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**Abstract**
We use molecular dynamics simulations to study the static properties of a single linear
multiblock copolymer chain under poor solvent conditions varying the block length $N$, the
number of blocks $n$, and the solvent quality by variation of the temperature $T$. We study the
most symmetrical case, where the number of blocks of monomers of type A, $n_A$, equals that of
monomers B, $n_B$ ($n_A = n_B = n/2$), the length of all blocks is the same irrespective of their
type, and the potential parameters are also chosen symmetrically, as for a standard
Lennard-Jones fluid. Under poor solvent conditions the chains collapse and blocks with
monomers of the same type form clusters, which are phase separated from the clusters with
monomers of the other type. We study the dependence of the size of the clusters formed on $n$,
$N$ and $T$. Furthermore, we discuss our results with respect to recent simulation data on the
phase behaviour of such macromolecules, providing a complete picture for the cluster
formations in single multiblock copolymer chains under poor solvent conditions.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Block copolymers have recently been the subject of many
experimental and theoretical studies, as such systems are
highly involved in industrial applications [1–54]. Block
copolymer melts are the most studied systems in this
respect [1–48]. We also note here that various copolymer
systems have been studied on many other occasions in different
geometries, i.e., in a selective nanoslit [55], on nanopatterned
surfaces [56–58], in nanopores [59], in the case of nanoparticle
aggregation [60], etc. Many theoretical, experimental, and
simulation studies deal with these systems. In particular,
theory predicts that melts of block copolymer chains for the
most symmetrical case (equal block length and composition)
form lamellar structure, given that the scaling parameter that
controls the phase behaviour ($\chi N$) is high enough to lead
to phase separation between the A and B blocks [11–13].

Simulations have confirmed that this parameter controls the
phase behaviour of such systems [4]. It has also been
discussed that the geometry of the microphase separated
regions is controlled by the number of blocks $n$, as well
as other parameters, i.e., relative size and arrangement of
blocks [4]. Subsequently, theoretical studies were extended
to cover the case of melts of multiblock copolymer chains
(two types of monomer compose each chain composed of
more than two blocks). It was shown that this case has
similar behaviour to a melt of diblock copolymer chains [35].
That is, a lamellar structure for the most symmetric case.
Nevertheless, in the case of infinitely dilute solutions, it is
sufficient to study isolated multiblock copolymer chains, where
only interactions (which can be of short range) within the
chain and the effect of the solvent are relevant [49–54]. The
phase behaviour of such systems has been studied by means
of computer simulations for chain lengths and temperature

ranges accessible to simulations [49, 50]. Also, the dynamic properties of such macromolecules have been the subject of recent simulation studies [54]. Interestingly, such systems are also closely related to various toy models (i.e., the HP model [61]), which try to mimic the behaviour of various biomacromolecules, which are formed by periodically repeated structural units ('monomers') along their chain, in order to understand complicated biological processes, i.e., protein folding [62], helical structures [63], etc.

Under Theta ($\Theta$) conditions or temperatures close to the $\Theta$ temperature, it is expected that a single linear symmetric multiblock copolymer chain would form a coil structure, where blocks of different type (A, B) hardly interact [49–54]. In fact, an expansion in the dimensions of the chain is taking place due to the repulsive interactions between neighbouring blocks A and B along the chain. Also, the spherical symmetry of the macromolecule should give way to an ellipsoidal overall formation [51–54]. The chain flexibility could also be restricted as a result of the neighbouring unfavourable interactions of different monomer types along the chain. However, the most interesting behaviour is observed under poor solvent conditions. In this case, chain collapses adopting a globular overall formation and different aspects of phase behaviour have been discussed depending on the block length $N$, the number of blocks $n$, and the temperature $T$, which can be used to tune the quality of the solvent [49, 50]. It has been discussed that three different regimes can be unambiguously distinguished. The first is a regime where only two domains of monomers of different type are formed. In this case all blocks of A monomers form a single cluster, while all the blocks of B-type monomers belong to another cluster without the occurrence of any variation in the number of clusters. This means that the clusters are always separated by an A–B interface and one cluster of A or B monomers never splits into two distinct clusters. Another scenario suggests that full phase separation, as defined above, takes place with a certain probability, which can be very high or very small according to the values of $N, n$, and $T$. The third scenario corresponds to the case where full phase separation as discussed above (formation of only two clusters with different types of monomers) cannot take place and a symmetric variation in the number of clusters $N_{cl}$ around an average value ($2 < N_{cl} < n$) is observed [49, 50].

Guided by theory [35], one would rather expect in the long chain limit that a ground-state-type structure would be a single lamellar domain, where an interface between all A- and B-type blocks is formed, similarly to what is known for multiblock copolymer melts. Such a structure would have much less (unfavourable) A–B contacts compared to a multidomain structure of A and B clusters, which is kinetically favoured in simulations. The phase behaviour of multiblock copolymer chains has already been rather extensively discussed [49, 50]. The overall properties of single multiblock copolymer chains have also been the subject of various studies [51–54]. In the following we focus our discussion on the static properties of the clusters formed for a single multiblock copolymer chain for a variety of parameters $N, n$, and $T$ accessible to our simulations. In this way, we provide a complete picture of
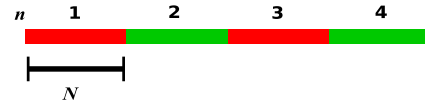


**Figure 1.** Definition of the structural parameters describing our linear multiblock copolymer chains. $n$ (in this case $n = 4$) is the number of different blocks A and B ($n_A = n_B = n/2$) denoted with different colours (or grey tones) and $N$ is the length of each block. All the blocks, irrespective of whether they are of type A or B, have the same length $N$. Then the total length of the chain is $nN$.

the cluster formations in a single multiblock copolymer chain under poor solvent conditions. Our results are discussed within the framework of recent results on the phase behaviour of such macromolecules [49, 50].

The rest of the paper is organized as follows. In section 2 we describe our simulation model and methods to analyse our results. In section 3 we present our results on the analysis of the size of the clusters formed, and in section 4 we give our concluding remarks.

## 2. Model and methods to analyse the results

We have considered symmetric linear multiblock copolymers, i.e., the length of all blocks, irrespective of their type, is $N$, the number of A-type blocks is equal to the number of B-type blocks, with $n$ being an even number denoting the total number of blocks. In our model the blocks of types A and B alternate along the chain. The above parameters are presented schematically in figure 1, where the different colours correspond to the different types of blocks. A single multiblock chain of four blocks is shown; two blocks of A-type monomers and two blocks of B-type monomers compose the multiblock chain in this figure.

Our chains are modelled by the standard bead–spring model [49, 50, 54, 64–69], where the beads interact via a cut and shifted Lennard-Jones (LJ) potential given by the following formula:

$$U_{LJ}^{\alpha\beta}(r) = 4\varepsilon_{LJ}^{\alpha\beta}[(\sigma_{LJ}^{\alpha\beta}/r)^{12} - (\sigma_{LJ}^{\alpha\beta}/r)^6] + C, \qquad r \leqslant r_c, \tag{1}$$

where $\alpha, \beta = $ A, B denote the different types of monomers, and the constant $C$ is defined such that the potential is continuous at the cut-off ($r_c = 2.5$). For simplicity, $\sigma_{LJ}^{\alpha\beta} = 1$, $k_B = 1$, but $\varepsilon_{LJ}^{AA} = \varepsilon_{LJ}^{BB} = 2\varepsilon_{LJ}^{AB} = 1$, in order to create an unmixing tendency between monomers A and B belonging to different blocks, as done in previous studies, and as is used for a standard system (LJ fluid) [70]. Therefore, $\Delta\varepsilon = \varepsilon_{LJ}^{AB} - 1/2(\varepsilon_{LJ}^{AA} + \varepsilon_{LJ}^{BB})$ was kept the same throughout our simulations and $\chi$ ($\chi \propto \Delta\varepsilon/T$) was varied by tuning the temperature $T$. The connectivity along the chain was maintained by the 'finitely extensible non-linear elastic' (FENE) potential

$$U_{FENE} = -\tfrac{1}{2}kr_0^2 \ln[1 - (r/r_0)^2], \qquad 0 < r \leqslant r_0. \tag{2}$$

$U_{FENE}(r \geqslant r_0) = \infty$, and the standard choices $r_0 = 1.5$ and $k = 30$ were used.

For this model we know rather roughly the $\Theta$ temperature [71], namely $\Theta \approx 3.0$. We also know that for
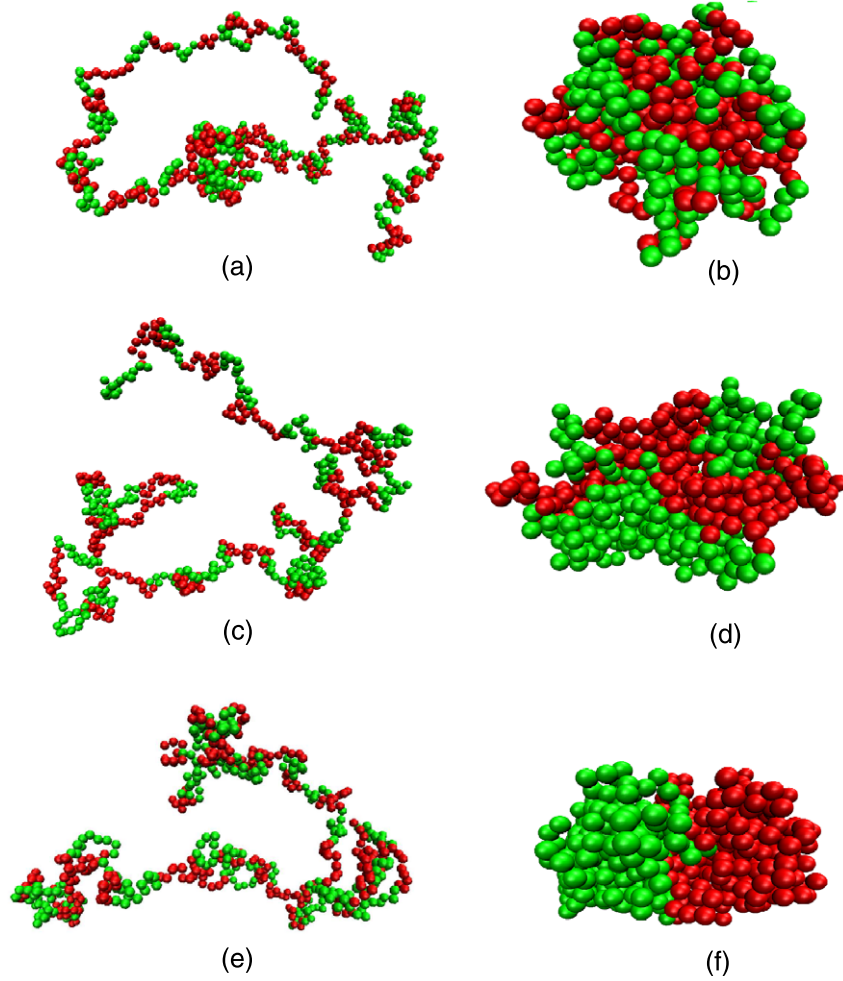
**Figure 2.** Snapshot pictures of different multiblock copolymers with the same total length $nN = 600$. Snapshots (a) and (b) refer to a multiblock copolymer chain with $N = 6$, (c) and (d) to $N = 15$, and (e) and (f) to $N = 60$. Different colours (or grey tones) correspond to different types of monomers. Cases (a), (c), and (e) are snapshots taken at $T = 3.0$. At this temperature the snapshots look rather similar and the chain obtains coil-like formations. Snapshots (b), (d), and (f) correspond to the temperature $T = 1.5$. In this case the chain collapses and different scenarios of phase behaviour are conceivable. In case (b) a symmetric variation of the number of clusters ($N_{cl}$) around an average value ($2 < N_{cl} < n$) takes place during the simulation. The formation of only two clusters containing different types of beads of all blocks never occurs. In case (d) the formation of only two clusters (of different beads) occurs with a certain probability, while in case (f) this probability is $P(N_{cl} = n = 2) = 1$ (one cluster contains blocks of monomers of type A and one cluster is composed of blocks of B-type monomers).

the LJ fluid, which is a standard system, phase separation occurs at a temperature close to $T = 1.5$. Moreover, the phase separation is favoured by the increasing degree of polymerization, and we expect to be able to observe phase separation at temperatures down to $T = 1.5$, also making use of our previous experience with this model [72, 73]. Indeed, phase separation is encountered for the systems under consideration (e.g., see figure 2). For many of the studied cases phase separation is already observed at temperatures close to $T = 2.4$, which is the temperature at which the system enters the regime where the chains collapse, i.e., effects due to the solvent are progressively becoming important. It is also clear that the use of symmetric structural and potential parameters facilitates our study. Moreover comparison with theoretical arguments could rather be more relevant. We use standard molecular dynamics (MD) simulations where the temperature is controlled by a Langevin thermostat, as was done in previous

studies [49, 50, 64–73]. Thus, the equation of motion

$$m \frac{d^2 \vec{r}_i}{dt^2} = -\nabla U_i - m\gamma \frac{d\vec{r}_i}{dt} + \vec{\Gamma}_i(t) \tag{3}$$

is numerically integrated using the GROMACS package. In equation (3), $t$ denotes time, $U_i$ is the total potential the $i$th bead experiences, $m$ is the mass which is taken as unity, $\gamma$ is the friction coefficient, and $\vec{\Gamma}_i(t)$ is the random force. $\gamma$ and $\vec{\Gamma}_i(t)$ are related by the standard fluctuation-dissipation relation

$$\langle \vec{\Gamma}_i(t) \cdot \vec{\Gamma}_j(t') \rangle = 6k_B T \gamma \delta_{ij} \delta(t - t'). \tag{4}$$

As in previous work [64–73], the friction coefficient was chosen as $\gamma = 0.5$. For the integration of equation (3) the leap-frog algorithm [74] is used with a time step of $\Delta t = 0.006\tau$, where the natural time unit is defined as $\tau = (m\sigma_{LJ}^2/\epsilon_{LJ})^{1/2} = 1$.

We simulated our systems at a temperature close to the $\Theta$ temperature ($T \approx 3.0$) with an integration time step $\Delta t = 0.006\tau$. For longer chains, we used higher temperatures for long equilibration runs, which were typically $30 \times 10^6 \tau$. After equilibration, we collected a number of independent samples (typically 500), which we used as initial configurations for slow cooling runs. We remind the reader that in our simulations the effect of the solvent is taken into account only implicitly, i.e., the solvent quality is tuned by variation of the temperature as is common practice. For our slow cooling runs, the temperature was lowered from a high temperature ($T = 3.0$) to a lower one ($T = 1.5$) in temperature steps $\Delta T = 0.1$, running the system at each temperature for a time range of $2 \times 10^6$ MD steps. For temperatures below $T = 2.1$ the intrinsic relaxation time of the chains starts to exceed the simulation time. Therefore, taking this large number of statistically independent 'cooling histories' is indispensable, in order to obtain meaningful statistical results. We also point out that the temperature $T = 1.5$ is low enough in order to access the most interesting regime where the chains collapse to form cluster formations. Of course, simulation of lower temperatures could also be interesting in order to try to compare our results with relevant theoretical arguments, given our rather short chain lengths, but then it would be impossible to simulate such a system with our method. We also note that the size $L$ of the simulation box was chosen such that the multiblock copolymer chain never interacts with its periodic images. For instance, for a chain of total length $nN = 600$, $L = 120$. For smaller or longer chains we used correspondingly smaller or larger simulation boxes, satisfying always the above criterion for the size $L$ of the simulation box. Further details on the simulated model have been discussed elsewhere [49, 50].

At temperatures close to $\Theta$, coil structures are formed and it seems visually (figures 2(a), (c), and (e)) that small differences exist for multiblock chains of different structural parameters $n$, $N$, as for example in figure 2. Of course, even at this high temperature differences in the overall formation of the coil structure occur, but here we mainly focus on the static properties of the clusters. The most interesting effect would be that the overall formation of the chains deviates from a spherical shape. At such temperatures, blocks of the same type of beads can only occasionally form clusters due to the high presence of thermal fluctuations. At temperatures below $T \approx 2.4$ the chains collapse and blocks of the same type of monomer form clusters with other monomers belonging to different blocks, due to the unfavourable interactions between A and B beads. Figure 2 also shows this case of phase separation, where in case (b) all blocks of the same type are not able to join together to a single cluster. In this case, we have a symmetric variation in the number of clusters, as has been discussed elsewhere [49, 50]. Then in case (d), the formation of only two clusters of dissimilar blocks is taking place with a certain probability, which might be high or small according to the choice of the parameters $n$ and $N$. In case (f) the blocks of different type are always phase separated and they form two different clusters, with an A–B interface formed between clusters. Here, the thermal fluctuations cannot overcome the incompatibility between dissimilar beads, and the clusters are

always phase separated. One would need to identify the beads belonging to each cluster in order to describe the overall sizes of these cluster formations. We used the Stillinger criterion and the standard choice $r_n = 1.5$ [75], as was done in previous work [49, 50, 72, 73]. We also used smaller values of $r_n$ and similar results were obtained, while higher $r_n$ values are hardly significant, due to the rapid fall-off of the LJ potential.

Properties, $F$, depending on the fluctuating number of clusters, should be averaged with the probability $P(x)$ that a number of clusters per block occurs ($x$), i.e.,

$$\bar{F} = \sum_x P(x) F(x). \tag{5}$$

Due to the symmetry of our model, the statistical analysis for A and B clusters should end up with the same results. This is confirmed in our analysis, validating also our simulation protocol. Therefore, results on the clusters' properties will refer either to clusters with monomers of type A or clusters with monomers of type B only, and nowhere are clusters of A and B monomers in a single cluster considered, although this is possible given our criterion $r_n$ due to thermal fluctuations.

## 3. Results and discussion

In figure 3 we present results for the density profiles of multiblock chains with the same total length $nN = 600$, but different combinations of parameters $n$ and $N$, mathematically expressed by the following formula:

$$\rho(|\vec{r}|) = \langle \sum_{i=1}^{nN} \delta(\vec{r} - \vec{r}_c - \vec{r}_i) \rangle, \tag{6}$$

where $\delta(\vec{x})$ is the Dirac delta function, $\vec{r}_c$ the position of the centre of mass of the whole chain and $\vec{r}_i$ are the positions of all monomers irrespective of their type (A or B). The angle brackets denote an average over all configurations as usual. At low temperatures (e.g., in figure 3(a), $T = 1.8$) the differences are more pronounced than they appear at higher temperatures, i.e., $T = 3.0$ (figure 3(b)). However, the differences between a homopolymer chain of the same length ($N = 600$) and multiblock chains ($nN = 600$) at both temperatures are rather high even at temperatures close to $\Theta$, showing that the case of multiblock copolymers strongly deviates from the case of a homopolymer chain. Multiblock copolymer chains are, overall, rather swollen in the radial directions due to the unfavourable interactions between neighbouring A and B blocks at 'high' temperature and all different blocks at lower temperatures. At $T = 1.8$ and for small $n$ (or equivalently high $N$, since $nN$ is fixed in this case) the multiblock copolymers have pronounced differences in their densities close to the centre of the macromolecule. This region of $n(2 < n < 20)$ for this total chain length corresponds to case (f) of figure 2, where full phase separation of the blocks of different types has taken place. Even though the chains exhibit the same phase behaviour, rather pronounced differences are observed in the density profiles, showing that the interface between A and B monomers is not the same in all cases. As $n$ increases, one would expect that the contacts between A and B monomers
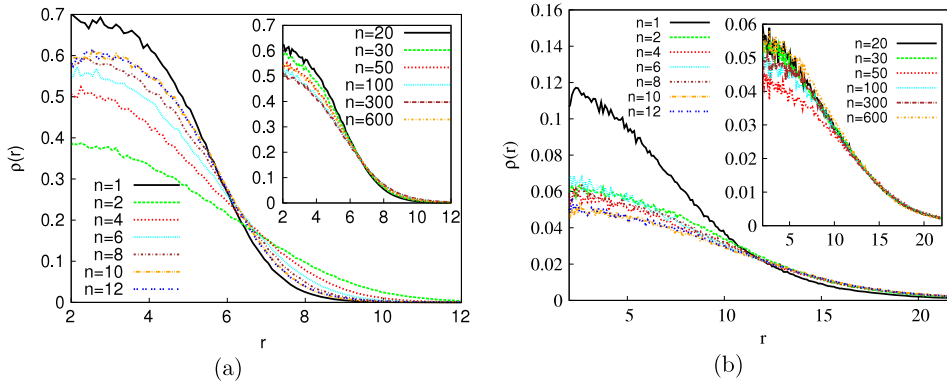
**Figure 3.** Density profile $\rho(r) = \rho(|\vec{r}|)$ plotted versus the radial distance $r = |\vec{r}|$ from the centre of mass of the chain. The temperatures $T = 1.8$ (a) and $T = 3.0$ (b) are shown.
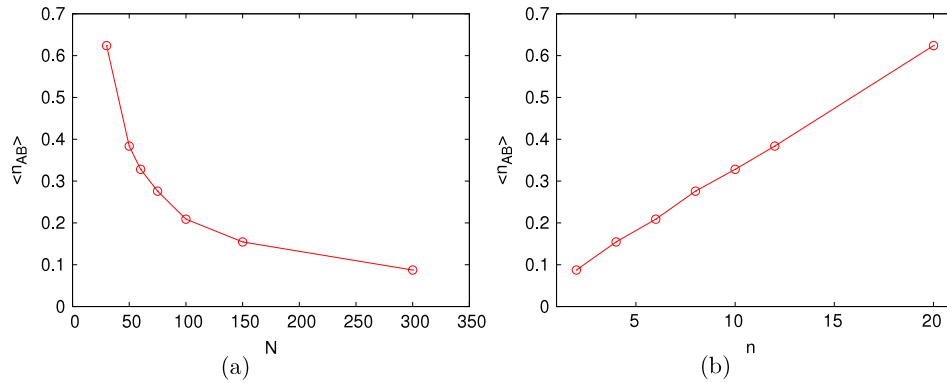


**Figure 4.** Average number of contacts $\langle n_{AB} \rangle$ between different types of monomers plotted versus block length $N$ (a) or versus number of blocks $n$ (b). In all cases $nN = 600$. The range of $N$ (or $n$) corresponds to the case where all blocks of type A are always joined together forming a cluster, while monomers of type B belong to another cluster and an A–B interface between these two clusters is formed.

at the interface should also increase in the collapse state ($T = 1.5$), and the cross-section should rather change from a double-cylinder-like to a dumbbell-like shape [68]. Therefore, it is relevant that we count the contacts between A and B beads, which is expressed by the following formula [69]:

$$n_{AB} = 4\pi \int_0^{r_n} g_{AB}(\Delta r)(\Delta r)^2 d(\Delta r), \qquad (7)$$

where $\Delta r$ is the absolute value of the distance between two sites of monomers $\vec{r}_i, \vec{r}_j$ in the multiblock copolymer chain, and $g_{AB}$ is the corresponding radial distribution function. Equation (7) means that a pair of monomers (A, B) is defined to have a pairwise contact if their distance is less than $r_n$. Similar quantities have been also used to characterize the incompatibility between linear and star chains in polymer melts and blends [76–78]. As can be seen from figure 4, the number of contacts A–B averaged over all conformations increases as the number of blocks $n$ increases. Also, we could see from figure 4(b) that the average number of blocks has a linear dependence on the number of blocks $n$, although we always have the formation of only two phase separated clusters, and the number of contacts per monomer remains less than 1.0. One would expect that $\langle n_{AB} \rangle < 1.0$ could be an indication for full phase separation. Lower values of unfavourable contacts

indicate the occurrence of only two phase separated clusters of A and B blocks (full phase separation) present at this low temperature. For high values of $n$ (figure 3(a)) there are rather small differences in the density profiles. In this regime a variation in the number of clusters has been observed. At $T = 3.0$ (figure 3(b)) the differences which were present for small $n$ at low temperatures have almost disappeared. Already at $T = 2.4$ the behaviour shown in figure 3(b) preempts that of figure 3(a), and is an indication that the chain leaves the collapsed state. For $T > 2.4$ differences should also result from the deviation of the overall formation from a completely spherically formation. We postpone such detailed discussion on these phenomena to a later communication.

We turn now to the properties characterizing the size of the clusters. Assuming that there should not be any preferential orientation, it is natural to characterize the size of our clusters by calculating the gyration radii of the formed clusters. Figure 5 shows results for $\langle R_g^2 \rangle$ and the temperature dependence of their size. For these results the total length of the multiblock copolymer chains is $nN = 600$. At first, we can clearly see (figure 5(a)) the effect of the temperature on the homopolymer chain. A major change in the slope of the cluster size with the temperature occurs at temperatures close to $T = 2.4$ and it is completed at temperatures close to $T \approx 2.2$. A smooth crossover from coil-like
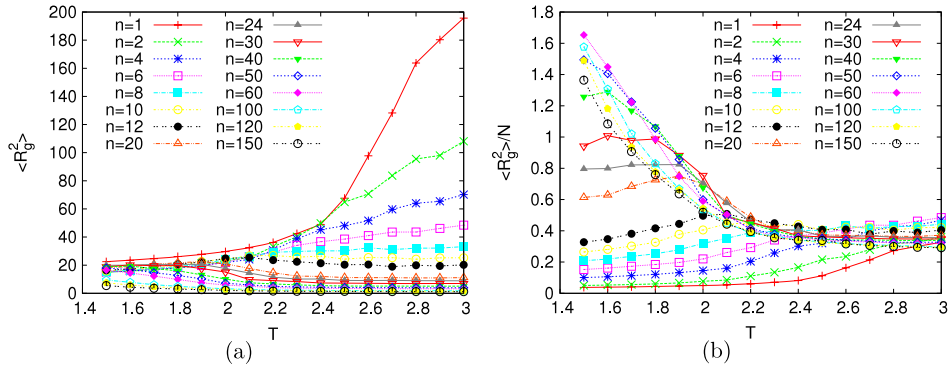
**Figure 5.** (a) The mean square gyration radius $\langle R_{\mathrm{g}}^2 \rangle$ of clusters A or B versus temperature. (b) The same data, normalized by the block length $N$. Data are shown for different numbers of blocks $n$. In all cases $nN = 600$.

structures to collapsed-chain structures takes place for this range of temperatures. This crossover becomes smoother in the multiblock copolymer cases. Also, it seems to be slightly shifted to lower temperatures, i.e., close to $T = 2.0$–$2.2$. For the multiblock copolymer chains, we can distinguish two different behaviours. For small $n$ (these cases correspond to phase behaviour like the one shown in figure 2(f)), the size of the clusters shows a monotonic behaviour with the temperature variation, i.e., the size of the cluster increases monotonically with the increase of the temperature. As $n$ increases, the variation with the temperature is smaller. Of course at high temperatures, where rather individual blocks compose each cluster, the size of these clusters has a straightforward dependence on the size of the individual blocks. Moreover, the length is rather high ($n$ low, since $nN = $ const in this case) and the probability for two clusters to join is 'high', due to the high length of the blocks and the high flexibility of the chain, which has a lower number of unfavourable A–B contacts. Then, we can distinguish a second behaviour, where the size of the clusters at higher temperatures is smaller than that of the clusters at low temperatures. In this case and at temperatures close to $\Theta$, the clusters, which are composed of rather individual blocks, have smaller dimensions compared to their size at low temperatures, where blocks join together, leading to the formation of clusters of monomers of the same type. Overall, as the number of blocks $n$ increases, the behaviour of multiblock copolymers deviates further from the homopolymer case. Moreover, the decrease of the block length $N$ results in clusters of smaller dimensions in all cases and at all temperatures. Only at low temperatures and in the regime where full phase separation occurs (small values of $n$, in the range of $N$ and $T$ presented here) can we see that the clusters have the same size. This is the case where the multiblock copolymer chain has only two clusters with monomers of different types, but each cluster contains the same number of monomers A or B for different $n$. This is the proof that the interface between A and B clusters is mainly held responsible for the differences arising in the density profiles for small $n$ at low temperatures. It is natural that the size of the single cluster of the homopolymer case should be the highest at 'high' temperatures (the block is longest, $N = 600$ in this case). However, plotting our data in a different way (figure 5(b)),

we can see that the dimensions of the clusters are on average (normalized by $N$) higher than the dimensions of the individual blocks at higher temperatures. In such a plot one can still distinguish between the different regimes discussed above.

In figure 6 we present results for the dependence of the average size of the cluster formations on the number of blocks $n/2$ of A-type monomers. Of course, as has already been discussed, the results are the same for B-type monomers due to the symmetry of our model. Therefore, keeping the block length $N$ constant, we altered the number of blocks $n$. Figure 6(a) presents such results at $T = 1.5$. When $N$ is small (e.g., $N = 5$), a rather small variation with the number $n/2$ of A or B blocks is seen. As the block length increases the slope of the curves also increases, showing that the variation with the number of blocks $n$ is high. It should be conceivable that also for high $N$ ($N = 160$) a plateau-like regime could be reached as in the case of $N = 5$, such that the system departs from the full phase separation regime. Yet, we are not able to access this regime with our simulations. On increasing the temperature, for instance to $T = 2.1$ (not shown here), the cases of small $N$ do not show any dependence on the variation of the number of blocks, whereas for high $N$ the linear dependence regime becomes smaller. We know that phase separation is favoured from higher block lengths. Therefore, blocks of small $N$ start to behave independently (leave a cluster) already at a lower temperature. At temperatures close to the $\Theta$ temperature (above $T = 2.4$, i.e., $T = 2.7$, figure 6(b)) cluster formations containing two or more blocks of the same type of monomer are hardly formed. Therefore, one should hardly observe any dependence on the number of blocks $n$ and the size of the clusters should rather reflect the size of individual blocks. However, we remind the reader that, even at these high temperatures, blocks with monomers of the same type do occasionally form clusters, and therefore the size of these clusters should not be considered absolutely as the size of the individual blocks.

It would be desirable to plot our results in such a way that the regime of rather individual clusters can be distinguished from the regime of the collapsed chain. Such plots are shown in figure 7. At low temperatures (i.e., $T = 1.5$, figure 7(a)) and for block lengths $N$ below 20 (for these systems a variation in the number of clusters is observed and occasionally only two
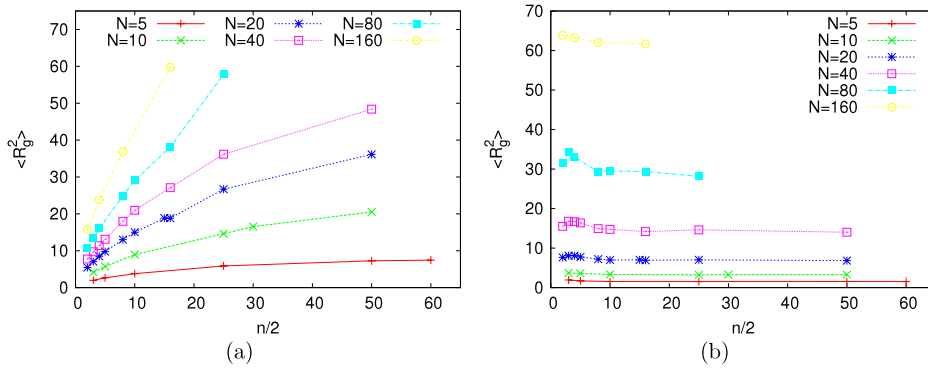
**Figure 6.** The mean square gyration radius $\langle R_g^2 \rangle$ of clusters A or B plotted versus the number of A or B blocks ($n_A = n_B = n/2$) for different block lengths. Two different temperatures are shown: $T = 1.5$ (a) and $T = 2.7$ (b).
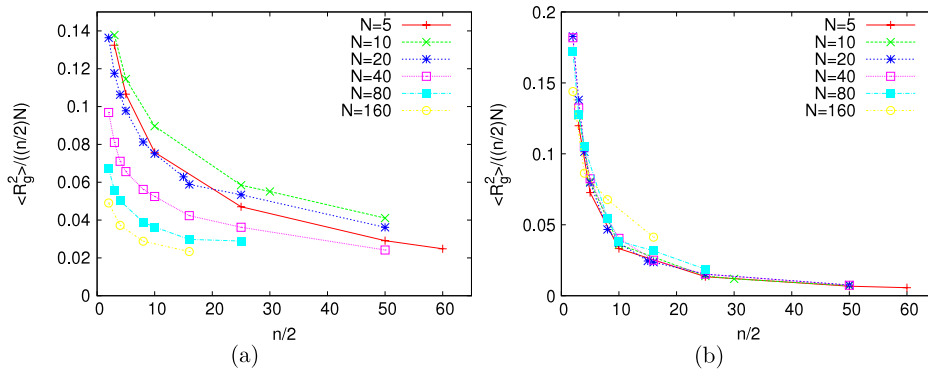


**Figure 7.** The mean square gyration radius $\langle R_g^2 \rangle$ of clusters A or B divided by the number of A or B blocks ($n_A = n_B = n/2$) and the block length ($N$) plotted versus this number of A or B blocks for different block lengths. Two different temperatures are shown: $T = 1.5$ (a) and $T = 2.4$ (b).

separated clusters of different monomers are observed [49, 50]) the curves do not show any systematic behaviour. It is only for higher block length $N$, where the block length is high enough to lead to phase separation between different blocks, that we can clearly see the different behaviour. A 'plateau regime' is accessed faster for higher $N$. As the temperature increases (above $T \approx 2.4$), we reach a temperature where the curves collapse onto a single curve for the different block lengths $N$ showing the same behaviour with the number of A or B blocks $n/2$. Our claim for a universal temperature boundary around $T = 2.4$ (figure 7(b)) seems to be correct. The effect of the solvent quality is proven to play an important role below this temperature, for all the multiblock chains. Further increase of the temperature increases the overall size of the chains. Thus, at $T = 3.0$ (not shown here) the curves are still on top of each other as in figure 7(b), but only a small change in the slope of the curves with the number of blocks $n/2$ can be observed. This shows that the increase of the temperature has the effect of weakening further the dependence on the number of blocks $n$. Also, increase of the temperature shifts the curvatures slightly to higher values of $(\langle R_g^2 \rangle)/(Nn_A)$, as is expected.

We can present correspondingly the dependence of the cluster sizes on the block length for different multiblock copolymer chains composed of different numbers of blocks ($n_A = n_B = n/2$). Such plots are presented in figure 8 for two different temperatures, i.e., a low temperature where

the chain is fully collapsed, and a temperature close to the $\Theta$ temperature. We have seen that full phase separation between blocks cannot take place when the block length is lower than $N = 20$ in the range of temperatures that are studied here. In the regime of full phase separation as has been discussed in this study (at rather low temperatures) the size of the clusters does not depend on the block length $N$ for different numbers of blocks, when the normalization of figure 8 is chosen. Below $N = 20$, full phase separation cannot take place, a variation in the number of clusters is observed, and higher dependence is seen on the block length $N$ for higher numbers of clusters, until a plateau is reached for $N > 20$. This behaviour is rather universal for multiblock chains of different numbers of blocks. Then, at $T = 3.0$ our data show the same behaviour exhibiting an almost linear dependence on $N$ for all the cases of different $n$. However, for small numbers of blocks ($n/2 = 4$) the curve is shifted. For higher numbers of blocks $n$ this shift is smaller as the number of blocks increases. This behaviour is compatible with the picture obtained from the overall properties, such as, for example, the density profiles of figure 3(b).

It is interesting to augment our discussion by dividing our data by the number of blocks ($n_A = n_B = n/2$, figure 9). At lower temperatures (i.e., $T = 1.5$) a universal boundary between two linear regimes is seen, when $N$ is small i.e., $N < 20$. Then a different regime is reached, where a linear
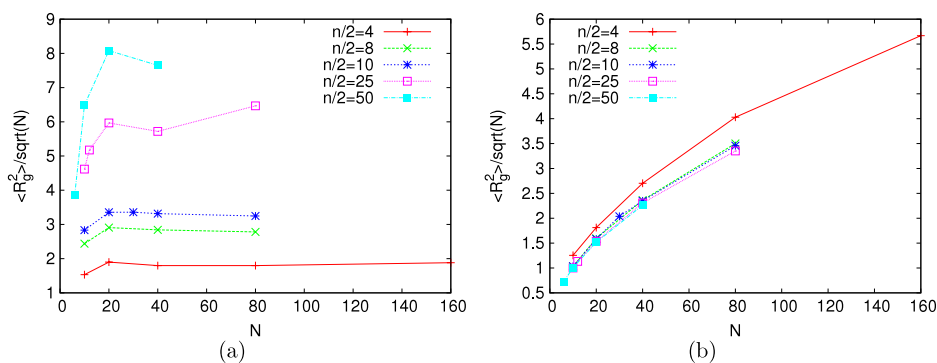
**Figure 8.** The mean square gyration radius $\langle R_g^2 \rangle$ of clusters A or B divided by the square root of the block length ($N$) plotted versus block length for different numbers of blocks as indicated. Two different temperatures are shown: $T = 1.5$ (a) and $T = 3.0$ (b).



**Figure 9.** The mean square gyration radius $\langle R_g^2 \rangle$ of clusters A or B divided by the number of blocks A or B ($n/2$) plotted versus block length for different numbers of blocks as indicated. Two different temperatures are shown: $T = 1.5$ (a) and $T = 3.0$ (b).
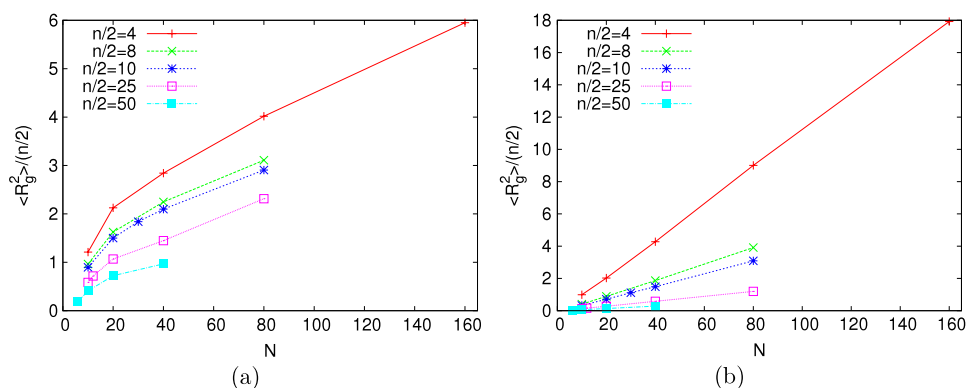
dependence with a different slope from the first linear regime is seen. As the temperature increases to close to $\Theta$, where the clusters are mainly composed of individual blocks, we can clearly see a single linear behaviour extending over all the considered block lengths $N$. When the number of blocks $n$ is small, the slope describing the dependence on the block length $N$ is higher. In this case blocks of monomers of the same type have higher probability than clusters occasionally. As the number of blocks $n$ increases, this probability of occasional clustering globally decreases as the number of unfavourable interactions decreases. Such a linear behaviour shows that the blocks individually behave 'locally' like homopolymer chains, and it is only the A–B contacts between connected blocks that control such behaviour. Plots like figure 9 provide an indication of the proximity of the $\Theta$ temperature for the chains.

## 4. Concluding remarks

In this study, we have investigated the static properties of a single multiblock copolymer chain under poor solvent conditions. The interactions were chosen symmetrically, as well as the structural parameters of the chains, i.e., the lengths of the blocks with monomers of type A or B were equal, and the number of blocks A was equal to the number of blocks B, while the blocks of different types alternated along the chain. We used standard molecular dynamics

simulations of a bead–spring model for our simulations, and we focused our discussion on the dependence of the size of the cluster formations occurring at low temperatures on the varied parameters, i.e., the block length $N$, the number of blocks $n$, and the temperature $T$, which was used to tune the quality of the solvent. Our analysis was presented in the context of recent results on the phase behaviour of such macromolecules. We showed that the number of contacts at the interface between A and B monomers, in the case where the multiblock copolymer chain at a low temperature (e.g., $T = 1.5$) is always split into two microphase separated clusters composed of blocks of the same type of monomers, varies linearly with the number of blocks and it is lower than 1.0 ($nN$ was kept constant).

Accordingly, we studied the dependence of the size of the clusters on the temperature, discussing our results in the context of recent results on the phase behaviour of such macromolecules. We could clearly distinguish the different regimes relating to the different phase behaviours. The dimensions of the clusters as a function of the number of blocks $n$ and the block length $N$ were independently studied. A comprehensive discussion of the dependence of the size of the clusters on the $n$ was given, discussing also the effect of the temperature. Furthermore, we showed (figure 7) that our data collapse onto a single curve when the chains leave the collapsed state and gradually adopt coil-like conformations. Thus, we could use such plots to identify this boundary. This

occurs at the temperature $T \approx 2.4$. Then, the dependence of the size of the formed clusters on the block length $N$ was presented. We showed that at lower temperature the collapsed state results in two different linear regimes with a smooth crossover between them. At temperatures close to the $\Theta$ temperature a linear dependence on the block length $N$ is seen for all block lengths with a different slope, i.e., as the number of blocks increases, there is a smaller dependence on the block length $N$, when the data for gyration radius are normalized by the number of blocks. Our results, in combination with recent results on the phase behaviour of symmetric linear multiblock copolymers, provide a complete picture of the behaviour of the cluster formations in such macromolecules for the range of parameters accessible to simulations.

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