(5) Tuzar, Z.; Petrus, V.; Kratochvil, P. *Makromol. Chem.* **1974**, *175*, 3181.
(6) Krause, S.; Reismiller, R. A. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 663.
(7) Stacy, C. J.; Kraus, G. *Polym. Eng. Sci.* **1977**, *17*, 627.
(8) de Gennes, P.-G. In *Solid State Phys. Suppl.* **1978**, *No. 14*.
(9) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(10) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443.
(11) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.
(12) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca (NY) and London, 1979.
(14) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(15) Casassa, E. F. *J. Polym. Sci., Part B* **1967**, *5*, 773.
(16) Daoud, M.; de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 85.
(17) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950** *18*, 1600.
(18) Hoeve, C. A. J.; DiMarzio, E. A.; Peyser, P. *J. Chem. Phys.* **1965**, *42*, 2558.
(19) Reference 13, pp 39–42.

Topological Constraints and Their Influence on the Properties of Synthetic Macromolecular Systems. 3. Triblock Copolymers Attached to a Surface

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ABSTRACT: Chain molecules with both ends strongly adsorbed to a surface are discussed as a model system for adsorption of triblock copolymers. Irreversible adsorption and absence of interaction between chain monomers and surface are assumed. Monte Carlo calculations are used to investigate the average conformation and the probability of knot formation for separate coils. A comparison is made with the probability of knot formation in ring polymers and scaling predictions. For overlapping coils scaling predicts that the layer thickness depends on the preparative stage due to the requirement of conservation of topological state, which leads to an additional excluded volume effect.

1. Introduction

Sterically stabilized colloidal suspensions are becoming increasingly important. Often polymers are used and various groups are currently investigating the forces between adsorbed layers of macromolecules.[1-8] Three essentially different systems can be distinguished, according to whether the adsorbed species are homopolymers, diblock copolymers, or triblock copolymers. To illustrate this, we will restrict ourselves to a discussion of the forces between layers adsorbed on mica involving polystyrene (PS) and poly(2-vinylpyridine) (PV2P). We will also assume that the polymer layer is irreversibly adsorbed.

The case of PS homopolymers adsorbed on mica and immersed in cyclohexane has been the subject of some controversy.[1,2,6,9,10] The force measured as a function of the distance between the micas contains a repulsive part followed by an attractive part for temperatures below and above the Θ-temperature (34.5 °C). Two explanations were put forward, a phase separation argument and a chain-bridging argument. Both may be present, but there are indications that bridging is the dominant factor.

Bridging can be avoided by using PS–PV2P diblock copolymers. The PV2P block adsorbs strongly on mica and if the surface is saturated, additional adsorption of PS will be negligible. In toluene, a good solvent for PS, the force is only repulsive with a steep uprise due to the onset of overlapping PS tails. This situation can be described well[8] by the Alexander–de Gennes theory[11,12] of terminally anchored chains. The overlapping coils force the PS chains away from the surface in a stretched conformation, leading to a flat concentration profile and a long-range repulsive force. Furthermore, the attractive part of the force reappears, but much smaller in magnitude than in the case of homopolymers, probably due to the absence of bridging.[8]

A third possibility is the use of PV2P–PS–PV2P triblock copolymers.[13] Again bridging is avoided. However, the repulsive layer now consists of loops instead of tails. In combination with the assumed irreversibility, this can have a significant effect since the topological constraints introduced in this way will lead to additional excluded volume effects.

There is another reason we are interested in triblock adsorption. In the dilute limit of separate coils, the situation closely resembles cyclization of linear polymers as described in a previous paper.[14] In particular, knots will again be present. Precisely how many is difficult to estimate off-hand, because the influence of the average monomer concentration inside the coil on the probability of knot formation is not well-known. That this is a problem of more than academic interest was pointed out by de Gennes recently.[15] In a short paper he suggested that the long-time memory effects in melts of crystallizable linear polymers may be related to tight knots. These might have been created during a previously conducted crystallization process accompanied by reeling in chains, containing a knot, from both ends. All these cases, ring polymers, loops, and unperturbed chains are characterized by different geometries and different average monomer concentrations.

The organization of this paper is as follows. In the next section a short description of the Monte Carlo method used to study the conformations and knot structure of ideal chain molecules attached with both ends to a plane will be given. Then in section 3 the results for the dilute limit of separate coils will be discussed. Finally, in section 4 the case of overlapping coils will be considered.

2. Monte Carlo Calculations

The Monte Carlo technique is used to create random walks which start and end at a flat surface and never cross the surface. As in the case of ring polymers we are con-

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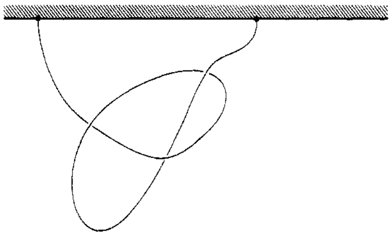

Figure 1. Example of a loop containing the simplest possible knot 3_1.

fronted with the fact that the probability of returning to the plane becomes vanishingly small for large walks. To avoid this problem a body-centered cubic (bcc) lattice is used and an enrichment factor is introduced. The bcc lattice has the advantage that a random walk on it is the product of three independent one-dimensional random walks in the x, y, and z directions.[14,16] For convenience the adsorbing plane is assumed to be at $x \equiv 1$ and the walks take place in the space $x \geq 1$. Only the one-dimensional random walk in the x direction will be considered here; the other two are trivial.

It is known[17] that the number of walks of k steps from an arbitrary point $x_0 \geq 1$ to $x = 0$, $N(x_0,k)$, satisfying $x \geq 1$ for all but the last point, is given by[17]

$$N(x_0,k) = \frac{x_0}{k}\binom{k}{\frac{k+x_0}{2}} \qquad (2.1)$$

starting from x_0, the next step goes to either $x_0 + 1$ or $x_0 - 1$. The number of different walks through these points is given by $N(x_0{+}1,k{-}1)$ and $N(x_0{-}1,k{-}1)$, respectively. Hence, if we look at all possible walks of k steps from x_0 to $x = 0$, satisfying $x \geq 1$ for all but the last point, a fraction

$$P(k,x_0,\delta) = N(x_0{+}\delta,k{-}1)/N(x_0,k) \qquad (2.2)$$

will be at $x_0 + \delta$ after the first step. Here $\delta = \pm 1$. Using eq 2.1, we find that this amounts to

$$P(k,x_0,\delta) = \frac{(x_0 + \delta)(k - \delta x_0)}{2x_0(k - 1)} \qquad (2.3)$$

In the following $P(k,x,\delta)$ will be used as the enrichment factor in the sense that a probability $P(k,x,\delta)$ will be given to the continuation $x + \delta$ if the previous $(N - k + 1)$th step ended at x. Here $N + 1$ is the length of the walk ending at $x = 0$, given the fact that we are interested in walks of length N ending at $x = 1$. As in the case of ring polymers the use of an enrichement factor implies that different steps of the random walk are no longer independent. However, the above discussion indicates that no serious errors will be introduced. For ring polymers this was actually verified by Chen.[18]

To investigate the knot structure of a thus obtained loop, the walk must be closed without introducing additional self-entanglements. Figure 1 illustrates a loop with the simplest knot possible and Figure 2 shows how loops are closed. Once a closed walk is obtained, the knot structure can be found by using a procedure described in a previous paper.[14] It is based on the Alexander polynomial and will not be discussed here again.

3. Separate Ideal Coils

In this section a single chain, strongly adsorbed with both ends to the surface, will be considered. The emphasis will be on the probability of knot formation in polymer loops as compared to polymer rings. We will restrict ourselves to Θ-conditions, since in a good solvent only a very small fraction of the chains will be knotted. For rings this was demonstrated by Vologodskii et al.[16] and Chen[18] and rationalized by Brochard and de Gennes.[19] In the case of polymer loops the fraction of knotted chains will even be less, due to a reduced average monomer concentration inside the coil.

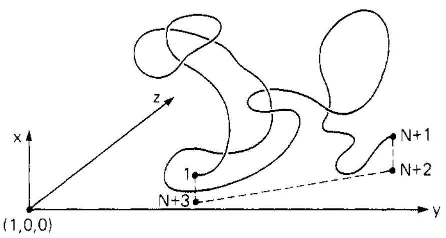

Figure 2. Loop closure. The beginning and ending points of the loop are indicated by 1 and $N + 1$, respectively. They are in the $x = 1$ plane. The walk satisfies $x \geq 1$. The loop is closed by adding the dashed line. Points $N + 2$ and $N + 3$ have the same coordinates as $N + 1$ and 1, respectively, except for the x coordinate, which is zero in both cases.

Brochard and de Gennes[19] argued that the number of self-entanglements in a coil is proportional to the number of nearest-neighbor contacts. In a Θ-solvent the probability for a binary encounter is proportional to c^{*2}, where c^* is the average monomer concentration inside the coil. The total number of self-entanglements N_s scales therefore like

$$N_s \sim Nc^*a^3 \qquad (3.1)$$

where N is the chain length and a the monomer length. For a given chain length, the number of entanglements and therefore also the probability of knot formation are determined by the average concentration inside the coil. Under Θ-conditions c^* can easily be found for polymer rings as well as for polymer loops. The mean square radius of gyration of ring molecules is given by[20]

$$R^2_{\mathrm{g,ring}} = Na^2/12 \qquad (3.2)$$

Hence, c^*_{ring}, defined as $N/(4\pi R^3_{\mathrm{g,ring}}/3)$, equals

$$c^*_{\mathrm{ring}} = (18(3^{1/2}))N^{-1/2}/(\pi a^3) \qquad (3.3)$$

To obtain a similar estimate for polymer loops we observe the following points. The model used to investigate this case consists of random walks which are products of two essentially different random walks: an ordinary two-dimensional random walk parallel to the surface with a step length $(2/3)^{1/2}\, a$ and a closed one-dimensional random walk perpendicular to the surface with a step length $a/3^{1/2}$. For the body-centered cubic lattice where the nearest neighbors of a lattice point (x,y,z) are given by $(x{\pm}1,y{\pm}1,z{\pm}1)$, $a = 3^{1/2}$. Let $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$ denote the average square of the x, y, and z coordinates with respect to the center of mass. For polymer rings the following relation holds:

$$\langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = Na^2/12 \qquad (3.4)$$

For polymer loops this becomes

$$2\langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = Na^2/6 \qquad (3.5)$$

To find the average concentration inside the coil in the case of loops we assume that it can be represented by an ellipsoid with long axis $e_2 = (Na^2/6)^{1/2}$ and short axis $e_1 = (Na^2/12)^{1/2}$. Furthermore e_1 is the axis of rotational symmetry. The volume is given by

$$V = \tfrac{4}{3}\pi e_1 e_2{}^2 \qquad (3.6)$$

Hence

$$c^*_{\mathrm{loop}} = q(3^{1/2})N^{-1/2}/(\pi a^3) \qquad (3.7)$$

It follows from eq 3.3 and 3.7 that

$$c^*_{\mathrm{ring}}/c^*_{\mathrm{loop}} = 2 \qquad (3.8)$$

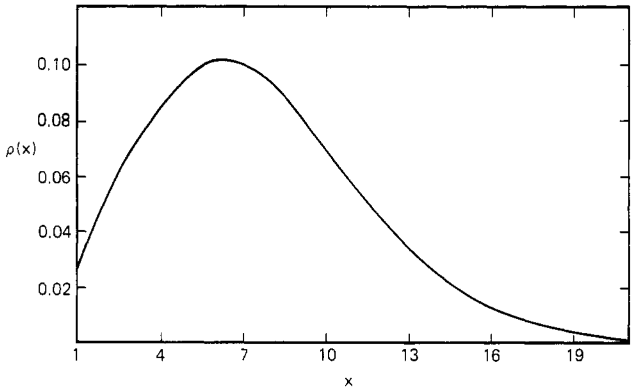

Figure 3. Average concentration profile for separate coils.

Table I
Fraction of Knotted Walks

no. of steps N	% knots rings[a]	% knots loops	ratio
20	2.3 ± 0.1	1.6 ± 0.1	1.44 ± 0.15
40	8.4 ± 0.6	5.6 ± 0.4	1.50 ± 0.20
60	12.8 ± 0.8	9.6 ± 0.6	1.33 ± 0.15
80	19.1 ± 1.0	14.0 ± 0.8	1.36 ± 0.15
100	25.6 ± 1.1	17.9 ± 1.0	1.43 ± 0.15
120	28.1 ± 1.3	23.1 ± 1.0	1.22 ± 0.10
140	33.1 ± 1.8	28.6 ± 1.4	1.16 ± 0.12
160	37.4 ± 1.9	30.8 ± 1.8	1.21 ± 0.12

[a] Reference 14.

Clearly, this is only a crude approximation. In reality the average monomer concentration depends on the distance to the center of mass and is moreover not the same for polymer rings and polymer loops. Figure 3 shows an example of the average monomer density $\rho(x) = \sum_{x,z}\rho(x,y,z)$ for walks of $N = 140$ as a function of the distance x to the wall. A depletion layer is clearly visible. The same calculations predict that besides the two end points on the average only two more monomers will be at the surface. Not unexpectedly, this number is just twice that found by DiMarzio et al.[21] for linear chains attached to the surface with only one end.

Table I and Figure 4 present the fraction of knotted conformations as a function of walk length. It is compared with previously obtained results for polymer rings.[14] It shows that the fraction of knotted conformations is less sensitive to the average monomer concentration than on the basis of eq 3.1 might be expected. This observation agrees well with our findings for polymer rings reported in ref 14. There it is shown that an increase in concentration of the order of 25% by taking an 8-choice instead of a 7-choice body-centered cubic lattice had no significant effect on the number of knotted walks.

4. Overlapping Coils

In this section we discuss the situation where the number of triblock copolymers adsorbed to the surface and the length of the end blocks is such that the middle block loops overlap. The most interesting case consists of relatively short end blocks and long middle blocks. As before, we assume that the interaction between the middle block and the surface can be neglected. Furthermore, it is also assumed that the layer was adsorbed under good solvent conditions for the middle block and that equilibrium was obtained. An important point for the present discussion is the assumption that equilibrium can be obtained as long as the surrounding solvent contains enough polymer. Adsorption is only irreversible, at least in the case of strong adsorption, if no exchange between adsorbed and free polymer is possible. Once the polymer solution is replaced by a pure solvent, polymers will remain attached to the surface.

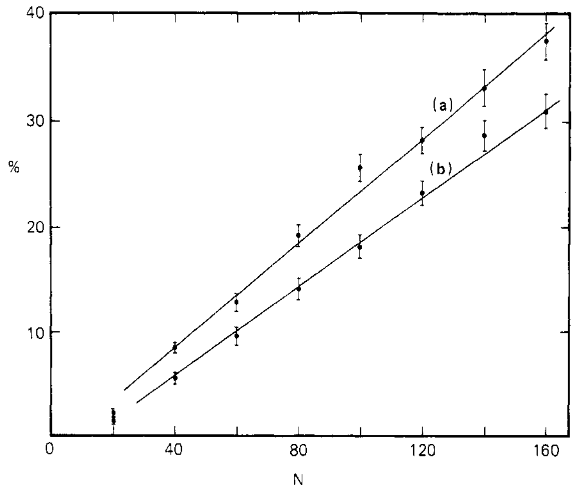

Figure 4. Probability of knot formation as a function of chain length N: (a) polymer rings;[14] (b) polymer loops.

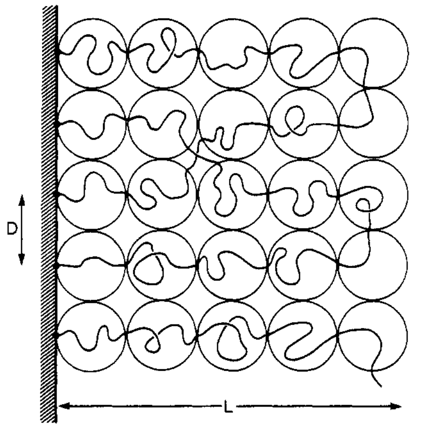

Figure 5. Strongly stretched situation for chains with both ends bound to the surface in the presence of a good solvent.

Quantitatively, the conformations of the polymer loops in a good solvent will not differ essentially from the one-side grafted (diblock) case discussed by Alexander and de Gennes.[11,12] The loops will be strongly stretched in the direction normal to the surface as illustrated in Figure 5. In both cases a lowering of the solvent quality will reduce the thickness L of the adsorbed layer. The only reason the triblock adsorption case will be considered briefly is the fact that the topological constraints between the different loops will influence the way in which this reduction takes place.

To demonstrate this, we start with a certain density of loop ends σ and a layer thickness L. The average distance between the loop ends is given by

$$D = a\sigma^{-1/2} \tag{4.1}$$

To obtain L as a function of the loop length N, the simple Flory approach[22,23] will be followed. In many cases it is known to give the correct prediction for the dimension because of a cancellation between the overestimates in repulsive and attractive interactions. Basically, the equilibrium dimensions are obtained by a competition between osmotic swelling and elastic retraction. The boundary conditions of loop ends being attached to the surface play a role similar to cross-link points in the case of swelling of networks.

The layer can be considered to consist of cylinders of length L and base surface $\simeq a^2/\sigma$ containing $N/2$ segments each. The average monomer concentration is given by

$$c \simeq \sigma N/(2La^2) \tag{4.2}$$

The repulsive energy density in this layer is in the mean field approximation given by

$$f_{\text{rep}} \simeq \tfrac{1}{2}kTv(T)c^2 \tag{4.3}$$

where $v(T)$ is the excluded volume parameter given by

$$v(T) = (1 - 2\chi)a^3 + v_{\text{top}} \tag{4.4}$$

The essential part is the presence of the additional positive term v_{top}. It takes the topological constraints into account.[24,25] However, it is very important to realize that v_{top} is determined by the experimental preparative protocol, i.e., the conditions under which the initial adsorption has taken place. What we propose here is essentially that in the preparative stage the topological state has been fixed, which implies that, even though certain rearrangements of the loops are possible without chain ends having to desorb completely from the surface, we assume that the topological situation is essentially frozen in on the time scale of the experiments to be conducted. In this respect, force measurements as a function of temperature are the ones to consider specifically.

The repulsive energy per loop is found to be

$$F_{\text{rep}} \simeq kTv(T)\sigma N^2/La^2 \tag{4.5}$$

where numerical coefficients have been dropped. The repulsive energy favors osmotic swelling as long as $v(T) > 0$ and is counteracted by the elastic retraction. Treating the elastic free energy of a loop of length N as being of the same order as the elastic free energy of two linear chains of length N/2, we obtain

$$F_{\text{el}} \simeq kTL^2/Na^2 \tag{4.6}$$

where numerical coefficients have again been dropped. To find the layer thickness L, the total free energy per loop given by

$$F/kT \simeq v(T)\sigma N^2/La^2 + L^2/Na^2 \tag{4.7}$$

has to be minimized with respect to L. Omitting numerical coefficients, we obtain the following result:

$$L \simeq (v(T)\sigma)^{1/3}N \tag{4.8}$$

This expression is identical with the de Gennes–Alexander result except for the fact that $v(T)$ may contain a contribution due to the topological constraints. Assuming equilibrium adsorption, v_{top} will be zero at the temperature of preparation. The effect of the topological constraints will become increasingly important upon approaching the normal Θ-conditions ($\chi = 1/2$). It is here that the largest difference between diblock and triblock adsorption is expected. At the Θ-temperature eq 4.7 probably still describes the triblock case correctly since v_{top} can be quite large. For instance, the second virial coefficient for polystyrene rings in cyclohexane at 34.5 °C was recently found[26] to be approximately 5×10^{-5} cm^3/g^2. The repulsive energy density of the diblock case, on the other hand, is now dominated by the third-order interaction term $\sim kTw^2c^3$, leading to a layer thickness $L \sim (w\sigma/a)^{1/2}N$.

Summarizing this rather speculative discussion we see that, although the layer thickness will be proportional to N, the prefactor will in general be different for triblocks compared to diblocks. Just how much is difficult to estimate in particular because hardly anything is known about V_{top}. But, it can in principle be investigated by force measurements between surfaces of copolymers adsorbed on mica. In this case, the onset of the repulsive barrier can be used as a measure of the layer thickness.

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References and Notes

(1) Klein, J. *Nature (London)* **1980**, *288*, 248.
(2) Klein, J. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 99.
(3) Klein, J.; Pincus, P. *Macromolecules* **1982**, *15*, 1129.
(4) Klein, J.; Luckham, P. *Nature (London)* **1984**, *308*, 836.
(5) de Gennes, P.-G. *Macromolecules* **1982**, *15*, 492.
(6) Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almog, Y. *Macromolecules* **1984**, *17*, 204.
(7) Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1985**, *18*, 1882.
(8) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem Soc.* **1986**, *108*, 2869–2876.
(9) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84*, 178.
(10) Scheutjens, J. M. H. M.; Fleer, G. J. *Adv. Colloid Interface Sci.* **1982**, *16*, 341.
(11) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.
(12) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(13) Patel, S.; Tirrell, M.; Hadziioannou, G. *Bull. Am. Phys. Soc.* **1986**, *31*, 259.
(14) ten Brinke, G.; Hadziioannou, G. *Macromolecules* **1987**, *20*, 480.
(15) de Gennes, P.-G. *Macromolecules* **1984**, *17*, 703.
(16) Vologodskii, A. V.; Lukashin, A. V.; Frank-Kamenetskii, M. D.; Anschelevich, V. V. *Sov. Phys.—JETP (Engl. Transl.)* **1987**, *39*, 1059.
(17) Feller, W. *An Introduction to Probability Theory and Its Applications*; Wiley: New York, 1968; Vol. 1.
(18) Chen, Y. J. *J. Chem. Phys.* **1981**, *75*, 2447.
(19) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(20) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(21) DiMarzio, E. A.; McCrackin, F. L. *J. Chem. Phys.* **1965**, *43*, 539.
(22) Flory, P. J. *Principles of Polymer Chemistry*, Cornell University: Ithaca, NY, 1953.
(23) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca (NY) and London, 1979.
(24) Frank-Kamenetskii, M. D.; Lukashin, A. V.; Vologodskii, A. V. *Nature (London)* **1975**, *258*, 398.
(25) Vologodskii, A. V.; Lukashin, A. V.; Frank-Kamenetskii, M. D. *Sov. Phys.-JETP (Engl. Transl.)* **1975**, *40*, 932.
(26) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.