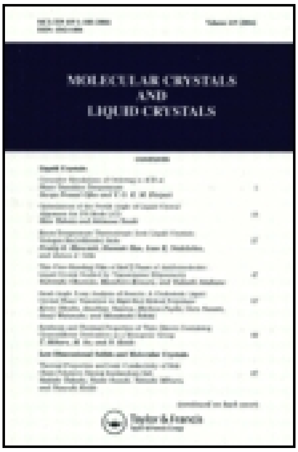

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Structure of Branched Polymer Chains Adsorbed on a Patterned Surface

Andrzej Sikorski [a] & Szymon Żerko [a]

[a] Department of Chemistry, University of Warsaw, Warsaw, Poland

Version of record first published: 16 Jun 2011

To cite this article: Andrzej Sikorski & Szymon Żerko (2011): The Structure of Branched Polymer Chains Adsorbed on a Patterned Surface, Molecular Crystals and Liquid Crystals, 547:1, 108/[1798]-115/[1805]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.572801

Mol. Cryst. Liq. Cryst., Vol. 547: pp. 108/[1798]–115/[1805], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.572801

Taylor & Francis
Taylor & Francis Group

The Structure of Branched Polymer Chains Adsorbed on a Patterned Surface

ANDRZEJ SIKORSKI AND SZYMON ŻERKO

Department of Chemistry, University of Warsaw, Warsaw, Poland

The model star-branched macromolecules were constructed of identical segments which positions were restricted to vertices of a simple cubic lattice. The chains were modeled at good solvent conditions and the excluded volume was the only interaction between the polymer segments. The model chain interacted via a simple contact potential with an impenetrable planar surface consisting of two kinds of points: attractive and repulsive arranged into strips. The properties of the system were determined by means of Monte Carlo simulations. The structure of adsorbed chains was found to be strongly dependent on the distance between the repulsive stripes when this distance was short and compared to the chain's size.

Keywords Adsorbed polymers; lattice models; Monte Carlo method; patterned surfaces

1. Introduction

Adsorbed polymer chains have recently been a subject of many experimental and theoretical works because of their practical importance, e.g., lubrication, colloidal stabilization, chromatography etc. [1]. The adsorption of a polymer chain is also interesting from the theoretical point of view as the presence of the surface changes the properties of the adsorbed macromolecule when compared with a chain in a solution and mean field theories remain the most popular treatment of adsorbed macromolecules [1]. Off-lattice Monte Carlo studies revealed some dynamic properties of adsorbed linear polymer chains [2–4] but it is still not clear if the self-diffusion coefficient scales with the chains length as N^{-1} or $N^{-3/2}$ [5–7].

The properties of branched polymer chains usually differ from those of their linear counterparts but this effect is especially pronounced at interfaces [1,8]. The simplest model of a non-linear macromolecule is a cyclic chain (ring) and these chains were found to be considerably stronger (ca. 40%) adsorbed when compared to linear ones [8,9]. Other non-linear polymer are uniform star-branched chains consisting of three branches of equal length emanating from a common origin. This class of polymers can be synthesized, their properties can be studied experimentally and they are especially useful for theoretical considerations [10]. It was shown that stars with the small number of arms are slightly (6%) stronger adsorbed than linear chains what

---

Address correspondence to Andrzej Sikorski, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland. Tel.: +(48 22) 822 0211; Fax: +(48 22) 822 5996; E-mail: sikorski@chem.uw.edu.pl

was explained by the compactness of the star polymer compared with the linear one [11].

Coarse-grained models of adsorbed star-branched polymer chains were recently developed and studied by means of lattice Monte Carlo simulation [8,12,13]. This model was also extended by the introduction of second adsorbing surface and, therefore, chains were confined in the slit and the structure of star-branched chains in confinement was determined and discussed: it was shown that chains fully adsorbed on one surface could jump from one surface to another [14].

The process of the adsorption of polymers and proteins on patterned surfaces became also recently a subject of studies. Such systems can be studied experimentally [15–21], theoretically [22–25] and by means of computer simulation [26–36] and quite different structures like homopolymers, copolymers, copolymer blends, polyelectrolytes and polymer brushes were the objects of these studies. In this paper we have studied regular star-branched homopolymers strongly adsorbed on a strip-patterned surface. The chains consisted of $f = 3$ arms (branches) and polymer segments were embedded to a simple cubic lattice (a coarse grained model). The model chains were studied at good solvent conditions as the excluded volume was the only intra-chain potential. The simulation Monte Carlo algorithm we used employed chains' local micromodifications of a Verdier-Stockmayer type. The structure of such macromolecules were studied and compared with those found for pure attractive surfaces [14].

2. The Model and the Method

Model star-branched chains consisted of $f = 3$ linear chains of equal length called 'arms'. The arms consisted of sequences of identical segments emanating from a common origin called the branching point. Each polymer segment can be treated as a representation of some monomers of a real polymer. In order to make the calculations more efficient the positions of polymer segments in space were restricted to vertices of a simple cubic lattice. The double occupancy of the same lattice site by polymer segments was forbidden what was equivalent to the effect of the excluded volume in the macromolecular system. No other polymer-polymer interactions were introduced into the model and it resembled good solvent conditions. The calculations were made for single chains, i.e., in the case of infinitely diluted polymer solution.

The macromolecules were located near a planar surface, which was parallel to the xy plane and put at $z = 0$. This surface was impenetrable for polymer segments and a square-well contact potential V was assumed between it and a polymer segment:

$$V(x_i, z_i = 1) = \begin{cases} \varepsilon_r & for\ \mathrm{mod}(x_i, d_v) = 0 \\ \varepsilon_a & for\ \mathrm{mod}(x_i, d_v) \neq 0 \end{cases} \tag{1}$$

where x_i and z_i are the coordinates of ith polymer segment along x and z axes respectively. The interaction V took place when a polymer segment was located near the surface ($z = 1$) and ε_a was a value of attractive contact potential, while ε_r was a repulsive contact potential. The repulsive points on the surface were arranged into strips. The repulsive strips were parallel to y axis and d_v was a distance between these strips. The width of each strip was one lattice point. This kind of surface patterning was rather common in real experiments where the surface is covered periodically [15–21]. The periodic boundary conditions were introduced along the x and y directions only. The size of the Monte Carlo box L was chosen large enough to minimize the influence of its size on the results.

The Monte Carlo simulations were carried out using a sampling algorithm in which the chain's conformation was locally changed by the following set of local moves [36]: (i) 2-segment motion, (ii) 3-segment motion, (iii) 3-segment crankshaft motion, (iv) 1- and 2-segment end reorientations and (v) the branching point collective motion. All these micromodifications were selected at random during the simulation. A new chain's conformation was accepted due to the chain connectivity and the excluded volume with the probability proportional to its Boltzmann's factor (the Metropolis scheme):

$$P_{old \to new} = \min[1, \exp(-\Delta E/kT)] \tag{2}$$

where $P_{old \to new}$ is the probability of the transition from an old to a new configuration, ΔE is an energy difference between the old and the new conformation, $k = 1$ is the Boltzmann constant and T is the temperature. Each simulation run consisted of 10^9–10^{10} time steps and was preceded by an equilibration run that lasted for 10^7–10^8 time units. This procedure was repeated about 10 times starting from different conformations of the chain.

3. Results and Discussion

The simulations were performed for star-branched chains consisted of $n = 17$, 34 and 67 segments in the arm what implied that the total number of segments in the macromolecule $N = f \cdot (n - 1) + 1 = 49$, 100 and 199. The distance between the repulsive stripes on the attractive surface was varied between $d_v = 2$ and $d_v = 50$: the distance 2 lattice units is the shortest possible ($d_v = 1$ corresponds to purely repulsive surface) while the distance 50 lattice units is larger than the diameter of the longest adsorbed polymer chain under consideration [8]. In order to keep the constant distance between the repulsive stripes in the entire Monte Carlo box along x and y axis its edge varied between $L = 180$ and 200 – one requires the condition $\mathrm{mod}(L, d_v) = 0$. The attractive potential of the surface was chosen as $\varepsilon_a = -1kT$ what corresponded to the strong adsorption regime [8] while the repulsive potential was chosen to be of the same strength $\varepsilon_r = 1kT$.

The size of a polymer chain was described as usual by the mean-squared radius of gyration of the entire star $<S^2>$. In order to make the results comparable for chains of different lengths the reduced quantities were introduced. The reduced size of chain was used $<S^2>/<S^2>_0$, where the index '0' refers to the chain adsorbed on a pure adsorbing surface. The reduced distance between the repulsive strips was calculated as $d_v/(2<S^2>^{1/2})$, because $2<S^2>^{1/2}$ is the approximate chain diameter. In Figure 1 we present the reduced size parameter $<S^2>/<S^2>_0$ as function of the distance between the repulsive strips $d_v/(2<S^2>^{1/2})$. The calculated parameter describing mean size of the macromolecule was rather statistically stable as the standard deviation did not exceed 3%. One can observe that curves are similar but not monotonic. The rapid increase of chain's size for lower values d_v is caused by the opening of the possibility of packing the chain along the y axis what was impossible in the

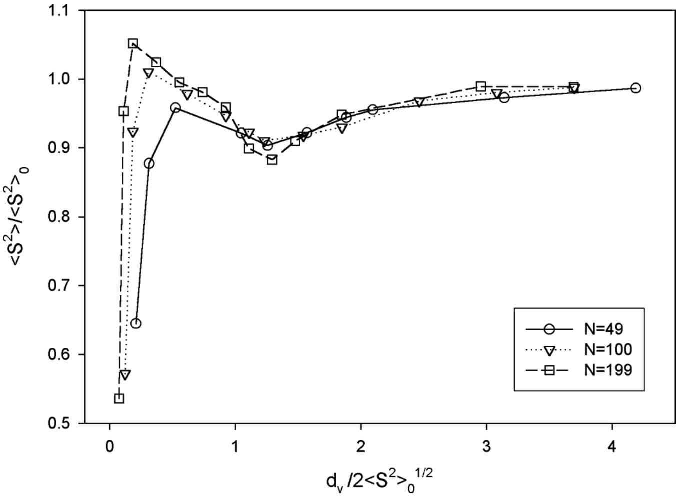

Figure 1. The reduced mean-squared radius of gyration $<S^2>/<S^2>_0$ as a function of the reduced distance between the repulsive stripes $d_v/<2S^2>_0^{1/2}$. The chain lengths are given in the inset.

case $d_v = 2$, as only rod structures could be packed there without energetic loses. The minima appear on all chain lengths near $d_v/(2<S^2>^{1/2}) = 1.3$, i.e., for distances longer that the mean chain diameter. The appearance of these minima can be explained by the asymmetry of the chain: at the minimum the longest axis of the shape ellipsoid becomes comparable with the distance d_v.

The surface contained the repulsive patterns along the y-axis and thus, one can expect some asymmetry of chain. For purpose this we also studied the changes of the contributions to the mean-squared radius of gyration along both x and y axes. The reduced size along both axes was expressed as the contributions to the reduced mean-squared radius of gyration. Figure 2 shows these contributions as functions of the reduced distance between the repulsive stripes. It appeared that the x components $<S_x^2>/<S_x^2>_0$ increase when the distance d_v increases. The changes in the y contributions are quite different. For the narrowest attractive strips ($d_v = 2$) S_y^2 is slightly larger than S_x^2 what implies that almost no direction is preferred in spite of the presence of the repulsive strips. It can be explained by the fact that for such narrow distances d_v the chain has to cross the strips many times because the probability of forming conformations with no energy losses (with few segments perpendicular to the y-axis: rod-like or Greek key-like) is rather small. The moderate increase of the distance between the repulsive strips (from $d_v = 3$ to $d_v = 5$) leads to the dramatic increase (approximately 3 times) of the chain's size along the y axis. This widening of attractive areas simply opened the possibility for more polymer segments to stay perpendicular to the y-axis. The same non-monotonic behavior of the chain's size in the direction parallel to stripes was found for linear charged homopolymers [26] and for linear stiff chains [28]. The further increase of the parameter d_v leads to the decrease of the radius of gyration: this decrease is more rapid for $d_v \leq 15$ and lower for $d_v > 15$. For longer distances d_v both contributions to the radius of gyration converge to the common value, i.e., the chain becomes isotropic along the xy plane. Thus, the presence of the minimum on $S^2(d_v)$ curve is obvious

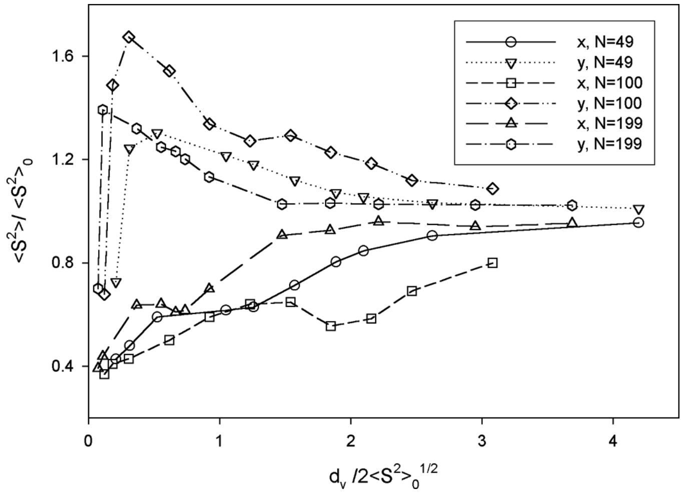

Figure 2. The x and y contributions to the reduced mean-squared radius of gyration $<S_x^2>/<S_x^2>_0$ and $<S_y^2>/<S_y^2>_0$ as a function of the reduced distance between the repulsive stripes $d_v/<2S^2>_0^{1/2}$.

as S^2 is a sum of two components: decreasing (S_y^2) and increasing (S_x^2). What is important, in the case of chains adsorbed on a patterning surface, one can show that the size of the chain is governed by the balance between the entropic losses and the energetic gains. This can be especially seen for very short distances between the repulsive strips.

The presence of anisotropic surface should induce some ordering of macromolecules. Figure 3 presents the changes of the fractions of polymer segments parallel to x and y axes with the distance between repulsive strips. One can observe that

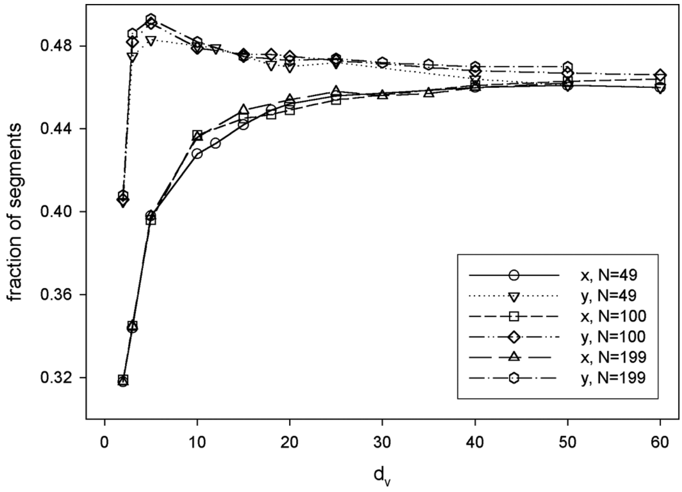

Figure 3. Fraction of polymer segments parallel to x and y axis as a function of the distance between the repulsive stripes d_v.

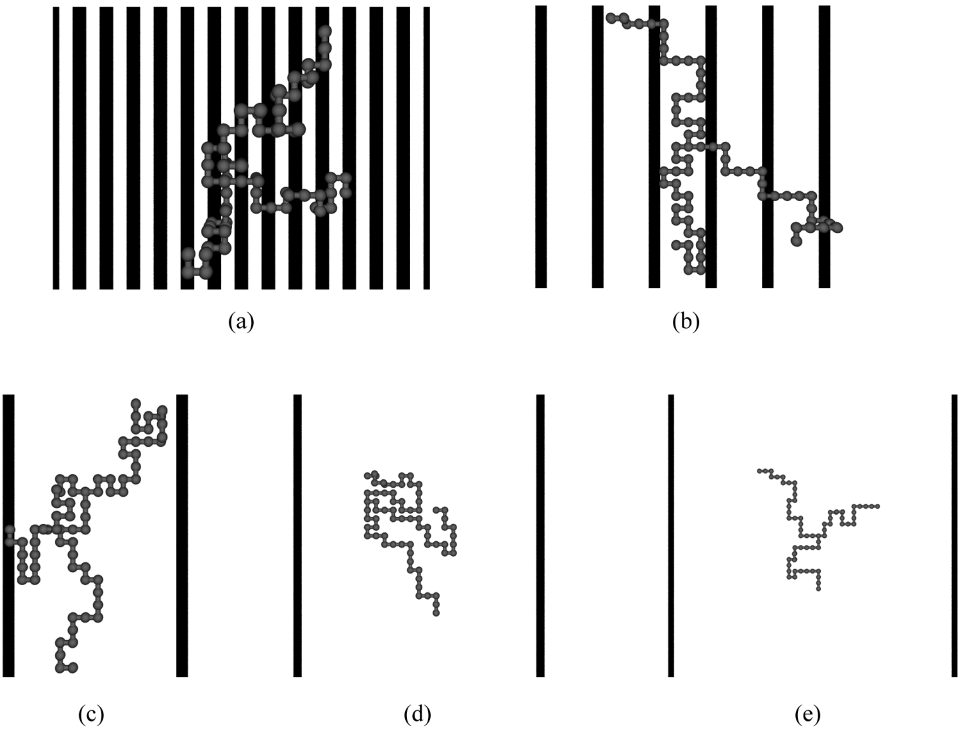

Figure 4. Typical snapshots of adsorbed chains: the chain consisted of $N = 199$ beads for $d_v = 2$ (a), 5 (b), 15 (c), 30 (d), and 50 (e).

the chain's length has almost no influence on the orientation of polymer segments. The number of segments parallel to x axis increases as the distance d_v increases and this increase is especially rapid for the shortest distances. Along the y direction one can observe the initial increase of the number of segments and then the smooth decrease. This initial increase of the number of polymer segments is caused by the decrease of the number of segments perpendicular to the xy surface. For longer distances between the strips both fractions converge to 0.47 (the remaining fraction of 0.06 segments is located perpendicularly to the surface). In Figure 4 we showed typical chain conformations for various distances between the repulsive strips. One can observe how the chain accommodates to the attractive area trying to minimize its energy while for short distances ($d_v = 2$ and 5) or is not able to avoid the repulsive stripes and a considerable number of segments becomes perpendicular to the surface.

4. Conclusions

In this work we present some results concerning simulations of star-branched chains adsorbed on a planar surface. The macromolecules were embedded to a simple cubic lattice with the coarse grained representation of chains. The system was at good solvent conditions and the excluded volume was the only intra-chain potential. The adsorbing surface was patterned with narrow and parallel repulsive strips. The properties of the model system were calculated using the Monte Carlo simulation method with a Metropolis-like sampling algorithm.

It was shown that the introduction of the attractive surface changed significantly the size and structure of chains – the strong adsorption leads to the formation of almost two-dimensional polymer structures. The introduction of the repulsive strips led to the further changes in the chain's size and these changes were dramatic for a very short distance between the repulsive strips only. For wider distances between these strips the chain is able to accommodate in attractive areas.

Acknowledgment

The computational part of this work was done using the computer cluster at the Computing Center of the Department of Chemistry at the University of Warsaw. This work was supported by the Polish Ministry of Science and Higher Education grant N N507 326536.

Reference

[1] Eisenriegler, E. (1993). *Polymers near Surfaces*, World Scientific: Singapore.
[2] Milchev, A., & Binder, K. (1996). *Macromolecules*, *29*, 343.
[3] Baschnagel, J., & Binder, K. (1996). *J. Phys. I (Fr.)*, *6*, 1271.
[4] Pandey, R. B., Milchev, A., & Binder, K. (1997). *Macromolecules*, *30*, 1194.
[5] Maier, B., & Rädler, J. O. (1999). *Phys. Rev. Lett.*, *82*, 1911.
[6] Sukhishvili, S. A., Chen, Y., Müller, J. D., Gratton, E., Schweizer, K. S., & Granick, S. (2000). *Nature*, *406*, 146.
[7] Sukhishvili, S. A., Chen, Y., Müller, J. D., Gratton, E., Schweizer, K. S., & Granick, S. (2002). *Macromolecules*, *35*, 1776.
[8] Sikorski, A. (2002). *Macromol. Theory Simul.*, *11*, 359.
[9] Kosmas, M. K. (1990). *Macromolecules*, *23*, 2061.
[10] Freire, J. J. (1999). *Adv. Pol. Sci.*, *143*, 35.
[11] Likos, C. N. (2006). *Soft Matter*, *2*, 478.
[12] Charmuszko, K., & Sikorski, A. (2009). *J. Non-Crystal. Solids*, *355*, 1408.
[13] Romiszowski, P., & Sikorski, A. (2005). *J. Chem. Phys.*, *123*, 104905.
[14] Rockford, L., Liu, Y., Mansky, P., & Russel, T. P. (1999). *Phys. Rev. Lett.*, *82*, 2602.
[15] Lei, S., Wang, C., Wan, L., & Bai, C. (2004). *J. Phys. Chem. B*, *108*, 1173.
[16] Shi, F., Wang, Z., Zhao, N., & Zhang, X. (2005). *Langmuir*, *21*, 1599.
[17] Denis, F. A., Pallandre, A., Nysten, B., Jonas, A. M., & Dupont-Gillain, C. C. (2005). *Small*, *1*, 984.
[18] Pallandre, A., De Meersman, B., Blondeau, F., Nysten, B., & Jonas, A. M. (2005). *J. Am. Chem. Soc.*, *127*, 4320.
[19] Wang, Y., Liu, Z., & Huang, Y. (2006). *Langmuir*, *22*, 1928.
[20] Glynos, E., Chremos, A., Petekidis, G., Camp, P. J., & Koutsos, V. (2007). *Macromolecules*, *40*, 6947.
[21] Petera, D., & Muthukumar, M. (1998). *J. Chem. Phys.*, *109*, 5101.
[22] Balazs, A., Singh, C., & Zhulina, E. B. (1998). *Macromolecules*, *31*, 6369.
[23] Seok, C., Freed, K. F., & Szleifer, I. (2004). *J. Chem. Phys.*, *120*, 7174.
[24] Kriksin, Y. A., Khalatur, P. G., & Khokhlov, A. R. (2005). *J. Chem. Phys.*, *122*, 114703.
[25] McNamara, J., Kong, C. Y., & Muthukumar, M. (2002). *J. Chem. Phys.*, *117*, 5354.
[26] Semler, J. J., & Genzer, J. (2003). *J. Chem. Phys.*, *119*, 5274.
[27] Cerda, J. J., & Sintes, T. (2005). *Biophys. Chem.*, *115*, 277.
[28] Jayaraman, A., Hall, C. K., & Genzer, J. (2005). *J. Chem. Phys.*, *123*, 124702.
[29] Patra, M., & Linse, P. (2006). *Macromolecules*, *39*, 4540.
[30] Chen, H., Peng, C., Ye, Z., Liu, H., Hu, Y., & Jiang, J. (2007). *Langmuir*, *23*, 2430.

[31] Al Sunaidi, A. (2007). *Macromol. Theory Simul.*, *16*, 86.
[32] Hoda, N., & Kumar, S. (2007). *Langmuir*, *23*, 1741.
[33] Chen, H., Peng, C., Sun, L., Liu, H., Hu, Y., & Jiang, J. (2007). *Langmuir*, *23*, 11112.
[34] Al Sunaidi, A. (2008). *Macromol. Theory Simul.*, *17*, 319.
[35] Koutsioubas, A. G., & Vanakaras, A. G. (2008). *Langmuir*, *24*, 13717.
[36] Sikorski, A. (1993). *Macromol. Theory Simul.*, *2*, 309.