Vol. 38 (2007) *ACTA PHYSICA POLONICA B* No 5

STRUCTURE OF POLYMER CHAINS IN AN ADSORBING SLIT*

Piotr Romiszowski, Andrzej Sikorski

Department of Chemistry, University of Warsaw
ul. Pasteura 1, 02-093 Warsaw, Poland

(Received November 11, 2006)

The aim of the study was to investigate polymer molecules located between two parallel and impenetrable attractive surfaces. The chains were constructed of united atoms (segments) and were restricted to knots of a simple cubic lattice. Each polymer consisted of three chains of equal length emanating from a common origin (a regular star). Since the chains were at good solvent conditions the only interaction between the segments of the chain was the excluded volume effect. The properties of the model chains were determined by means of Monte Carlo simulations with a sampling algorithm based on chain's local changes of conformation. The influence of the chain length, the confinement and the strength of adsorption on the structure of the system was studied. The differences and similarities in the structure (tails, trains, loops and bridges) for different adsorption regimes and size of the slit were shown and discussed. The dynamic behavior of the chain's structural elements was also studied.

PACS numbers: 02.50.Ng, 05.10.Ln, 61.25.Hq, 83.10.Nn

1. Introduction

Properties of polymer chains put into a slit comparable with their size are important because to their practical applications like colloidal stabilization, lubrication *etc.* [1]. Theoretical considerations concerning confined polymers go back to the pioneering works of de Gennes [2]. Computer simulation methods are also useful tools for studying the confined polymer systems because it is difficult to solve exactly analytical theories as well as to study such systems experimentally. Monte Carlo simulations of lattice models of confined linear polymer chains show a universal behavior disregarding the chain length and the size of the slit and give information about the density profiles [3–5]. Star-branched polymers are interesting model systems of

---

[*] Presented at the XIX Marian Smoluchowski Symposium on Statistical Physics, Kraków, Poland, May 14–17, 2006.

branched macromolecules for theoretical studies and real experiments [6]. Recently, simulations concerning idealized models of star-branched and linear polymers were carried out [7–9]. The universal behavior of the polymer size, the short- and long-time dynamic properties was shown. The changes of the mechanism of chains motion when going from a chain in a bulk to a slit were discussed. The structure of a polymer chain in the slit can be described in terms of trains, loops, bridges and tails. A train consists of adjacent beads which are adsorbed on one surface, a loop is a connection between trains on the same surface, a bridge is a connection between trains on different surfaces and a tail is loop at the end of a chain. The schemes of these elements are presented in Fig. 1. The structure of polymer chains adsorbed on one surface is usually described in terms of trains, loops and tails was given in the mean-field theory of Scheutjens and Fleer [10, 11]. Numerous computer simulations were also carried out for adsorbed chains with different internal macromolecular architecture on various surfaces. In our previous work we studied the structure of star-branched chains on one surface and these results can be treated as the reference state [12].

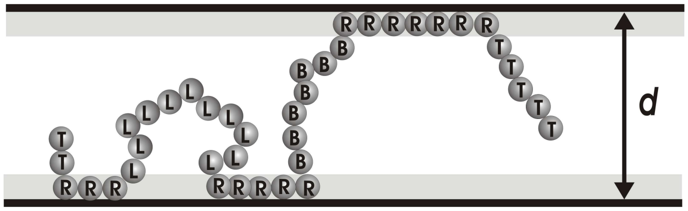

Fig. 1. The structure of a chain in a slit (a linear chain is shown for the sake of simplicity). From the left: a tail (T, consisting of 2 beads), a train (R, 3 beads), a loop (L, 11 beads), the second train (R, 5 beads), a bridge (B, 7 beads), the third train (R, 7 beads) and the second tail (T, 5 beads).

The main goal of this work was to study the structure of a single star-branched polymers confined between two parallel walls. The influence of this pure geometrical confinement combined with the attraction of the confining surfaces should change the structure of a polymer chain significantly. For the purpose of these calculations we built a united atom model of polymer chains on a simple cubic lattice models. The structure of star-branched chains adsorbed on one surface was recently determined and, hence, we have a good reference state. The model chains were simulated at good solvent conditions with the exclude volume potential only and a contact attractive potential was assumed between polymer segments and both confining surfaces. The properties of model macromolecules were determined from the Monte Carlo simulations, which were performed basing on a Metropolis sampling algorithm.

2. Model and the simulation algorithm

In our model all atomic details of the chains were suppressed and each polymer was constructed as a sequence of identical united atoms (beads) representing some real monomers. The positions of these beads were restricted to the vertices of a simple cubic lattice. The model chain represented a star-branched macromolecule consisted of $f = 3$ arms of equal length. It was assumed that there was no distinction between segment–segment, segment–solvent and solvent–solvent interactions and, therefore, the polymer was studied at good solvent conditions. The forbidding of the double occupancy of lattice sites by polymer segments (excluded volume) was introduced into the model. All chains were fully flexible because no local conformational biases were introduced. The chain was put into a Monte Carlo box with periodic boundary conditions employed in x and y directions only. The size of the Monte Carlo box, $L = 200$ lattice units, was large enough to avoid the interaction of chain with its image. The surfaces confining the polymer chains were parallel to the xy plane and separated by d consecutive lattice sites in the z-direction. The surfaces interacted with polymer segments with a simple contact potential:

$$V(z_i) = \begin{cases} 0 & \text{for} \quad 1 < z_i < d\,, \\ \varepsilon & \text{for} \quad z_i = 1 \text{ or } z_i = d\,, \\ \infty & \text{for} \quad z_i < 1 \text{ or } z_i > d\,, \end{cases} \tag{1}$$

where z_i is the z-coordinate of i-th segment and $\varepsilon < 0$. Thus, the surfaces were impenetrable for polymer segments and attractive for polymer segments adjacent to the surfaces. The inverse of the attractive potential can serve as the measure of the temperature of the system $T^* = -kT/\varepsilon$ [9]. The properties of the model chains were studied by means of the Monte Carlo simulation. The algorithm used was based on the asymmetric Metropolis scheme. In this algorithm an initial conformation of the chain underwent a series of local modifications. The following set of these micromodifications was used: two-bond motion, three-bond motion, three-bond crankshaft motion, chains ends reorientations, and branching point collective motion [13]. These micromodifications were selected randomly and one attempt of each micromodification per polymer segment defined a time unit. A new conformation obtained after such a change was accepted due to topological constraints, the intrachain excluded volume condition and the Metropolis criterion. The Monte Carlo simulation run consisted of 10^8 time units and before the production run, an equilibration run was always performed. The equilibration run consisted of 10^6–10^7 time units. The proper sampling of the phase space for each model chain was provided by the simulations carried out 20–30 times starting from quite different initial conformation. The initial chains conformations were produced by three different procedures which were described in detail elsewhere [7].

3. Results and discussion

The simulations were carried out for star-branched chains consisting of n = 17, 34, 67 and 134 segments in each of three arms what corresponded to the total number of segments in the chain N = 49, 100, 199 and 400. The distance between the surfaces was assumed as constant with $d = 7$. It was shown that this size of the slit star-branched chains enable, at certain conditions, the jumps of chains between the surfaces [10]. The strength of the adsorbing potential was varied from $\varepsilon = -0.1kT$ to $-1kT$ as it was previously shown that for this range the free (unconfined) polymer chain underwent the transition from a random coil state to a dense collapse globule [13]. Star-branched chains adsorbed on one surface also exhibits at this conditions a transition from a weak to a strong adsorption regime [12].

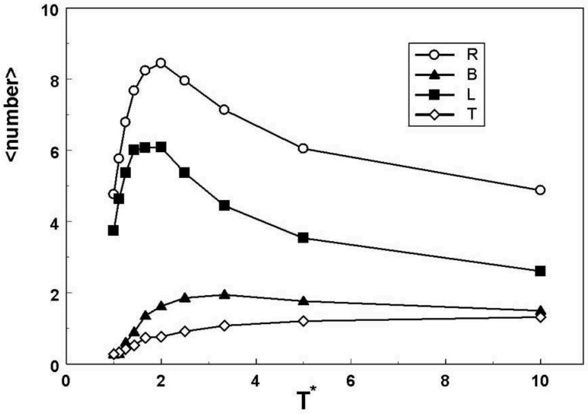

Fig. 2. The mean number of trains $\langle n_{\mathrm{tr}} \rangle$, bridges $\langle n_{\mathrm{br}} \rangle$, loops $\langle n_{\mathrm{lo}} \rangle$, and tails $\langle n_{\mathrm{ta}} \rangle$ of a chain consisting of $N = 199$ beads *versus* the reduced temperature T^*.

Figure 2 presents the temperature dependencies of the mean number of trains $\langle n_{\mathrm{tr}} \rangle$, loops $\langle n_{\mathrm{lo}} \rangle$, bridges $\langle n_{\mathrm{br}} \rangle$ and tails $\langle n_{\mathrm{ta}} \rangle$ for the chain consisting of $N = 199$ beads. At high temperature ($T^* > 3$) the numbers of trains and loops increase monotonically but moderately during the cooling of the system. The further annealing leads to the more rapid increase of $\langle n_{\mathrm{tr}} \rangle$ and $\langle n_{\mathrm{ta}} \rangle$. For temperature $T^* < 2$ the number of trains and loops decreases rapidly approaching values well below their high temperature limit. The existence of these maxima suggests that during the annealing process a rearrangement of the entire polymer chain takes place. The behavior of bridges is similar but their mean number $\langle n_{\mathrm{br}} \rangle$ is considerably lower and the maximum on the curve appears at higher temperature. It was shown that at low temperature the chain was almost fully adsorbed on one surface and sometime jumped to the opposite surface [9]. The number of tails decreases slowly in the entire range of temperature. The structure of an adsorbed chain is also described by the mean length of trains $\langle L_{\text{tr}} \rangle$, loops $\langle L_{\text{lo}} \rangle$, bridges $\langle L_{\text{br}} \rangle$ and tails $\langle L_{\text{ta}} \rangle$. The changes of these parameters with the temperature are presented in Fig. 3.

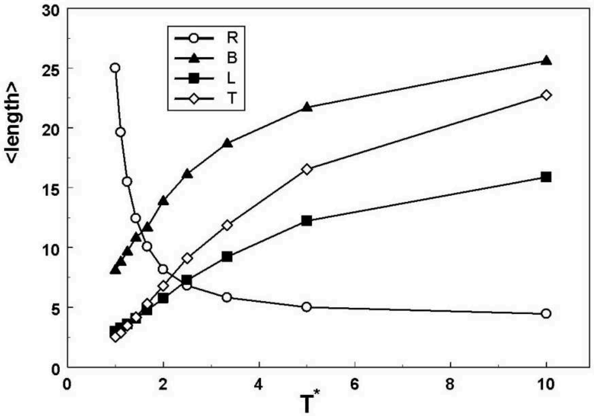

Fig. 3. The mean length of trains $\langle L_{\text{tr}} \rangle$, bridges $\langle L_{\text{br}} \rangle$, loops $\langle L_{\text{lo}} \rangle$ and tails $\langle L_{\text{ta}} \rangle$ of a chain consisting of $N = 199$ beads *versus* the reduced temperature T^*.

At high temperature bridges are the longest and, thus, dominate in the structure of the adsorbed polymer. At the lowest temperature under consideration the bridges were almost fully extended as their length $\langle L_{\text{br}} \rangle \sim 8$. The length of trains is the smallest one; the chain has only a few neighbor contacts with the surfaces. One can observe that at temperature $T^* < 2$ the mean length of bridges, loops and tails decrease smoothly with the decreasing of the temperature. This behavior is different when compared to that of a chain adsorbed on one surface where the length of loops had a maximum near the temperature $T^* = 2$ [12]. In the case of a polymer in the adsorbing slit the lengths of loops are limited because of the presence of the second surface (longer loops become bridges and the length of bridges is always higher than the length of loops).

The influence of the chain length on the number and the length of the structural elements at low temperature is presented in Figs. 4 and 5, respectively. The mean number of trains and loops is growing although non-linearly with the chain length. The number of bridges and tails remain very small and almost unchanged. The length of all structural elements remains almost unchanged. Scheutjens and Fleer predicted the same behavior for the linear chains [11]. The stability of structural elements of the star-branched polymer was also studied.

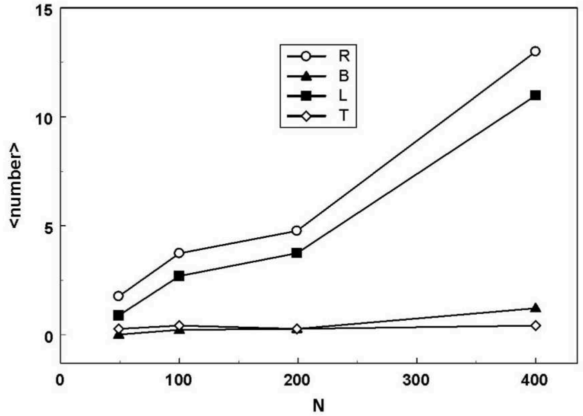

Fig. 4. The mean number of trains $\langle n_{\rm tr}\rangle$, bridges $\langle n_{\rm br}\rangle$, loops $\langle n_{\rm lo}\rangle$, and tails $\langle n_{\rm ta}\rangle$ *versus* the chain length N. The case of the temperature $T^* = 1.25$.

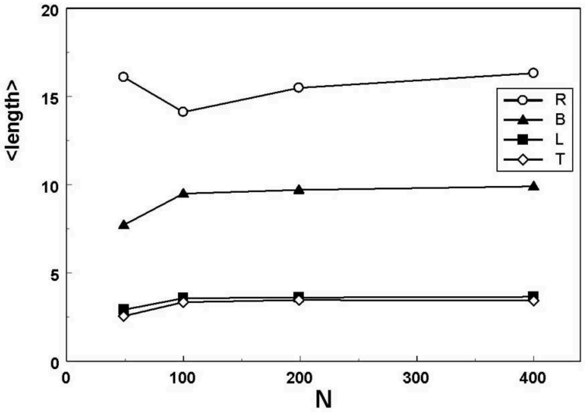

Fig. 5. The mean length of trains $\langle L_{\rm tr}\rangle$, bridges $\langle L_{\rm br}\rangle$, loops $\langle L_{\rm lo}\rangle$ and tails $\langle L_{\rm ta}\rangle$ *versus* the chain's arm length N. The case of the temperature $T^* = 1.25$.

Figures 6 and 7 show the mean lifetimes of trains, loops, bridges and tails for high and low temperature. The numbering of beads in these figures started from the branching point and goes to the arm's end. At high temperature the lifetimes of trains, loops and bridges prevail in the middle part of the chain. On the other hand, the number of tails is larger for ends of arms. The lifetimes of the structural elements at low temperature appeared to be quite different. The lifetimes of trains were almost constant along the entire chain contour and were close to 0.4 what means that, in average, in every time unit, a train disappears. The lifetimes of bridges and loops were approximately 5 and 15 times smaller, respectively. The lifetimes of tails were very close to zero for the entire polymer with the exception of very ends of the chain where they grow rapidly. One can also observe a different behavior of the vicinity of the branching point. This exceptional behavior of vicinity of the branching point could be explained by larger density of polymer segments in this region [12]. Therefore, the lifetimes of trains are higher here while the lifetimes of bridges and loops are lower.

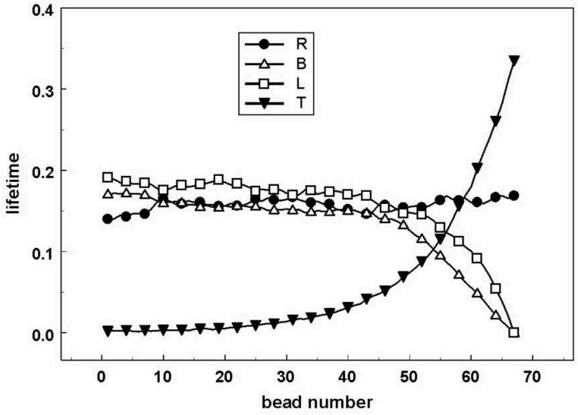

Fig. 6. The mean lifetimes of trains, bridges, loops and tails *versus* the bead number for the chain with $N = 199$ beads. The case of the temperature $T^* = 3.3$.

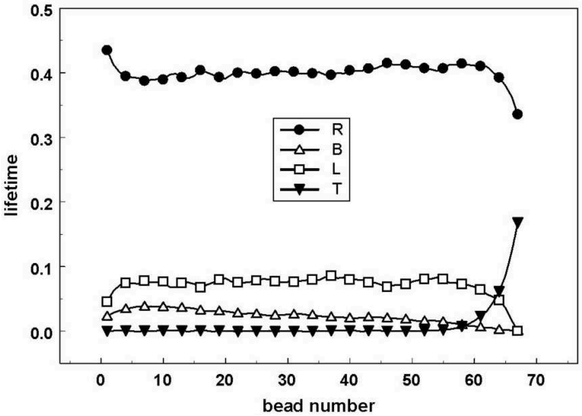

Fig. 7. The mean lifetimes of trains, bridges, loops and tails *versus* the bead number for the chain with $N = 199$ beads. The case of the temperature $T^* = 1.25$.

4. Conclusions

In this work we studied the structure of polymer chains confined in the adsorbing slit in the term of trains, loops, bridges and tails. The influence of the temperature and the length of the chain on these parameters was also studied and discussed. For this purpose we used an idealized lattice model of star-branched macromolecules and employed a Monte Carlo sampling algorithm. The main conclusion from this work is that the presence of the confinement and the attraction of the confining surfaces have impact on the structure of a chain and its dynamic properties. It was shown that the presence of the adsorbing slit changed significantly the structure of a star-branched polymer. The difference is especially visible at high temperature where the chain is involved in interaction with both confining surfaces. At low temperatures the chain is fully adsorbed on one side of the slit and this structure is qualitatively the same as that found for the chain adsorbed on one surface.

The computational part of this work was done at The Computer Center of the Department of Chemistry, University of Warsaw.

REFERENCES

[1] R. Eisenriegler, *Polymers Near Surfaces*, World Scientific, Singapore 1993.

[2] I. Teraoka, *Prog. Polym. Sci.* **21**, **89** (996).

[3] J.H. van Vliet, G. ten Brinke, *J. Chem. Phys.* **93**, 1436 (1990).

[4] A. Milchev, K. Binder, *Eur. Phys. J.* **B3**, 477 (1998).

[5] P. Cifra, T. Bleha, *Macromol. Theory Simul.* **8**, 603 (1999).

[6] G.S. Grest, L.J. Fetters, J.S. Huang, D. Richter, *Adv. Chem. Phys.* **94**, 67 (1996).

[7] A. Sikorski, P. Romiszowski, *J. Chem. Phys.* **116**, 1731 (2002).

[8] A. Sikorski, P. Romiszowski, *J. Chem. Phys.* **120**, 7206 (2004).

[9] P. Romiszowski, A. Sikorski, *J. Chem. Phys.* **123**, 104905 (2005).

[10] J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* **83**, 1619 (1979).

[11] J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* **84**, 178 (1980).

[12] A. Sikorski, *Macromol. Theory Simul.* **10**, 38 (2001).

[13] A. Sikorski, *Macromol. Theory Simul.* **2**, 309 (1993).