolymer chains is identified as an associate if it has more interchain contacts than an average cluster (or “associate”) formed by the same number of homopolymer chains in a good solvent. As an interchain contact we consider a pair of neighbor lattice sites occupied by insoluble segments each of which belongs to a different chain. A detailed description of this recognition criterion has been presented in reference<sup>34</sup>.

### Parameters of Studied Systems

The studied copolymer chains consist of two different types of segments, A and B, with different affinity to the solvent. Segments A are well soluble in the given solvent, segments B are insoluble. The total number of both types of segments is the same in all simulated polymers,  $N_A = N_B = 30$ . Individual systems differ in the sequence of A and B segments. The composition profiles are depicted in Scheme 1. Linear diblock copolymers were selected as a



SCHEME 1  
Composition profiles

reference system (sample 1). In other copolymer systems, the units A and B are more and more intermixed starting from the middle of the chain (samples 2–5). The last system (sample 5) is a copolymer with changing composition along the whole chain length. For the purpose of this work, we will refer to sample 5 as a “full gradient profile”. In experimental and theoretical works the term “full gradient” has referred to samples with linear composition profiles where the probability of finding segment A increasing linearly from 0 to 1 along the chain<sup>10,30,31</sup>. In this paper, sample 5 represents the discrete realization of the linear probability distribution.

The solvent quality is controlled by the values of pair interaction parameters. They are set so as to represent unfavourable interactions between insoluble segments B and solvent molecules S,  $\epsilon_{BS}$ , and between insoluble segments B and well soluble segments A,  $\epsilon_{AB}$ . All other interactions are set to zero. In this paper we show the results for two qualities of selective solvent, for  $\epsilon_{AB} = \epsilon_{BS} = \epsilon = 0.27$  ( $kT$  units) which correspond to the theta solvent for B segments, and for  $\epsilon_{AB} = \epsilon_{BS} = \epsilon = 0.30$  for the poor solvent. Concentration of polymers (fraction of occupied lattice points) is varied from 0.05 up to 0.15 and the size of the lattice is  $66 \times 66 \times 66$  lattice points. The number of chains is thus on the order of hundreds and the total number of segments is on the order of thousands. The size of the lattice and the number of chains is chosen to be large enough to avoid finite size effects. At least  $10^3$  statistically independent conformations have been used for the analysis.

## RESULTS AND DISCUSSION

At first we focus on the sizes of aggregates. For this purpose we calculate the weight distribution function of association numbers,  $W(A_s)$ ,

$$W(A_s) = \frac{A_s \cdot N(A_s)}{\sum_{A_s} A_s \cdot N(A_s)} \quad (1)$$

where  $N(A_s)$  is the number of associates with association number  $A_s$ . The summation runs over all possible association numbers and the denominator gives the total number of copolymers in the simulation box. In Fig. 1, the weight distribution functions of association numbers of associates formed by chains with different composition profiles are shown. There are shown curves for the poor solvent,  $\epsilon_{AB} = \epsilon_{BS} = \epsilon = 0.30$ , and for the fraction of occupied lattice sites  $c = 0.10$ . The differences in the association behavior of chains with different composition profiles are significant. The weight

distribution functions of samples 1–3 reach maxima which are only little shifted with respect to each other. It means that aggregates (micelles) with association numbers around 40 are preferentially formed and their sizes almost do not depend on the detailed structure of the central part of polymer chain. It is caused by relatively long soluble block on one end and insoluble block on the other end of the polymer chain. They are long enough to form a dense core and relatively stretched corona protecting the core. It will be shown later that the differences in middle parts of chains lead to differences in the internal structure of micelles. In the case of sample 4, where the central gradient part is fairly long and both, soluble and insoluble, ends of chains are relatively short, the situation is different. The aggregates are formed but the distribution function of association numbers does not show any preference value. The probability that a chain is a part of an associate with a particular association number,  $A_s$ , decreases with increasing  $A_s$ . On the other hand, aggregates with a high number of chains, even higher number than that of the corresponding diblock copolymers, are formed. As we will show below these associates do not have structure similar to the micelles of linear diblocks. This open association behavior is even more pronounced for the “fully gradient” copolymer (sample 5).

Several snapshots of the simulation box are shown to illustrate the differences between individual samples (Fig. 2). The solvent quality and concentration are the same as in Fig. 1. In the snapshot of sample 1, well defined

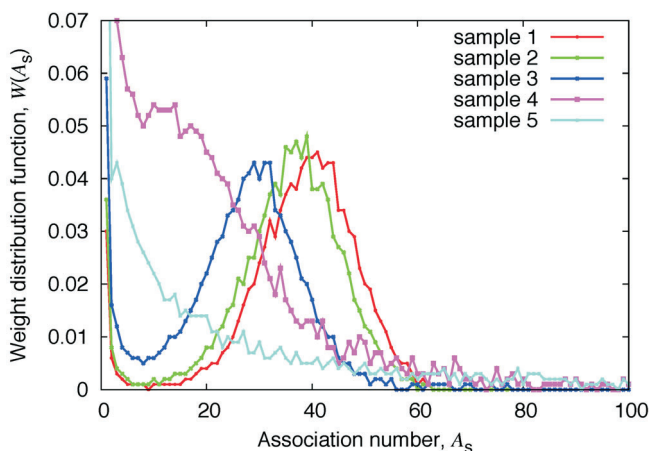


FIG. 1

Weight distribution function of association numbers,  $\varepsilon = 0.30$ ,  $c = 0.10$ . For composition profiles see Scheme 1

micelles with nicely segregated cores and coronas are clearly seen. For samples 2 and 3, defined associates are also seen, but the particles are more and more spread. There is a significant difference between the first three samples, samples 1–3, and the remaining samples 4 and 5, similar to the difference in the case of distribution functions of sizes. We can recognize insoluble domains in the snapshot of sample 4 but the solution of sample 5 seems to be “homogeneous” without any domains.

Next we are going to show how the size of aggregates and the size of domains depends on the concentration and on the quality of solvent. Sample 2 (Fig. 3) shows the behavior which is well known for linear diblocks<sup>1–9</sup>. The most probable association number,  $A_s$ , increases with increasing concentration and with deteriorating quality of the selective solvent. An interesting behavior, which is completely different from that of the previous samples, can be observed for samples 4 and 5. In the case of sample 4, the associates with a high value of  $A_s$  do not form at concentration  $c = 0.10$ . For both qualities of the solvent the  $W(A_s)$  curves smoothly decrease. When the concentration is set to  $c = 0.15$ , aggregates with high number of chains appear in the solution. The number of chains belonging to one “associate” in theta solvent can attain any value. It can also reach almost the maximum

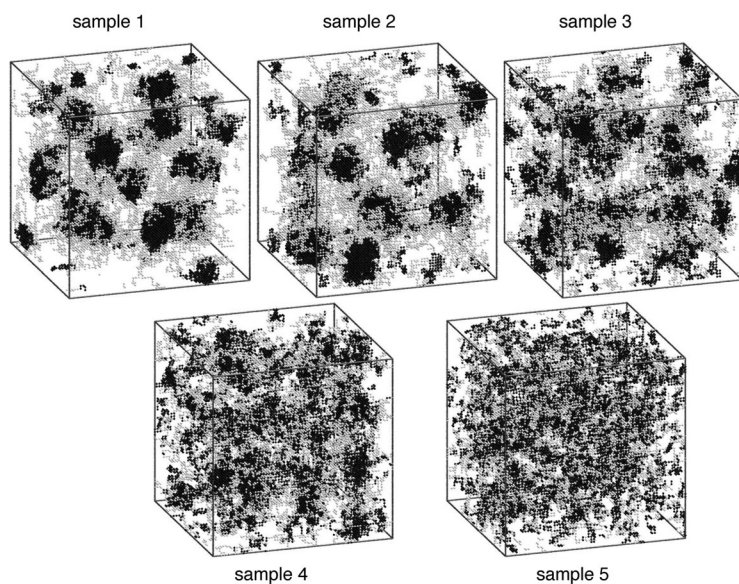


FIG. 2

Snapshots of simulation boxes,  $\epsilon = 0.30$ ,  $c = 0.10$

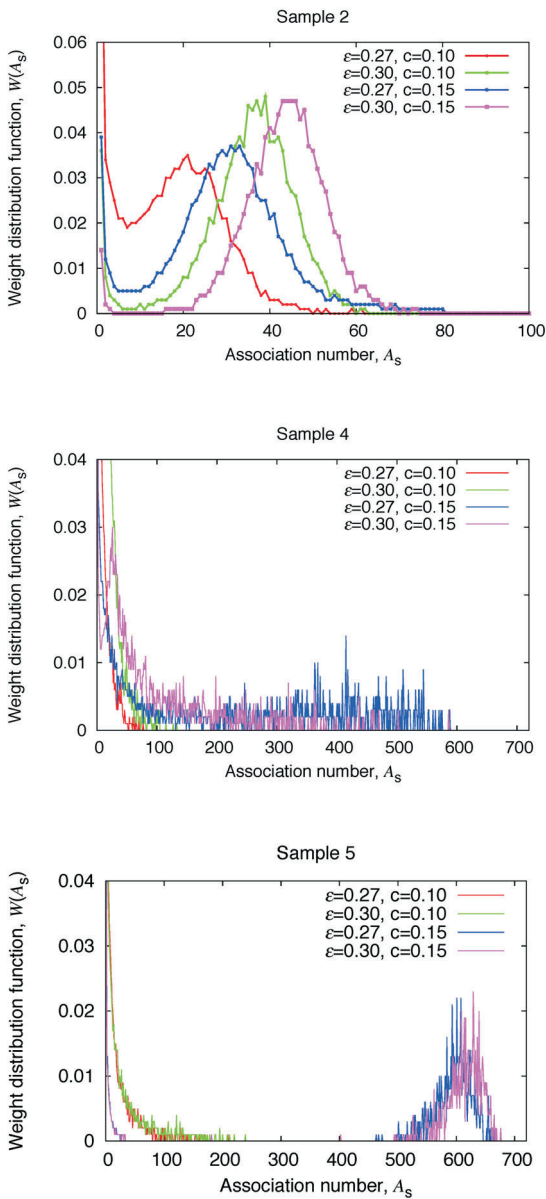


FIG. 3  
Weight distribution functions of association numbers



number of chains in the simulation box. In poorer solvent, a peak appears for small values of  $A_s$  but also aggregates with numbers of chains exceeding one half of the total number of chains in the simulation box are formed. From the snapshot of sample 5 we can see that associates are not formed at all in solutions with concentration  $c = 0.10$ . This fact is confirmed also by distribution functions. The situation changes at higher concentration,  $c = 0.15$ . Under these conditions, the maxima of distribution functions appear for  $A_s$  which correspond to the total number of chains in the box. It means that almost every chain is a part of one single aggregate which is formed in the solution. However, this aggregate is not a micelle or an associate with core and corona, any domains of insoluble segments are not seen (see snapshot in Fig. 4). Every chain is connected to other chains directly or through other chains and the copolymer creates an infinite network. This behavior resembles the formation of gels. In further text we will focus our attention on polymers which form defined aggregates. A more detailed analysis of the polymers forming gel-like structures is still in progress and will be the subject of a separate study.

In Fig. 5, the densities of segments A and B in associates as functions of the distance from the centre of mass of the associate are shown. The associates formed by linear diblocks (sample 1) and associates formed by polymers of sample 2 have similar profiles. They consist of a dense core, where only insoluble segments are present and a relatively large corona consisting

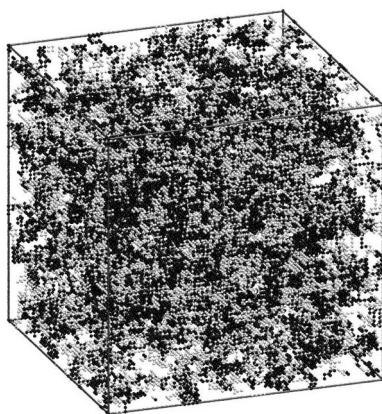


FIG. 4  
Snapshot of simulation box, sample 5,  $c = 0.15$ ,  $\epsilon = 0.30$



of soluble parts of chains, which is a typical structure of micelles of linear diblocks. The structure of the associates formed by sample 3 is slightly different. It still forms defined associates (see Figs 1 and 2) but from Fig. 5 it can be seen that their cores do not consist of insoluble segments only. The soluble segments are also present close to the centre of mass. The interface between the core and corona is wide and diffuse and the peripheral soluble part containing the soluble segments only is narrow. Similar differences between micelles of block copolymers and micelles of gradient copolymers were also observed experimentally<sup>17,25–27</sup>.

The shape of associates can be estimated from the asphericity parameter  $\alpha$  (refs<sup>36,37</sup>),

$$\alpha = \frac{\sum_{i>j=1}^3 (\langle R_i^2 \rangle - \langle R_j^2 \rangle)^2}{2 \left( \sum_{i=1}^3 \langle R_i^2 \rangle \right)^2} \quad (2)$$

where  $R_i$ ,  $R_j$  are the principal components of gyration tensor of associate. The asphericity parameter can vary from  $\alpha = 0$  for perfect spheres to  $\alpha = 1$  for long thin cylinders. Nonzero values of  $\alpha$  correspond to ellipsoids. In practice, when  $\alpha \leq 0.1$  associates are considered to be spherical<sup>36,37</sup>. The asphericity parameters as functions of the association number,  $\alpha = \alpha(A_s)$ , are shown in Fig. 6. For better understanding, the weight distribution functions of association numbers have been also included in these figures. The most populated micelles, i.e., those corresponding to the most probable

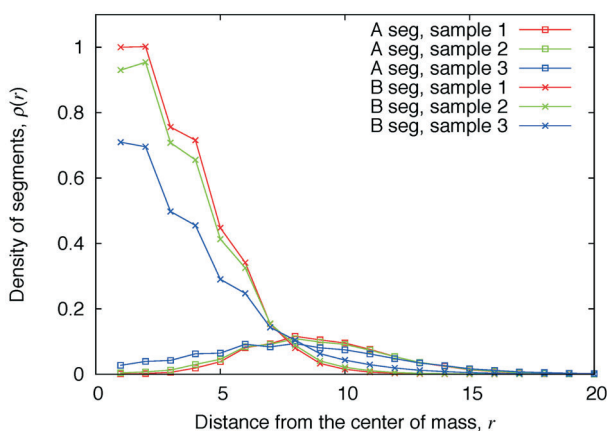


FIG. 5

Density of soluble and insoluble segments A and B as a function of distance from the center of mass of associate,  $c = 0.15$ ,  $\epsilon = 0.27$

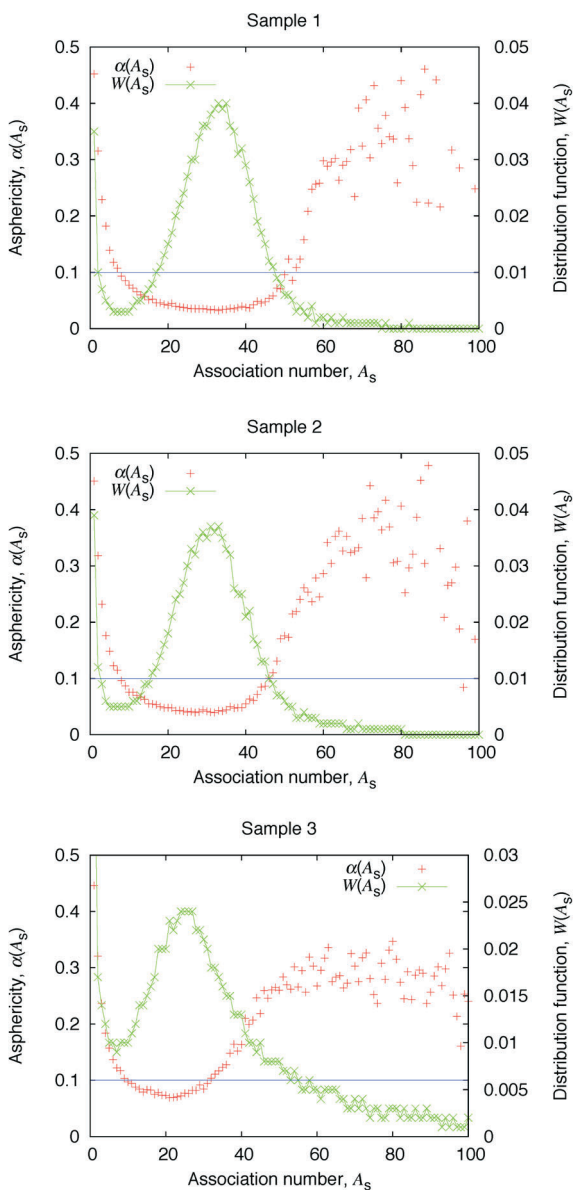


FIG. 6

Asphericity as a function of association number for  $c = 0.15$  and  $\varepsilon = 0.27$  (left y axes) and weight distribution functions (right y axes). The line  $\alpha = \alpha(A_s) = 0.1$  is dividing micelles to spherical (below the line) and non spherical (above the line) according to the asphericity parameter  $\alpha$

association numbers, formed by samples 1 and 2 are spherical ( $\alpha$  is less than 0.1). The asphericity reaches higher values only for associates with low and high association numbers which are only rarely found in the samples. Noisy data for high values of  $A_s$  are caused by very low statistics of Monte Carlo data for these associates. Differences in asphericity as well as in distribution functions of associates formed by chains of sample 1 and 2 are really small. More significant differences are seen for micelles formed by sample 3. The curve  $\alpha = \alpha(A_s)$  has qualitatively the same shape as those for samples 1 and 2 but its values corresponding to the most probable associates are significantly higher. Micelles formed by chains with such composition are more like ellipsoids.

## CONCLUSION

In this paper we have presented work concerning the association behavior of copolymer chains with different composition profiles. It was shown that even small changes in sequences of soluble and insoluble segments can lead to significant differences in their solution behavior.

Chains with longer soluble and insoluble ends form associates with dense insoluble cores and soluble coronas. These associates resemble well known micelles of linear diblock copolymers but some differences in their shape and structure were detected: the presence of a longer middle gradient part causes deviations from the spherical shape of micelles and interpenetration of soluble and insoluble segments in the middle part of a micelle.

When the soluble and insoluble chain ends are shorter, the copolymers do not form micelles with sufficiently segregated cores and shells. Their behavior resembles that of gels. We can recognize domains of insoluble segments and large particles consisting of these domains under certain conditions. But in case of copolymers with fully gradient composition profile, the aggregates have not been seen at all. Such copolymers do not aggregate at low concentrations and form a gel-like structures at higher concentrations.

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