

Computer Simulation
of Linear and Comblike Copolymers
at an Interface



Dissertation

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Introduction

For a long time, chemical industry was interested in polymers mainly from the viewpoint of obtaining unique construction materials (plastics, rubbers, fibers, etc.). Couple of decades ago the main focus of interest shifted to functional polymers (superabsorbents, membranes, adhesives, etc.). In the nineties scientific and industrial polymer community started to discuss "smart" or "intellectual" polymer systems (e.g., soft manipulators, polymer systems for controlled drug release, field-responsive polymers); the meaning behind this term is that the functions performed by polymers become more sophisticated and diverse. This line of research concentrating on polymer systems with more and more complex functions will be certainly in the mainstream of polymer science in the 21st century.

One of the ways to obtain new polymers for sophisticated functions is connected with the synthesis of novel monomer units where the required function is linked to the chemical structure of these units. However, the potential of this approach is rather limited, because complicated and diverse functions of polymer material would then require a very complex structure of monomer units, which normally means that the organic synthesis is more expensive and less robust.

The alternative approach is to use known monomer units and to try to design a copolymer chain with given sequence of these units. There are practically infinite possibilities to vary sequences in copolymers: from the variation of some simple characteristics like composition of monomer units, average length of blocks (for the chains with blocky structure), availability of branching, etc. to more sophisticated features like long-range correlations or gradient structure. Therefore, in this approach a wide variety of new functional copolymers can be tailored. It is important to emphasize that the nature has chosen this way in the evolution of main biological macromolecules: DNA, RNA, and proteins. These polymers in living systems are responsible for functions, which are incomparably more complex and diverse than the functions,

which we are normally discussing for synthetic copolymers. The molecular basis for this ability to perform sophisticated functions is associated with unique primary sequences of units in biopolymers, which emerged in the course of biological evolution.

Thus, one of the promising approaches in the sequence design of functional copolymers is biomimetic in its nature: it is tempting to look at the main features of sequences of monomer units in biopolymers, understand how these sequences define functional properties, and then try to implement similar ideas for synthetic copolymers.

Copolymers have been studied extensively for several decades, partly because of their biological and industrial importance, and partly because of their interesting and sometimes perplexing properties.

For some recent years, the theoretical investigation of the properties of comb copolymers has received considerable interest. The comb copolymers with a high density of side chains (such polymers are sometimes called "molecular bottle-brushes") display many specific properties, including the formation of highly ordered microstructures arising as a result of microphase separation both in solution and in bulk, liquid-crystalline ordering in a dilute good solvent, etc.

The linear copolymers can have different sequences of monomer units (from alternating to statistical). Although recent years have witnessed an impressive confluence of experiments, simulations, and analytic theories, nowadays there is no comprehensive understanding what role copolymer primary sequences play for the structural and functional properties of copolymer systems.

In this thesis the different copolymer systems at an interface have been studied using computer simulation approach.

The literature observation is done in the first chapter of the thesis. It includes common information about comblike copolymers, short description of conformational-dependent sequence design, etc.

The chapters 2-4 include original results.

In the second chapter of this thesis the equilibrium structure and dynamical behavior of comblike copolymers are studied, using the bond-fluctuation model and cellular-automaton (CA)-based simulation technique.

In the third chapter the computer-aided sequence design of two-letter (AB) quasirandom copolymers with quenched primary structure near an infinite planar surface is performed using Monte Carlo simulations and the lattice bond-fluctuation

model. Main aim here is to explore in detail the statistical properties of generated sequences.

In the fourth chapter, both molecular dynamics and Monte-Carlo simulation of a simple model of molecular motor is performed. The model realizes long-range directional motion (reptation) of a single block AB copolymer chain, which is strongly adsorbed on a molecularly structured stripe-patterned surface.

Chapter 1

Review

1.1. Comblike copolymers

1.1.1. Short description of comblike copolymers

Macromolecule of comblike copolymer consists of backbone (main chain) and branches (side chains), grafted to the main chain **Figure 1**.

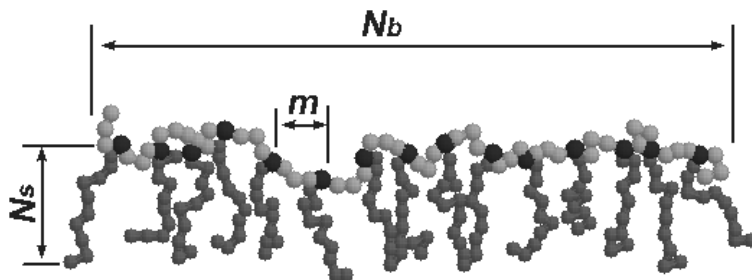


Figure 1. Schematic representation of comblike macromolecule. Here, N_b – main chain, N_s – side chain, m – distance between the branching points.

Comblike copolymers are capable of structuring in solutions, melts and at interfaces (micellization^{1,2,3,4}, liquid-crystalline ordering^{5,6}, microphase separation⁷, formation of mono-, bi- and multilayers^{8,9,10}). By varying the chemical structure of macromolecules and external conditions, it is possible to obtain various three- and two-dimensional structures with a unique set of mechanical and physicochemical characteristics.

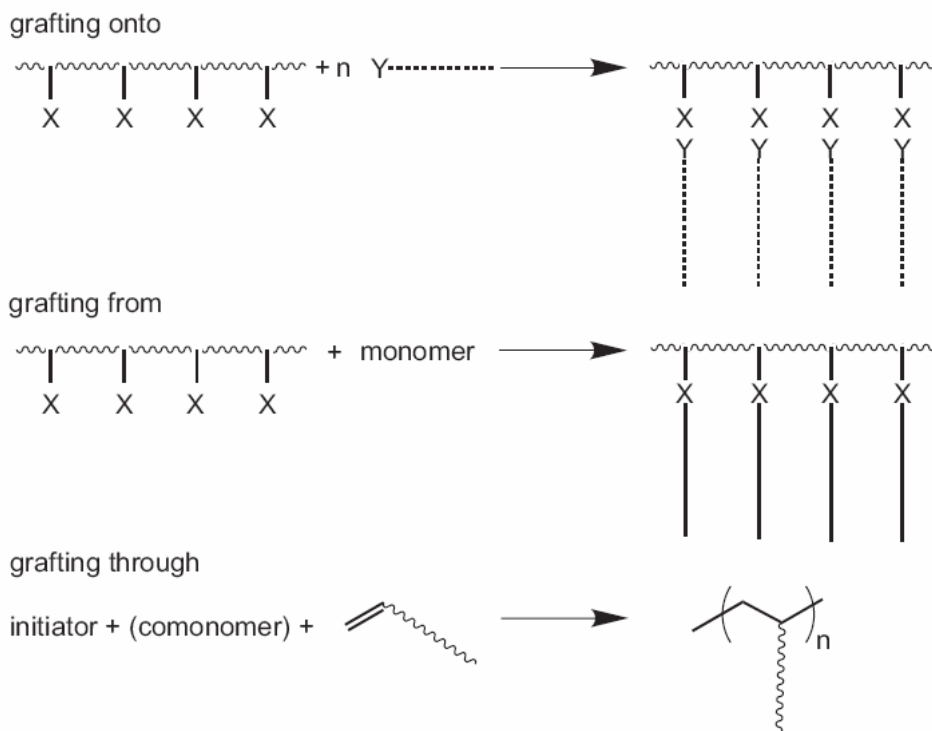


Figure 2. Schematic illustration of different methods of preparing graft copolymers (figure from book of K.A. Davis and K. Matyjaszewski¹¹).

There are three general methods for preparing graft copolymers:

- 1) grafting onto (requires the presence of complimentary functionalities on the graft unit and the backbone;
- 2) grafting through (utilizes macromonomers, which are polymer chains that contain a copolymerizable moiety at the chain end. Homo- or copolymerization with another monomer produces the graft copolymer);
- 3) grafting from (employs a backbone containing reactive sites that are capable of initiating a polymerization).

Figure 2 illustrates these three approaches.

There is a possibility of controlling the system morphology in various fashions through modifying the molecular architecture. This can be done using two different approaches. In one case molecular bottle-brushes are obtained by polymerization of macromonomers, which serve as building blocks^{12, 13, 14}. Such synthesis leads to long backbones with covalently linked oligomeric side chains. Recently, it has been demonstrated that noncovalent bonding can also be used in creating comb copolymer-like structures. The latter arise due to a strong association between end-functionalized

oligomeric chains and homopolymers^{15,16,17,18,19}. The physical association involves hydrogen bonding, ion-ion, dipole-dipole, or ion-dipole interactions, charge-transfer complexes, metal-ligand coordination complexes, etc. If associative bonding interaction is rather strong, the comb shaped structures resemble in many ways conventional chemically synthesized comb copolymers. However, due to the reversible nature of the side chain attachment there are important differences resulting in very rich phase behavior observed for these systems^{15-19, 20,21,22}.

Recently, different synthetic strategies have been developed to prepare comb-like polymers with a high grafting density ($m \ll N_b$) of linear side chains^{23,24,25}. One might call this type of polymers cylindrical brushes as the radius of curvature is determined by the brush length. Both theoretical analysis and computer simulation report on the enhancement of the persistent length of macromolecules caused by steric repulsion between the side chains. Due to these steric interactions macromolecules have “bottle-brush”-like structure.

Competition between the entropic flexibility of the main chain and the excluded volume interaction of the side-chains results in many interesting properties such as lyotropic ordering²⁶, axial contraction of the main chain²⁷, and microphase segregation.

The cylindrical brushes with diblock copolymer side chains can be easily hydrolyzed to amphiphilic core-shell nanocylinders. Such brushes have two-layer (core-shell) structure, where stretched cylindrical core is occupied by shell of side-chains²⁸ (Figure 3).

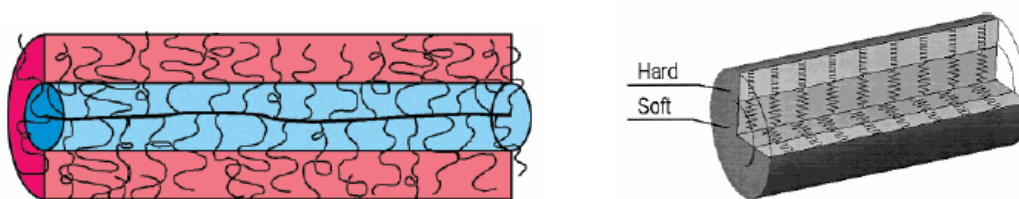


Figure 3. (a) Schematic illustration of cylindrical brush in solution (Picture from 29). (b) Idealized structure of the segment of cylindrical core/shell brush (Picture from 25).

The resulting core/shell cylindrical brushes can be used for a number of applications in nanotechnology, e.g., for the preparing nanoscopic channels, wormlike micelles, and other complex architectures²⁵, for the synthesis of metal clusters and wires within such a macromolecular template²⁹, as cylindrical nanoreactors with well-defined dimensions for the synthesis of novel nanosized organic/inorganic hybrid systems²⁸.

1.1.2. Conformational behaviour in a dilute solution

The conformational properties of comblike macromolecules in a dilute solution have been studied by several authors using both analytical approaches and computer simulations.

Ptitsyn³⁰ and Kron and Ptitsyn³¹ were the first who have shown that the presence of branches causes an increase in the excluded-volume effect. They have derived equations showing that the expansion factor of branched macromolecules in a good solvent α is larger than that of the corresponding linear polymers. The same conclusion was made by Berry and Orofino³² and Tsvetkov³³.

In refs. ^{30,31,32,33} it was assumed that the backbone and side chains obey the same random-flight (Gaussian) statistics and they have the same stiffness as for isolated chains. On the other hand, numerous experimental data^{34,35} demonstrate that even at Θ -conditions the mean dimensions of a comb copolymer are much greater than the unperturbed dimensions of the homopolymer used as a backbone.

In the literature, there are different interpretations of this important observation, e.g., (i) at the theta point for the corresponding unbranched linear polymer, the expansion factor of the branched macromolecule, α , is essentially larger than unity and the osmotic second virial coefficient B is larger than zero, whereas according to the Flory-type theory^{30,31,32,33} it should be $\alpha=1$ and $B=0$ under these conditions (in other words, the dimensions of the comb polymer determined for theta conditions are not unperturbed)^{36,37,38,39}; (ii) the equilibrium stiffness of chains increases markedly when they are consolidated in a comblike structure^{40,41}.

At this stage it is worth-while to remind the concept of quasimonomers, introduced by one of us in ref. 38. This concept is based on the fact that the local density $\rho(\vec{r})$ of monomer units near the given unit is not low and does not decrease even for an infinitely long chain. Therefore, the intrachain interaction must be expressed in terms of an effective renormalized second virial coefficient B^* , instead of the "bare" second virial coefficient B . The renormalized coefficient B^* is the sum of the contributions from the "bare" monomer-monomer interactions, which are characterized by B , and of the renormalizing contribution arising as a result of the "interference" between other monomers. In the case of branched polymers, there is an effective intramolecular repulsion that is due to the "extra interference" in the interaction of bare monomers,

additional to the "normal interference" existing in a linear infinite chain. This fact leads to the additive renormalization of an effective second virial coefficient for the interaction between two quasimonomers i and j of a branched polymer. Using these arguments, in ref. 38 the Θ -behavior of comb-branched polymers was studied and the essential Θ -swelling of such chains was calculated.

As to the good solvent, the local conformational structure and dimensions of the long comblike polymers in a dilute solution have been studied on the basis of simple scaling approach by Birshtein et al.⁴². They found that in the wide range of the solvent quality, the local structure of the polymer is characterized by elongation of both the backbone and side chains as a result of strong repulsion between their monomer units. For the size of the backbone, it was obtained the following expression⁴²:

$$R \sim N_b^{3/5} (N_s / m)^{9/25} \quad \text{Equation 1}$$

where N_b is the number of monomer units in the backbone and $m \sim \varpi^{-1}$ is the number of chain segments between two successive side chains, ϖ is the grafting density. Taking into account the elasticity of the main chain between two successive branching points and minimizing the free energy of side chains of length n attached to the backbone with a fixed grafting density, Birshtein et al.⁴² derived the scaling relation for the size of the side chains:

$$R_n \sim N_s^{18/25} \varpi^{3/25} \quad \text{Equation 2}$$

This result implies that the strongly overlapping side chains behave similarly to two-dimensional self-avoiding walks. However, the corresponding exponent $18/25 = 0.72$ in Eq. (2) is slightly smaller than the 2d-SAW value of $3/4$. Also, Birshtein et al.⁴² concluded that the strong repulsion between side-chain units in the high coverage regime should result in increase of rigidity of the main chain to scale of the same order as the dimensions of the side chains. This conclusion is in line with the experimental data of Tsvetkov et al.⁴¹.

Fredrickson⁴³ took a somewhat different representation for the free energy of a comb copolymer structure. On the basis of a classical Flory approach he explored the intermediate coverage regime ($N_s^{-9/10} \ll \varpi \ll N_s^{-3/5}$) in which the behavior of the system is determined by a balance between the unfavorable elastic stretching of the backbone and the corresponding reduction in excluded volume interaction of side-chain units. For the size of the main chain, his consideration gives:

$$R \sim N_b^{3/5} N_s^{9/25} \varpi^{2/5} \quad \text{Equation 3}$$

This dependence happens to be nearly identical to the expression (1) obtained by Birshtein et al.⁴². In the high coverage regime, i.e., under conditions of dense grafting of long side chains ($\varpi \gg N_s^{3/5}$ or $m \ll R_s$), Fredrickson predicts the usual 2d-SAW behavior for the side chains

$$R_s \sim N_s^{3/4}. \quad \text{Equation 4}$$

for the case of a backbone that can be treated as a solid cylinder of a given fixed length. In addition, he studied the chain stretching in this regime and found that the persistence length of the main chain is expected to scale as $\lambda \sim N_s^{15/8} \varpi^{17/8}$.

Rouault and Borisov⁴⁴ also studied the conformational properties of comb copolymers using a Flory-type approach. They found that, if the effect of the induced rigidity is weak and the grafting density is not too high, the size of the main chain behaves as $R \sim N_b^{3/5} (N_s \varpi)^{9/25}$ that coincides with Eq. (1). On the other hand, at high densities of long side chains when the simple Flory arguments break down, they obtained:

$$R \sim N_b^{3/5} (N_s \varpi)^{27/50} \quad \text{Equation 5}$$

Note that this expression was derived for the system with variable chain rigidity, i.e., when the induced rigidity was taken into account. If very long side chains are considered, then

$$R \sim N_s^{87/100} \varpi^{77/100} \quad \text{Equation 6}$$

Using a mean-field approach and a simplifying assumption, which was tested by computer simulation, Subbotin and co-workers found that the persistence length λ of the brush, consisting of a semiflexible backbone and rodlike side chains, scales as $\lambda \propto N_s^2 / \ln N_s$ for large values of the side chain length N_s . Also it was found, that for flexible side chains $\lambda \propto R_s N_s^{5/4}$, and for rigid side chains $\lambda \propto R_s N_s$.

Since the theoretical treatments considered above involve many simplifications it is very difficult to access the consequences for realistic polymer systems. Indeed, compared to the systems studied theoretically, the side chains in real bottle-brushes used so far are considerably smaller (~ 10 - 10^2 monomer units). In addition, some of the theoretical results are rather conflicting by itself. In this situation, computer simulations become quite desirable. Only a few studies have deal with the simulation of comb copolymers^{45,46,47,48}.

Gallacher and Windwer⁴⁵ used a Monte-Carlo (MC) procedure to simulate flexible branched macromolecules on the tetrahedral lattice. The branched-polymer model selected for investigation in this study was the random-comb polymer, i.e., a

structure consisting of a relatively long backbone chain (of up to 200 lattice steps) with short branches of equal length distributed randomly on the backbone. It has been found that branched polymers have higher expansion factor in a good solvent than their linear counterparts with the same molecular weight, and this effect increases with the length and frequency of branches.

Using MC simulation technique, McCrackin and Mazur⁴⁶ studied the Θ behavior of comblike macromolecules. Note that the theoretical dependencies obtained by Birshtein et al.⁴² for comblike macromolecules in Θ -solvent are in reasonable agreement with these simulation data.

Lipson⁴⁷ used the Rosenbluth MC algorithm to generate lattice combs with branches evenly placed along the backbone. The number of monomer units in the branches was 3, 6, or 9, and the total number of units in the system was ranged between 20 and 210. Three particular cases were studied, associated with different values of the ratio of branch length to interbranch spacing. It was shown that the critical exponent, ν , in the N -dependence of R_N remains unchanged from its value for linear self-avoiding walk. However, in analyzing the comb results, it was found that correction-to-scaling terms made significant contributions.

Rouault and Borisov⁴⁴ performed a lattice MC simulation, using the bond fluctuation model, in order to check the validity of the theoretical prediction, developed in the same paper⁴⁴. However, the comblike structures studied were too small to make possible the reliable comparison between the corresponding scaling theory and the simulation. Evidently, due to this and because the degree of side-chain overlap was rather weak, Rouault and Borisov found the "unperturbed" dependence $R_n \sim N_s^{0.6}$ for the size of the side chains. In addition, the authors draw attention to the fact that the topological constraints at the branching points induce a very slow relaxation of the comb macromolecule in the case of high grafting densities.

Saariaho et al.⁴⁸ presented the results of continuous space MC simulation for freely jointed hard sphere side chains grafted on the backbone. The largest structure studied by these authors consisted of a backbone of $N_b = 100$ beads with $n = 50$ side chains of $N_s = 20$ beads each. The main chain beads, from which a side chain is grafted, were chosen equally along the backbone, i.e., every other main chain bead carried a side chain. It was found that the mean size of the side chains behaves as $R_s \sim N_s^{0.682}$, that is, the corresponding scaling exponent is slightly smaller than that predicted by Fredrickson⁴⁵, (see Eq. (4)) and by Birshtein et al.⁴² (see Eq. (2)). At the

same time, this exponent is undoubtedly larger than the well-known three-dimensional SAW value of 0.588. The radius of gyration of the main chain R_g as a function of side-chain length N_s was found to increase monotonously with n as $R_g \sim N_s^{0.54}$, giving an indication of side-chain induced stretching. It should be noted that the calculated exponent 0.54 agrees surprisingly well with the value of 27/50, which follows from the scaling prediction of Rouault and Borisov⁴⁴ for the systems with long side chains at high grafting density. In addition, it was concluded that a correct description of the backbone conformations must be based on two characteristic length scales: at a small length scale, the main chain behaves as a flexible chain; at a larger length scale, the extension of the backbone occurs.

The same model was used to simulate the influence of the excluded volume interactions between the side chains on the enhancement of the persistence length of a molecular bottle-brush in a dilute athermal solution⁴⁹. In this study, the diameter of the side-chain beads was varied. The ratio between the persistence length and the bottle-brush diameter was found to increase considerably with increasing size of the side-chain beads, but almost independent of the side-chain length. The size of the side chains was found to scale as $R_s \sim N_s^v$ with v ranged from 0.687 to 0.718, depending on the side bead diameter.

Rouault⁵⁰ employed the pivot algorithm to study lattice comb polymers, large enough to have side-chains obeying scaling behavior. For the end-to-end distance of the main chain as a function of side-chain length, he observed $R \sim N_s^{0.34}$. This dependence is in good agreement with the theoretical one $R \sim N_s^{9/25}$, predicted in the absence of induced rigidity⁴⁴. The dependence of $R_g \sim N_s^{0.7}$ obtained for the side-chain dimension is also in reasonable good agreement with the theoretical prediction of refs.^{42, 44} (see also Eqs. (2) and (4)). It should be noted that, unlike the bond fluctuation algorithm, the dynamics of the pivot algorithm is unphysical and, hence, this method cannot be used for simulating the relaxation of macromolecules.

1.1.3 Conformational behaviour at an interface

Macroconformation and flexibility of molecular brushes are expected to change considerably when the brush molecules are adsorbed on a flat solid substrate⁵¹. The system becomes essentially two-dimensional when each monomer unit gets in contact with the surface. The strong adsorption prevents overlapping of the side chain and induces in-plane directionality of the excluded volume interactions. Also the



Figure 4. Schematic illustration of the brush in the bulk (axial) and the brush adsorbed on the flat solid surface (plane).

symmetry of the system is changed from the uniaxial symmetry of a cylindrical brush in solution towards plane symmetric distribution of the side chains in a strongly adsorbed brush (**Figure 4**). In this quasi-two-dimensional state, the side chains strongly repel one another. In this case, the macroconformation can strongly depend on the relative number of the side chains at the opposite sides of the main chain.

Conformational changes in a strongly adsorbed comblike macromolecule with a flexible backbone and densely attached flexible side chains depend on the interplay of the intramolecular and surface forces^{51, 52}. Moreover, it is known that strong adsorption of macromolecules from solution onto a flat substrate can lead to stretching of the main chain^{53,54}.

Ten Brinke and co-workers⁵⁵ presented the results on the off-lattice Monte-Carlo simulation for molecular brushes in thin films. The effect of intramolecular excluded volume interactions on the conformations of isolated cylindrical brushes in athermal solvents confined between two hard impenetrable parallel plates was studied. Equilibrium conformational properties of molecules with $N_b = 100$, $m = 2$, $N_s = 6$ -30 was determined as a function of the width of the slit, including the pure two-dimensional (2d) case. It was demonstrated that the root-mean-square end-to-end distance of the side chains R_{side} as a function of the side chain length N_s is:

$$R_{side} \sim N_s^{0.89} \quad \text{for } 2d \text{ case} \quad \text{Equation 7}$$

$$R_{side} \sim N_s^{0.68} \quad \text{for } 3d \text{ case} \quad \text{Equation 8}$$

The several conclusions were made. Both the backbone and the side chains start to extend due to the squeezing: the backbone at around $\Delta Z = 40$ and the side chains at $\Delta Z = 10$. The root-mean-square end-to-end distance of the side chains R_{side} has a clear minimum whereas the root-mean-square end-to-end distance of the main chain R_{main} of the backbone increases quite monotonically. As shown both by theory and by simulations⁵⁶, isolated linear chains confined between two hard parallel plates behave qualitatively in the same manner as the side chains.

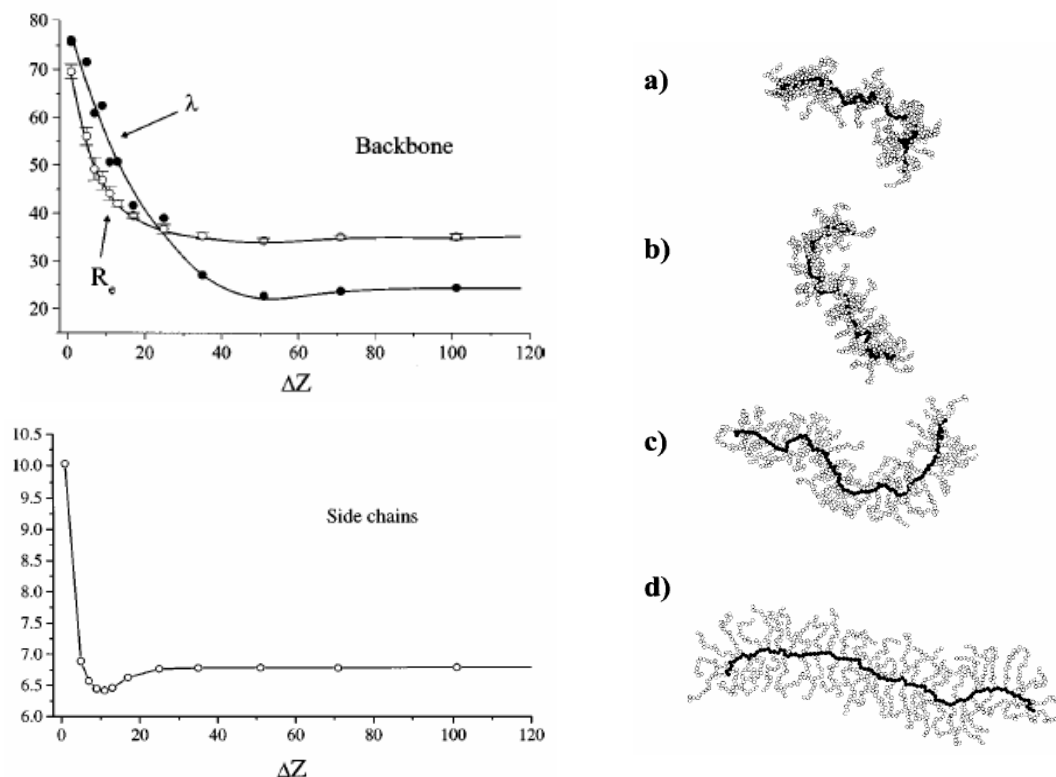


Figure 5. Left side: root-mean-square end-to-end distance of the backbone, persistence length λ of the backbone and root-mean-square end-to-end distance of the side chains as a function of the separation between the confining plates ΔZ . Right side: snapshots from the simulation, conformations of a brush confined between two parallel plates separated by a distance, (a) $\Delta Z = \infty$ (3d case), (b) $\Delta Z = 17$, (c) $\Delta Z = 5$, (d) $\Delta Z = 1$ (2d case). Figures from 52.

It was also found, that the ratio between the persistence length and the brush diameter, λ/D , increases considerably as the molecules are squeezed between confining plates. Moreover this ratio increases as a function of the side chain length (for $N_s > 10$) in 2d, whereas it remains approximately constant in 3d for the chain lengths studied. This then would imply that lyotropic behaviour exclusively due to intramolecular excluded volume effects can be obtained for flexible polymers.

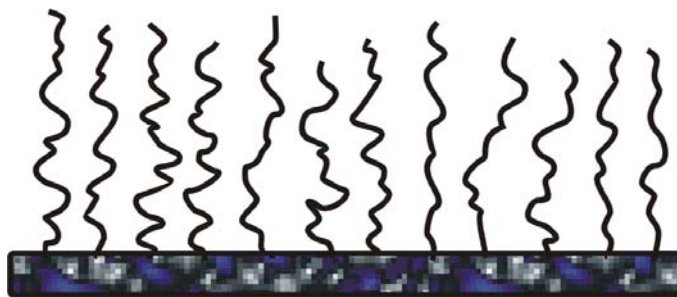


Figure 6. Schematic representation of grafted polymer layer (“polymer brush”).

Grafted polymer layers.

A grafted polymer layer is formed by polymer chains grafted at one end at impenetrable interfaces (Figure 6). When the grafting density to the surface Ω is small, the different chains do not overlap, this is often referred to as the mushroom regime. When the grafting density is larger than the overlap value $\Omega \cong 1/R^2$ (where R is the gyration radius of a chain in the bulk), the chains stretch from the surface and form a semidilute polymer brush⁵⁷.

Polymer brushes are promising objects for various practical applications: steric stabilization of colloidal systems, lubrication, adhesion, biocompatibility, chromatographic separation, the design of drug-delivery systems as well as membranes with adjustable permeability, modifications of adhesive and wetting properties of materials, etc. The brushes can be used to simulate weakly crosslinked gels, branched polymers and microsegregated copolymers. They serve also as convenient model systems for investigating the wetting phenomena and phase transformations in thin polymer films.

The equilibrium properties of polymer brushes were first described by Alexander⁵⁸, de Gennes⁵⁹ and, latter, Birshtein⁶⁰ for the uniform layer model using scaling arguments or blob concept. It was demonstrated, that in the good solvent (above the Θ -point) the brush layer height h is increase with the grafting density Ω :

$$h \sim N\Omega^{1/3} \quad \text{Equation 9}$$

, in the Θ -point :

$$h \sim N\Omega^{1/2} \quad \text{Equation 10}$$

More recently Semenov⁶¹ has introduced a self-consistent field (SCF) theory which allows an explicit calculation of the monomer distribution. Zhulina et al.⁶² and Milner, Witten, and Cates^{63,64} have carried out detailed calculations for a semidilute brush in the strong stretching limit (high grafting density) showing that the monomer

concentration profile is parabolic at the mean field level. The same behaviour (Eq. 9, 10) was demonstrated for all these self-consistent models.

Lai and Binder⁶⁵ have obtained the same results (Eq. 9) by Monte Carlo simulation using the bond fluctuation model. In the simulation, chain length ranged from $N=20$ to 50 beads.

Experimentally, polymer brushes (PS-PEO copolymers adsorbed on quartz from deuterated toluene) have been studied by Field et al⁶⁶. They also found that $h \sim N\Omega^{1/3}$.

Lateral Contraction

Stable surface modification is important in a wide range of applications in biotechnology and materials sciences. Studies on polymers in a restricted geometry near the interface is of great current scientific and technological importance, since the polymer chain organizations at the interfaces crucially influence the dissolution and etching characteristics, mechanical and biological properties, adhesion, wet ability, liquid crystal aligning properties and so forth⁶⁷.

Recently, Holland with co-workers⁶⁸ investigated the surface active properties of novel surfactant polymers at the air-water and graphite-water interfaces. Here, the surfactant polymers are comblike polymers consisting of a poly(vinylamine) backbone with poly(ethylene oxide) (PEO) and hexanal side chains (**Figure 7**). The polymers were prepared with various grafting ratios of the two side chains. In the compression of spread monolayers, desorption of the PEO side chains from the interface into the aqueous subphase results in two transitions. At high pressures, the hexanal side chains confine the surfactant polymers to the interface. For the surfactant polymers at the water-graphite interface, using tapping mode atomic force microscopy (AFM) it was found that with high hexanal:PEO content (e.g., 8:1), the surfactant polymer rapidly forms a compact and complete monolayer. At lower hexanal:PEO content (e.g., 4:1), a disordered layer is formed. After several hours, this layer rearranges into small scattered domains with banded structures. Due to such behaviour, adsorbed monolayers consist of PEO surfactant polymers can play bacterial resistance role.

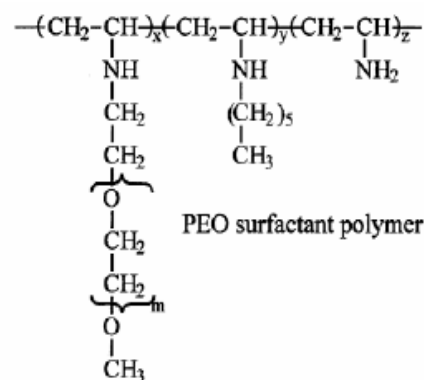


Figure 7. Chemical composition of surfactant polymer consists of a poly(vinylamine) backbone with poly(ethylene oxide) and hexanal side chains (PEO-hex). Figure from 68.

Miller, Richards and Webster^{69,70} investigated the organisation of a well-defined graft copolymer with a polynorbornene backbone ($N_b = 50$) and poly(ethylene oxide) grafts ($N_s = 15, 25$, and 50), grafted to each monomer unit of backbone (Figure 8), which has been spread at the air-water interface as Langmuir films.

Neutron reflectometry has been used to determine the layer organization and the distribution of water in the near surface region occupied by the spread film.

It was found, that the backbone region has a constant thickness over the whole surface concentration range explored whereas the poly(ethylene oxide) graft layer increases in thickness monotonically as the surface concentration of the spread film increases. As the surface concentration is increased, the reduction in separation distance between the PEO grafts is accompanied by an expulsion of water from the PEO-containing layer and a stretching of the grafts deeper into the subphase. The thickness of the PEO-containing region increases linearly with the grafting density at the water surface (assuming all PEO grafts become immersed). A more detailed examination of the reflectivity due to the poly(ethylene oxide) layers suggests that it is composed of two layers, one of which has a uniform density of ethylene oxide segments with the second having a parabolic decay of segments. The exponent for the dependence of the poly(ethylene oxide) total layer thickness on the density of grafting of the water surface was

$$h \sim N\Omega^{2/3}$$

Equation 11

i.e., much stronger than predicted by theory for a brush like layer (Eq.9).

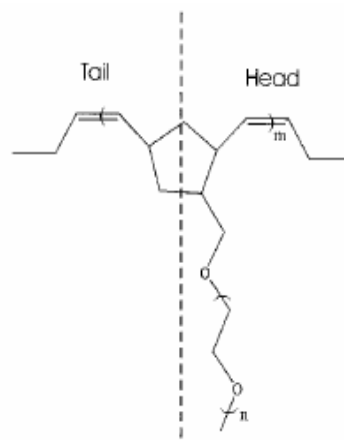


Figure 8. Schematic structure of poly(norbornene)-g-poly(ethylene oxide) copolymer. Figure from 69.

1.2. Linear polymers at an interface

Polymers at an interface has attracted continuous attention because of both the practical importance and the theoretical interest for many years^{71,72}. Numerous experimental^{73, 74,75,76}, theoretical^{77,78,79,80} and computer simulation^{81,,82,83,84,85} research has been devoted to the static and dynamics properties of polymers near an interacting surface.

The first reason of such interest is that the presence of polymeric materials can drastically modify the interfacial properties and hence is of relevance in many technological applications such as stabilization of colloidal suspension, wetting, chromatography, adhesion, lubrication, corrosion-protective coatings, design of biocompatible materials, interaction with membranes etc. From the other side, predicting the effect of surfaces on the properties of polymers is highly desirable in many surface-oriented technologies. It is also very interesting from the theoretical point of view as the presence of the attractive surface distorts the properties of the adsorbed chain comparing with the case of the free chain in solution. Furthermore, as it was noted in⁸³ the polymer adsorption has distinct phase transition properties and thus provides a realistic system for the fundamental understanding to the statistical mechanics of phase transitions.

Polymer chains adsorb onto the solid surface when attractive adsorption interactions compensate for the loss of entropy.

Most of the studies concerned the case of “weak” adsorption (for ex., when the energy of interaction between monomer unit and the surface $\varepsilon_a < kT$; of course, total energy of entire long polymer chain interaction $\varepsilon_a \times n_a \gg kT$, where n_a is number of adsorbed units). When a polymer chain in dilute solution under good solvent conditions interacts with a weakly attractive solid surface, it may undergo an “adsorption transition”^{140,71,72} from a three-dimensional 3d (nonadsorbed) to a quasi-two-dimensional 2d (strongly adsorbed, “pancake”) configuration (Figure 9). Weakly adsorbed chain can have three different morphological elements: adsorbed section (“train”), nonadsorbed section with two ends connected to the surface (“loop”) and nonadsorbed section with one end connected to the surface (“tail”).

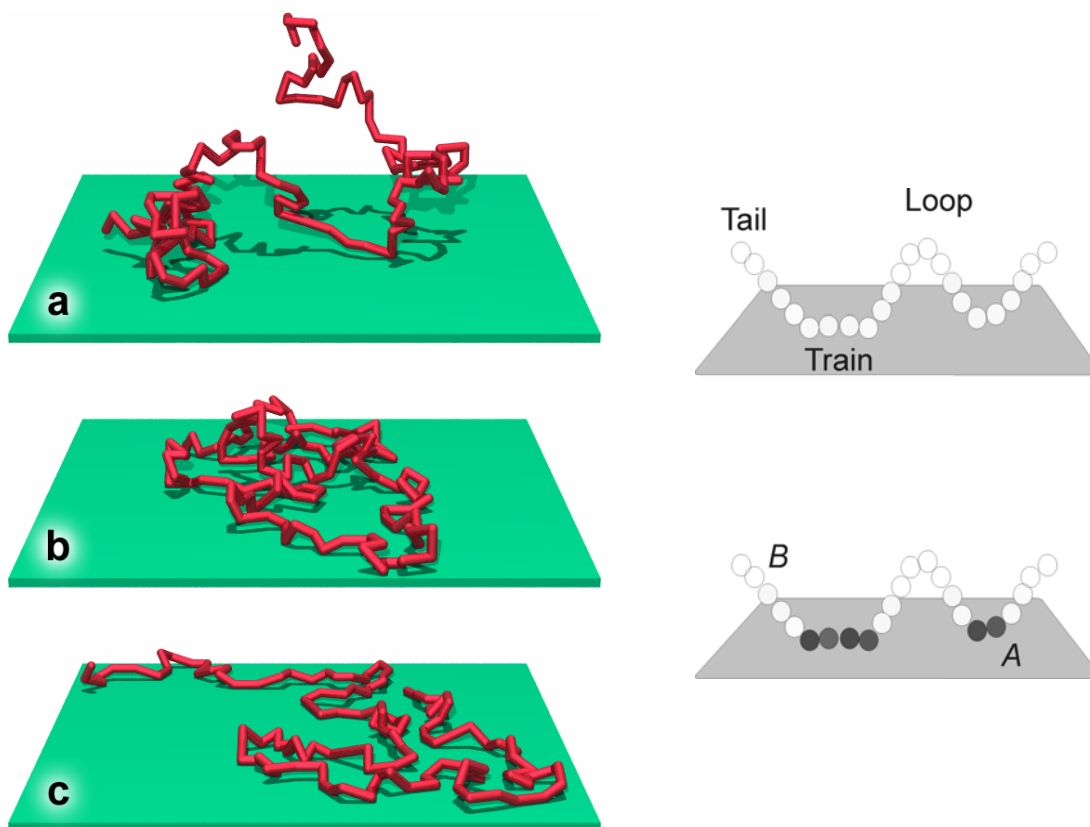


Figure 9. Configurations of polymer chain at a flat interface: (a) weak adsorption regime; (b) point near the adsorption transition; (c) strong adsorption regime; (d,e) chain in weak adsorption regime, monomeric units are represented as circles; (d) parts of the adsorbed chain - tail, loop and train; (e) adsorbed monomeric units (A) are coloured in grey and nonadsorbed units (B) – in white.

Simple scaling considerations led to the conclusion that at the adsorption transition the number of adsorbed monogenic units $n_a \propto N^\chi$, for $N \rightarrow \infty$. Here, χ is the so-called “crossover exponent”. For polymer chain in good solvent de Gennes¹⁴⁰ proposed a scaling relation $\chi \propto 1-\nu$ which would yield $\chi \approx 0.41$ when taking the established value for the exponent ν , relating the radius of a long chain in a good solvent to its length, i.e., $R \propto N^\nu$, $\nu \approx 0.59$ (in the three-dimensional case).

Computer simulations of single polymer chains are important because it is very difficult to experimentally study the adsorption of isolated polymer chains contrary to solutions of free chains. In recent years, intensive computer simulation studies have been performed in this direction. Particularly, crossover exponent has been found to test the theoretical predictions (see **Table 1**).

A polymer chains under good solvent condition near a short-range attractive impenetrable wall had been investigated in Ref. 82, 83 by Monte Carlo simulation us-

ing bond-fluctuation model. Author measured the equilibrium properties for various chain lengths ($N=30\div 100$) at wide range of adsorption energy ($\varepsilon_a = 0\div -1,5kT$). It has been found that for the sort chains ($N=40$) adsorption transition is less pronounced than for the chains with $N=100$.

Binder et al.⁷⁹ carried out Monte Carlo simulations for a coarse-grained bead-spring model of a flexible polymer chain interacting with the surface by the simple contact attractive potential. The adsorption transition of a polymer chain at a weakly attractive surface was studied. It was found that despite all the simplifications of model, it allows a description of many features of real polymers (e.g., it exhibits a glass transition at low temperatures). Also obtained results support the expectation that the exponents describing the adsorption transition are universal, i.e., they are not influenced by the precise form and the long-range character of the adsorption potentials used.

In Ref. 81, the adsorption of polymer chains from a solution onto a solid surface had been studied by MD simulations. Particularly, the influence of the chain stiffness on the adsorption had been investigated. Also the morphology of the adsorbed chain with variable stiffness has been studied in detail. In particular, such quantities as average length of loop and train sections, monomer density profiles, and segment orientation were calculated. It was found that stiffer chains adsorb more easily; moreover the average lengths of loop, train and tail sections strongly depend on the adsorption energy and on the chain stiffness.

Table 1. Comparison of values crossover exponent χ (for relation $n_a \propto N^\chi$) obtained by computer simulation with the theoretical predictions (all values are done for good solvent conditions).

Author(s)	Method and values N	crossover exponent χ
De Gennes ¹⁴⁰	Scaling theory, $N \rightarrow \infty$.	0.41
Eisenriegler, Kremer, Binder ⁸⁶	Lattice MC-simulation, $N \leq 100$	0.58
Kramarenko, Winkler, Khalatur, Khokhlov, Reineker ⁸¹	MD-simulation, $N \leq 128$	0.58
Mierovitch, Livne ⁸⁷	Lattice MC-simulation, $N \leq 260$	0.53
Metzger, Muller, Binder, Baschna- gel ⁷⁹	Lattice MC-simulation, $N \leq 256$	0.50
Hegger, Grassberger ⁸⁸	Lattice MC-simulation, $N \leq 2000$	0.496

1.3. Conformational-dependent sequence design of copolymers

In a series of publications,^{89,90,91,92,93} a concept of conformation-dependent sequence design of copolymers has been introduced. The essence of the proposed approach⁸⁹⁻⁹³ is based on the assumption that a copolymer obtained under some bare ("parent") preparation conditions is able to "remember" features of its original conformation in which it was built up and can then manifest these features when the conditions are changed. In other words, this concept takes into account a strong coupling between the conformation and primary structure of copolymers during their synthesis. Ideologically, the approach⁸⁹⁻⁹³ bears some similarities with that proposed earlier in the context of the problems of protein physics,^{94,95,96,97} however, it aims at synthetic copolymers rather than biopolymers with a unique (target) conformation.

The first ideas connected with biomimetic sequence design of functional copolymers were formulated in 1998^{98,99,100,101}. They were based on the simple and well-known fact that the functioning of all globular proteins depends on two main factors: (i) they are globular; (ii) they are soluble in aqueous medium. It should be mentioned that the combination of these two factors is non-trivial, e.g., for homopolymers and random copolymers the transition to globular conformation is usually accompanied by the precipitation of globules from the solution^{102,103}. Protein globules are soluble in water because of the special primary sequence: in the native conformation, most of hydrophobic monomer units are in the core of the globule while hydrophilic and charged monomer units form the envelope of this core. Of course, the division of 20 types of monomer units available in globular proteins in only two classes (hydrophobic and hydrophilic) is rather rough, but still this viewpoint gives a correct general picture of the structure of a protein. Now, having in mind the biomimetic approach described above, we can formulate the following problem: whether it is possible to design such sequence of synthetic AB copolymer (copolymer consisting of monomer units of two types, A and B) that in the most dense globular conformation all the hydrophobic B-units are in the core of this globule while hydrophilic A-units form the

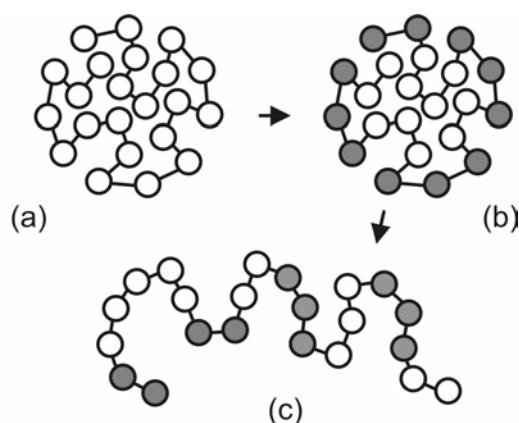


Figure 10. Main steps of the sequence design scheme for proteinlike copolymers: (a) homopolymer globule; (b) the same globule after "coloring" procedure; (c) proteinlike copolymer in the coil state.

envelope of this core? This question was first addressed in Ref. 98 (see also Refs. 99-101) and the corresponding polymers were called proteinlike AB copolymers.

The proteinlike AB sequences were first obtained in computer experiments⁹⁸⁻¹⁰¹, which can be described as follows. We start with arbitrary homopolymer globule conformation formed due to the strong attraction of monomer units [Figure 10a] and perform for it a "coloring" procedure [Figure 10 b]: monomer units in the center of the globule are called A-type (hydrophobic) units, while monomer units belonging to globular surface are assigned to be B-type (hydrophilic) units. Then this primary structure is fixed, attraction of monomer units is removed and proteinlike copolymer is ready for the further investigation [Figure 10 (c)].

In particular, in Refs. 98-101 the coil-globule transition for thus generated AB copolymers was studied. This transition was induced by the attraction of only A-units (the interactions B-B and A-B were chosen to be repulsive). The properties of this transition were compared with those for random AB copolymers with the same composition and random-block AB copolymers with the same composition and the same "degree of blockiness" as for designed proteinlike AB copolymers. The calculations were performed by Monte-Carlo method using the bond-fluctuation model.

It was shown⁹⁸⁻¹⁰¹ that the coil-globule transition in proteinlike copolymers occurs at higher temperatures, leads to the formation of denser globule, and has faster kinetics than for random and random-block counterparts. The reason for this is illustrated in Figure 11 where the typical snapshots of globules formed by proteinlike and random AB copolymers with the same AB composition are shown. One can see

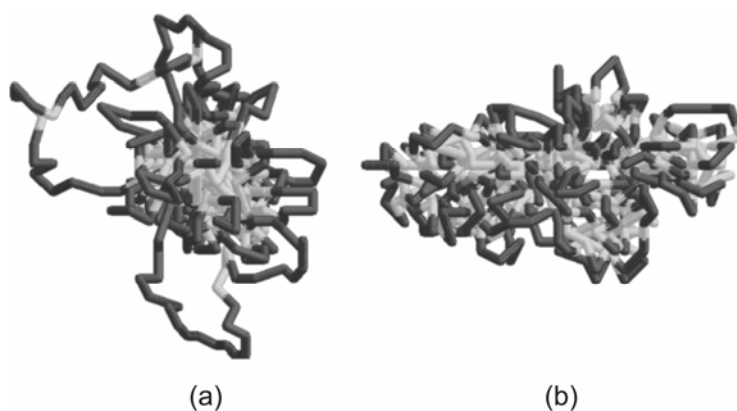


Figure 11. Typical snapshots of globular conformation for (a) proteinlike and (b) random copolymers.

that the core of proteinlike globule is much more compact and better formed, it is surrounded by the loops of hydrophilic units, which stabilize the core. Apparently, this is due to some memory effect: the core which existed in the "parent" conformation [this is the term introduced in Ref. 98 to describe the conformation of **Figure 11b** where the coloring is performed] was simply reproduced upon refolding caused by the attraction of A units. One may say that the features of "parent" conformation are "inherited" by the proteinlike ABcopolymer.

Looking at the conformations of **Figure 11**, it is natural to argue that proteinlike copolymer globule should be soluble in water (see also Refs. 104,105) and thus open to further modification in the course of biological evolution, while random copolymer globules will most probably precipitate and thus drop out of the evolution.

Returning to the computer-generated proteinlike sequences **Figure 10**, it is clear that they should exhibit long-range correlations along the chain, since the type of monomer unit (A or B) depends on the conformation of globule as a whole, not on the properties of some small part of the chain. In Refs. 106,107 it was shown, both by exact analytical theory and by computer simulation, that this is indeed the case and that the long-range correlations in the proteinlike sequences can be described by the so-called Levy-flight statistics¹⁰⁸.

In Ref. 145 it was shown that the corresponding primary sequence is nonalternating and demonstrates the specific long-range correlations (LRC), which can be described by the statistics of the Lévy-flight type.¹⁰⁹ These correlations are shown to be directly related to the conformation-dependent sequence design scheme. Certainly, owing to finite size of the bare globule, the longest correlations that can be found in

this case are also finite and should be understood as long-wave fluctuations of the chemical composition.^{145,146}

After the idea of sequence design of proteinlike copolymers was presented and realized in computer simulations, several teams started experimental research aimed to obtain such copolymers in synthetic chemical laboratory.

In particular, Prof. H. Tenhu at the University of Helsinki studied grafting of short poly(ethylene oxide) (PEO) chains to the copolymer of thermosensitive N-isopropylacrylamide (NIPA) and glycidyl methacrylate^{110,111}. At room temperatures, such copolymer is in the coil state and grafting takes place in a random manner. At elevated temperatures, the transition to globule occurs, and grafting proceeds mainly in the globular surface, thus leading to its hydrophilization and to the creation of proteinlike copolymer in the sense described above. Indeed, it was shown that proteinlike copolymer prepared in this way exhibits solution turbidity at higher temperatures than the random one, and gives smaller aggregates in the turbid solution.

In the group of Prof. V. Lozinsky (Institute of Organoelement Compounds of Russian Academy of Sciences) the redox-initiated free-radical copolymerization of thermosensitive N-vinylcaprolactam (NVCa) with hydrophilic N-vinylimidazole (NVIz) was studied at different temperatures¹¹². At room temperatures, such polymerization gives a random copolymer. On the other hand, when polymerization takes place at elevated temperatures (ca. 65°C) growing chains form globules, and the concentration of monomers around the active radical is influenced by this fact. The conditions were found when proteinlike copolymers are emerging as a result of such synthesis. These copolymers were not precipitating at all when the solution is heated up to 80°C; on the other hand, dense globules were formed already around 30°C. Qualitatively similar results were later reported for other pairs of comonomers.^{113,114,115}

In the group of Prof. B. Mattiasson (the University of Lund, Sweden) similar type of proteinlike copolymers were obtained for the pair of monomers NIPA/NVIAz synthesized in aqueous solution¹¹⁶. It was demonstrated that the copolymer with virtually random distribution of NVIAz units along the chains did not interact with the metal chelate adsorbent, Cu²⁺-iminodiacetate-Sepharose, whereas the copolymer, possessing the proteinlike sequence, was absorbed specifically by the resin, since the hydrophilic pendant imidazole groups were accumulated in the outer hydrophilic shell of macromolecular coil.

Recently, we performed computer experiments specially designed to describe the process of copolymerization with simultaneous globule formation in order to give more careful theoretical foundation for this synthetic method proposed in Ref. ¹¹². We have shown that such copolymerization process does indeed lead to the formation of a globule with proteinlike sequences ¹¹⁷.

The possibility to obtain the copolymers capable of forming core-shell microstructures via radical copolymerization of the monomers differing in hydrophilicity/hydrophobicity was confirmed by recent simulations¹¹⁸ where the process of copolymerization was modeled in a selective (polar) solvent. The composition of an emerging copolymer chain was such that macromolecule adopted a globular conformation, and the preferential absorption of hydrophobic monomers in the core of the globule was taken into account. It was shown¹¹⁸ that such copolymerization process, based on the so-called "bootstrap effect",¹¹⁹ automatically leads to the formation of the core-shell microstructure in the resulting globule and to the well-pronounced LRC in the primary sequences.

The idea of conformation-dependent sequence design can be generalized. Indeed, the special primary sequence can be obtained not only from globular conformation; any specific polymer chain conformation can play the role of a parent one. The simplest example of this kind is connected with the conformation of a homopolymer chain adsorbed on a flat substrate.

Let us "color" the chain segments being in direct contact with the surface in some typical instant conformation. This corresponds to the assumption that the surface catalyses some chemical transformation of the adsorbed segments. Then we will end up with an AB copolymer for which the sequence design was performed in the parent (adsorbed) state. One can expect that, after desorption, such an AB copolymer will have special functional properties: it will be "tuned to adsorption" (**Figure 12**). Following this line, Zheligovskaya et al. ⁹² have compared the adsorption properties of copolymers with special "adsorption-tuned" primary structures (adsorption-tuned copolymers, ATC) with those of truly random copolymers and random-block copolymers. Monte Carlo simulations revealed that specific features of the ATC primary structure promote the adsorption of ATC chains, compared to their random and random-block counterparts under the same conditions. In other words, the resulting copolymer sequence "memorizes" the original state of adsorbed homopolymer chain. It was shown

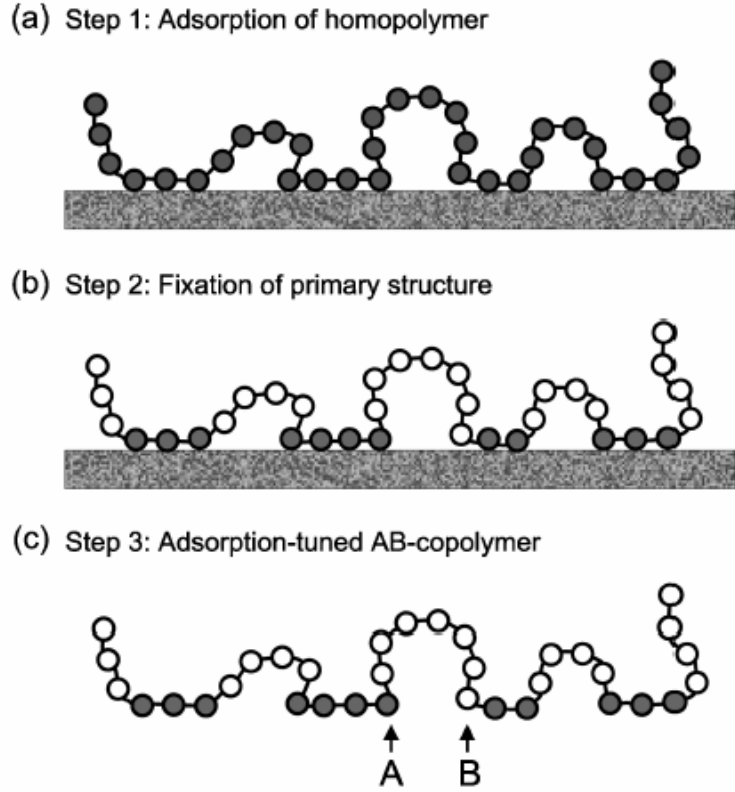


Figure 12. Schematic representation of the sequence design procedure leading to an adsorption-tuned primary structure.

that its statistical properties exhibit LRC of the Levy-flight type similar to those known for copolymers obtained via "coloring" of a homopolymer globule.¹²⁰

Recently, Velichko et al.¹²¹ have suggested the model of so-called molecular dispenser that is a further development in the direction of conformation-dependent sequence design. The authors simulated a homopolymer chain adsorbed on a spherical colloidal particle of nanometer size and performed design of sequence for this state of the chain: the non-adsorbed loop-like chain sections were transformed into soluble ones while the segments directly contacting with the surface remained adsorbable and were partly cross-linked. This resulted in fixing the cage structure of the central cavity. It was shown that after eliminating the "parent" particle, the cross-linked copolymer obtained in this way was tuned to selectively adsorb from a polydisperse colloidal solution other particles of the same size as in the preparation conditions.

Chapter 2

Comblike copolymers at an interface

In this chapter, the conformational behavior and some dynamic properties of molecular bottle-brushes are studied using the so-called cellular-automaton-based simulation technique.

2.1 Cellular-automation-based (lattice) molecular dynamics for the bond-fluctuation model of polymer

The static and dynamic properties of polymers can be simulated using numerical Monte Carlo (MC) or molecular dynamics (MD) techniques. MC methods, in which subsequent configurations of the system are generated stochastically, can be applied to both lattice and off-lattice polymer models. For studying dense polymeric systems, one of the best MC models is the bond-fluctuation model (BFM), which was first introduced by Carmesin and Kremer¹²². This lattice, coarse-grained, model has turned out to be much more efficient than other MC models of polymer chains^{123,124,125}. The second numerical method, the molecular dynamics, is based on continuum models, for which the integration of Newton's equations of motion of particles interacting via continuous or discontinuous potentials is performed. Generally, the continuum MD simulations are more flexible compared to MC. However, the full description of the microscopic properties such as the interparticle potential allows only to simulating the behavior of a relatively small number of particles. For the athermal case, which means that only the excluded volume interaction is taken into account, the MC bond-

fluctuation model (MC/BFM) is approximately an order of magnitude faster than the MD simulations^{123,124,125}. Also, the typical stability problems arising in the MD algorithm should be mentioned.

In the present section, we describe an attempt to combine the best features of lattice BFM and dynamic simulations in one algorithm. We will call this approach *lattice molecular dynamics* (LMD). It turns out that the LMD method requires about one order of magnitude less computer time than the standard MC/BFM method. The LMD procedure gives much more rapid convergence to the limiting distribution and can explore configuration space approximately an *order* of magnitude more efficiently than an equivalent MC simulation.

A first attempt to get correct microscopic properties from a coarse-grained description was done by Broadwell¹²⁶ for a gas in which the possible molecular velocities are restricted to a finite set. Then, Frisch et al.¹²⁷ devised a cellular-automaton-(CA-) based model for fluid mechanics. A new simulation scheme, maximally discretized molecular dynamics (MDMD), based on a lattice-gas automaton was proposed by Colvin et al.¹²⁸. They showed that the coarsest discretization of positions and velocities in MD leads to qualitatively correct transport coefficients. More recently, a CA-based algorithm for simulating the dynamic behavior of two-dimensional polymer solution was presented by Koelman^{129,130}.

We present here a brief description of the LMD model and some of its variants.

We consider particles which occupy the sites of square ($d=2$) or simple cubic ($d=3$) lattice. A polymer chain is represented by a sequence of N_p consecutive particles (monomer units or "beads") connected by N_p-1 effective bonds. In the BFM, each monomer unit occupies 2^d lattice sites. Double occupancy is excluded. Chain crossings are prohibited with a proper choice of the maximum separation, b_{max} , of connected monomers i and $i+1$. Thus, the bond length can range from $b_{min}=2$ ($d=2,3$) to $b_{max}=13^{1/2}$ ($d=2$) or $b_{max}=10^{1/2}$ ($d=3$) in units of the lattice spacing σ . This corresponds to 36 ($d=2$) or 108 ($d=3$) allowed bond vectors $\mathbf{b}$ with different choices of the bond length: $b_{2d}=\{2, \sqrt{5}, \sqrt{8}, 3, \sqrt{10}, \sqrt{13}\}$ and $b_{3d}=\{2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10}\}$. Generally, the system is modeled as an ensemble of $n_p N_p$ -unit chains (where n_p is the number of chains, N_p – number of monomer units in chain) and n_s solvent particles (equivalent in size to monomer units). $N(=n_p N_p + n_s)$ particles are placed inside an L^d box with periodic boundary conditions. The volume fractions of polymer and solvent are given by $\Phi_p = n_p N_p (2\sigma/L)^d$ and $\Phi_s = n_s (2\sigma/L)^d$, respectively. We consider particles moving on a

square (simple cubic) lattice with unit "velocity" v_α in direction α [$\alpha = \pm x, \pm y$ ($d=2$) or $\alpha = \pm x, \pm y, \pm z$ ($d=3$)] between a given lattice cell occupied by particle i and one of its four (six) nearest neighbors. The changes in particle "velocities" are caused by "elastic collisions" between pairs of particles i and j . The collisions take place if

$$\begin{cases} r_{ij} < 2 & \text{for all pairs } i \text{ and } j & (d = 2, 3) \\ r_{ij} > b_{\max} & \text{when } i \text{ and } j \text{ are chain neighbors} & (d = 2, 3) \\ r_{ij} = \sqrt{8} & \text{when } i \text{ and } j \text{ are chain neighbors} & (d = 3) \end{cases}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\mathbf{r}_i$ and $\mathbf{r}_j$ are the corresponding position vectors.

The collision laws of the discrete coarse-grained model give the transition rules for the internal states of each cell occupied by particles. The choice of the collision laws is somewhat arbitrary. For the simplest version of LMD, we use the following highly simplified collision law: $\mathbf{v}_i \Leftrightarrow \mathbf{v}_j$, for any two colliding particles i and j . In other words, the motion of the particles is such that, if their relative positions do not satisfy the constraints presented above, the particles move freely; in opposite case, an elastic collision takes place between the corresponding pair of particles, thereby interchanging their "velocities". Therefore, linear momentum and kinetic energy are conserved in all collisions. The simulations reported in this study are performed for the case when all particles have nonzero "velocities" and $\mathbf{v}\mathbf{v}^T = 1$. Thus, in the model under consideration, each collision between pairs of particles can only change the direction of the move but not the length of a jump.

At each time step the particles attempt to move in the corresponding directions; their trajectories between collisions are straight lines. If a collision occurs, the "velocities" of the two colliding partners are interchanged, but the particles are not moved until the next time step. As a result, in each configuration the excluded-volume condition and the bond-length restrictions are strictly met.

It should be noted that the coarse graining inherent in our model introduces multiple collisions. If such collisions take place, we chose randomly one of the possible binary collisions. Thus, as in MDMD¹²⁸, a stochastic element is present in the model.

We have also used a variant of this model in which the coupling to a heat bath is simulated. In this case, the "velocity" of a randomly selected particle is chosen afresh with the probability γ . Each stochastic collision is an instantaneous event that affects the "velocities" of the corresponding particles, that is, their directions of the

move. Then the particles are moved according their new "velocity", i.e., in some new directions. This physical picture corresponds to collisions between real particles and virtual heat-bath particles. At $\gamma = 0$, the system evolves in accordance with the usual collision rules. It is clear that the limiting case $\gamma \rightarrow 1$ corresponds to the standard MC scheme. If $\gamma > 0$, kinetic energy is conserved in all collisions, but since the model includes the fluctuations of "velocity" directions, momentum is conserved only on the average. It appears that, if the virtual collisions occur very frequently (i.e., $\gamma \approx 1$), this slows down the speed at which the particles in the system explore configuration space. On the other hand, when $\gamma = 0$, one disadvantage is that the calculated trajectories are not necessary ergodic. Such a problem arises for a single 3d polymer without surrounding solvent. LMD simulations with $\gamma > 0$ do not have this problem because they can improve ergodicity by making random changes to the configurations. In fact, most of the simulations discussed below were done with the model including virtual heat-bath particles, at $\gamma = 0.1$.

Note that at $\gamma = 0$ the system must satisfy the following conditions: (i) $\sum_{i=1}^N v_{ai} = 0$ and (ii) $N = 2dn$, where $n = 1, 2, \dots$ (the last condition can be fulfilled by adding the required number of 1-mers (i.e., solvent particles)).

All results presented below are expressed in internal units: lengths are measured in lattice constants σ , and time, t , is measured in units of time steps.

As has been noted, for simulating the behavior of polymer systems, the lattice bond-fluctuation model used in MC simulations is much more efficient than the continuum models. In this respect, the cellular-automaton-based molecular dynamics applied in the present study to the same model turns out to be still more efficient. The next question is: how does the LMD achieve this improved sampling efficiency? One clue to answer this question comes from examining the self-diffusion in a lattice gas. In the standard MC procedure, all the particles are moved with equal probability, in directions chosen at random. This limiting case corresponds to the coupling to a heat bath, when collisions between real particles and virtual heat-bath particles take place at each time step, with the probability $\gamma = 1$. At $\Phi \rightarrow 0$, the single-particle diffusion coefficient is given by $D = \langle \delta \mathbf{r}^2 \rangle / 2d$, where $\langle \delta \mathbf{r}^2 \rangle = \sigma^2$ is the mean-square displacement between two successive collisions. On the other hand, if we use cellular-automaton rules to introduce dynamics, the particle has unit velocity, and its trajec-

tory between two virtual collisions is a straight line. In this case, $\langle \delta \mathbf{r}^2 \rangle = \frac{\delta^2}{\gamma} (\frac{2}{\gamma} - 1)$. Then, it is clear that the simulation method in which the virtual collisions take place infrequently will generate larger moves between collisions and hence leads to larger D . Using diffusion in the configuration space as a criterion, we expect that such a method may well win out over a method that generates small moves. At $\Phi > 0$, one might say that advantages of the LMD method over MC simulations are due to the fact that at small γ a given particle passes through empty space located between other particles much faster than at $\gamma = 1$ (when the trajectory of the particle corresponds to a random walk). Intuitively, it is clear that the lower we make the volume fraction of particles the more pronounced are the differences in D . On the other hand, at high densities LMD becomes less useful. Note that, since the LMD algorithm is simple and involves only local operations, the computational effort increases only linearly with increasing system size.

2.2. 3d- and 2d- molecular cylindrical brushes: conformational behaviour and dynamics

2.2.1. Model

In this section we present the results of our LMD simulations on molecular bottle-brushes consisting of a main chain of N_b monomer units linked with n side chains of N_s monomer units; the total number of monomer units is $N = N_b + n \times N_s$. The length of the main chain was varied from 15 to 120 units (at $d=3$) and from 32 to 2048 units (at $d=2$). The side chains of lengths $N_s = 0\div 48$ were considered. The distance between grafted points along the backbone is denoted by m . The grafting density is given by $\varpi = n / N_b$. The maximum value of ϖ is equal to 2; in this case, $m = 1$ and each backbone monomer unit is linked with two side chains. In the present paper, we will consider the structures in which backbone monomer units are linked with not more than one side chain. In this case, $\varpi_{\max} = 1$. A starting configuration was created in the following way. First, the main chain was generated in the xy plane as a self-avoiding random walk. Then n side chains were grown from this backbone in the z direction. Depending on the total number of monomer units, between 5×10^5 and 2×10^6 time steps were necessary to obtain a fully equilibrated configuration. After equilibration, the simulation was carried out during time intervals ranged from 5×10^6 to 2×10^7 time steps. The structures under study were placed inside L^d box ($L = 256$ at $d = 3$ and $L = 4096$ at $d = 2$) with periodic boundary conditions. The box sizes are sufficiently large to ensure that no lattice effects take place.

Besides the "standard" geometric characteristics, such as chain sizes which have been considered in the numerical and theoretical works cited above, we will discuss some other quantities of interest, including the local fractal dimensionality, the particle scattering factor, time autocorrelation functions, etc.

2.2.2. Results and discussion

2.2.2.1. Dependence on the main-chain length and size scaling

The simplest ("customary") way of demonstrating the scaling behavior of polymers is to plot the mean square size of the chain versus the number of monomer units. We have calculated the root-mean-square size $R_g \equiv \sqrt{\langle R_g^2 \rangle}$ ($\langle R_g^2 \rangle$ being the mean-square radius of gyration) of the polymer backbone, R_b , for different main-chain lengths, N_b , at fixed grafting densities and side-chain lengths.

Figure 13 shows a typical plot of R_b vs. N_b for $\varpi = 1$ and $N_s = 6$. The usual procedure in analyzing data of this type is to fit it to the equation $R_b = AN_b^\nu$, where parameters A and ν are adjusted to obtain the best fit. This often requires that a few points for the smaller chains be omitted from the analyses. It was found that at $N_b > 45$ the value of R_b scales with N_b as $R_b \sim N_b^{0.588 \pm 0.065}$. Because only a few chains of finite length were studied, it is rather difficult to extract a convincing result for N_b -dependence from our data; a more extensive calculation involving much larger chains would be useful. Nevertheless, in Figure 13 we see the well-defined trend in data to approach the expected theoretical power law $R_b \sim N_b^\nu$ (with $\nu = 0.588$) for sufficiently long chains.

A more detailed scaling analysis of simulated data can be made by using the static structure factor $S(q)$ of backbone chain. Clearly, in an infinite dilute system the function $S(q)$ is just the average intramolecular correlation function defined as

$$S(q) = \frac{1}{N_b} \sum_{i,j}^{N_b} \langle \exp[\mathbf{i}q \cdot (\mathbf{r}_i - \mathbf{r}_j)] \rangle \quad \text{Equation 12}$$

where $\mathbf{i} = \sqrt{-1}$, $\mathbf{r}_i$ is the position vector of monomer unit i belonging to the main chain,

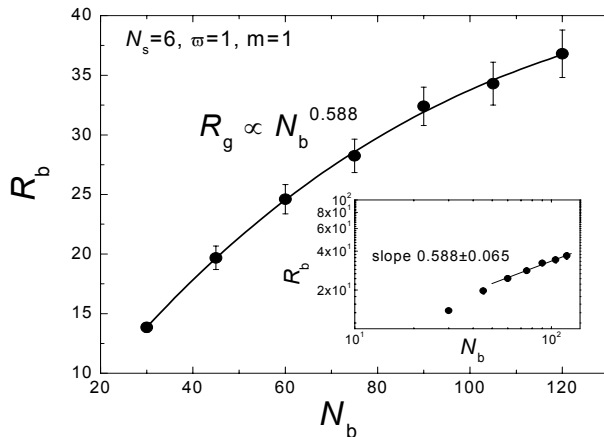


Figure 13. Radius of gyration of the main chain R_g as a function of N_b , at side chains length of $N_s = 6$ and grafting density of $\sigma = m^{-1} = 1$.

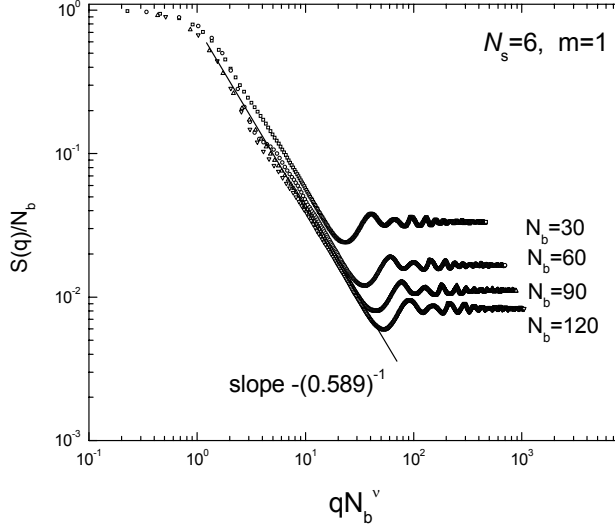


Figure 14. The intrachain static structure factor of the main chain vs. qN_b^v for four different values of N_b , at $N_s = 6$ and $m = 1$.

and $q = |\mathbf{q}|$ is the wave number. The corresponding scaling plot of $S(q)/N_b$ vs. qN_b^v (with $v = 0.588$) is shown in **Figure 14** for various main-chain lengths at side-chain length $N_s = 6$ and grafting density $m = 1$. For $N > 30$, we find excellent agreement with expected behavior: it is seen that there is a universal behavior for $1/q$ larger than a mean bond distance. For these intermediate values of q , the intrachain excluded volume interaction causes the scattering function to behave like $S(q) \propto q^{-1/v}$ that corresponds to the usual swollen state of linear polymer chains. As it can be seen, for $q \lesssim 10N_b^v$ the curves coincide. The insensitivity to N_b indicates that even ~ 10 -unit sections are near the scaling limit in this q region when $N_b \gtrsim 30$. For larger values of q , the chain units are uncorrelated at any N_b and $S(q) \rightarrow 1/N_b$ as it follows from **Figure 14**. At $q \rightarrow 0$, one observes: $S(q) \rightarrow N_b$.

Thus we conclude that, if the main-chain length is large enough, the backbone of the molecular bottle-brushes exhibits a universal scaling behavior $R \sim N_b^v$ well known for linear polymer chains in a good solvent. This result is in good agreement with all theoretical predictions considered above in Section 1.1.2.

Figure 15 shows a typical instantaneous configuration of the bottle-brush structures with the largest backbone $N_b = 120$ simulated in the present study for the case of three-dimensional space. This snapshot reflects many of the features which are characteristic for molecular bottle-brushes at high grafting density of side chains.

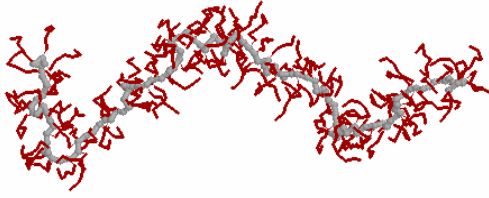


Figure 15. Typical configuration of the bottle-brushes structures: 120-unit main chain grafted with the 6-unit side chains at $m = 1$. Spheres depict monomeric

2.2.2.2. Dependence on the length of side chains

The typical results obtained for the mean radius of gyration of the main chain and the overall structure are plotted versus side-chain length in Figure 16a. In both cases we observe an increase of the mean dimensions as the side-chain length is increased. Such a behavior gives an indication of side-chain induced stretching. In order to get estimates for the exponent, the simulation data should be fit to the functional form $R_g(n) = R_g(0) + An^x$, since the correction-to-scaling term $R_g(0)$ is nonnegligible. In Figure 16a, the data points are the simulation results and the curves are nonlinear least-squares fits obtained by using only one of the correction-to-scaling terms in each case. One sees that use only one correction term leads to an excellent fit over the whole data set in all cases.

We found $R_g \sim n^{0.398 \pm 0.040}$ for the backbone and $R_g \sim n^{0.517 \pm 0.052}$ for the overall structure at $N_b = 60$ and $m = 1$. The exponent 0.398 governing the size of the main chain is in reasonable agreement with the corresponding value $9/25 = 0.36$ theoretically predicted by Birshtein et al.⁴², by Fredrickson⁴³, and by Rouault and Borisov⁴⁴ for the case when the branch density is not very high (see Eqs. (1) and (3)). However, the calculated exponent is smaller than that predicted for the situation of dense grafting with long side chains (Eqs. (5) and (6)). Probably, only for larger values of n used in the simulation this agreement would be possible. It should be recalled that the similar dependence $R_g \sim n^{0.34}$ has also been obtained in the Monte-Carlo simulation of Rouault⁵⁰.

The dependence $R_g \sim n^{0.517}$ observed in our calculation for the overall structure is much stronger than that found for the backbone. This is due to the swelling of the side chains. Note that the exponent 0.517 happens to be nearly the same as predicted by Eq. (5). On the other hand, taking into account that $N = N_b + N_b N_s / m$, from Eq. (1) one has⁴²:

$$R_N \sim N^{3/5} (m / N_s)^{6/25}$$

Equation 13

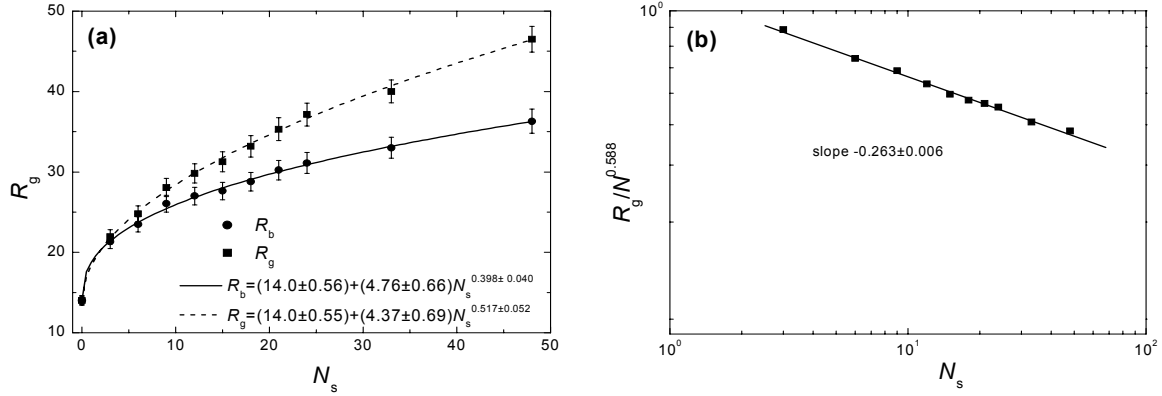


Figure 16. Radius of gyration of the backbone R_b and of the overall structure R_g as a function of side chain length N_s , at $N_b = 60$ and $m = 1$.

That is, the ratio $R_g/N_s^{3/5}$ should decrease as $N_s^{-0.24}$ with N_s increasing. The same dependence follows from the theoretical prediction of Fredrickson⁴³ (see Eq. (3)).

In Figure 16b we present the ratio $R_g/N_s^{0.588}$ calculated for the overall structure at different N_s and $m = 1$. The least-squares fit for $N_s = 6 \div 48$ yields $R_g \sim N_s^{-(0.263 \pm 0.006)}$. This scaling dependence seems applicable even for rather small side chains in the highly branched case and is in reasonable agreement with that theoretically predicted in the limit $N_s/m \gg 1$. Such a numerical proof was not given in the previous simulations^{45,46,47,48,49,50}.

2.2.2.3. Dependence on the grafting density

Figure 17a shows the mean radius of gyration calculated for the main chain at various grafting densities, $\varpi = m^{-1}$, for the fixed values of $N_b (=60)$ and $N_s (=12)$. As can be seen, the value of R_g is an increasing function of ϖ . At low densities, the ϖ -dependence of R_g exhibits an induction region as the branch density increased. In this case, the side chains are well separated and weakly interact. Although the induction effect makes it difficult to determine the limiting behavior of R_g as a function of ϖ without generating long side chains, its presence does demonstrate the extent of the residual effects of the "unperturbed" system. Taking this circumstance into consideration, we put into the data set the results obtained for the bottle-brushes with two side chains attached to one common monomer of the backbone. For sufficiently large values of ϖ , the least-squares fit performed on the postinduction R_g data gives $R_g \sim \varpi^{0.32 \pm 0.01}$. The obtained exponent (0.32) is comparable to that (0.36-0.4) predicted

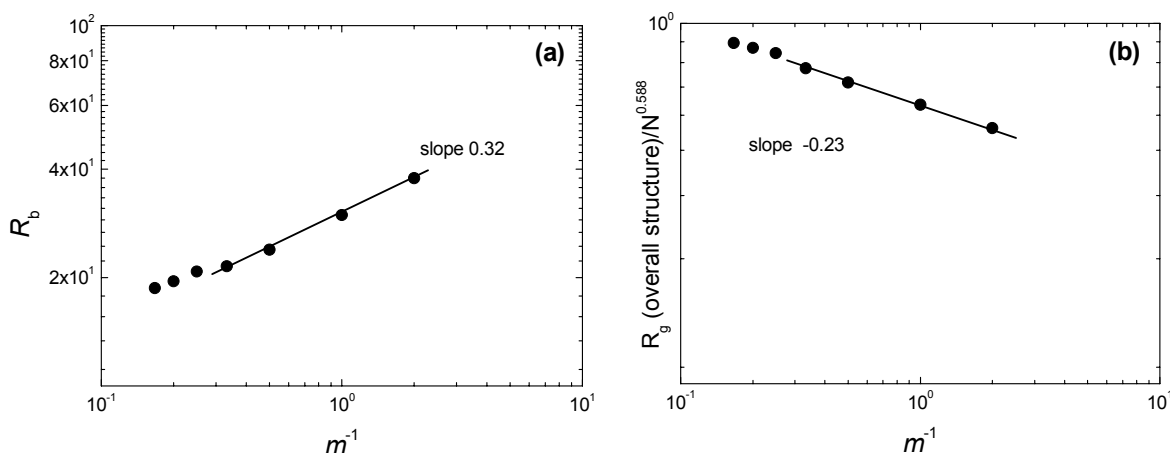


Figure 17. Radius of gyration (a) of the main chain and (b) of the overall structure as a function of grafting density m^{-1} ($=\sigma$), at $N_b = 60$ and $N_s = 12$.

by Birshtein et al.⁴² and Fredrickson⁴³ (see Eqs. (1) and (3)) and seems to be not even close to the prediction of Rouault and Borisov⁴⁴ for the system with densely grafted side chains.

It has been mentioned above that, according to the classical Flory-type theories, the expansion factor of a branched polymer, α , should be greater than that of a linear counterpart of the same molecular weight and should increase with an increase in the degree of branching. The similar conclusion follows from the simulation of Gallacher and Windwer⁴⁵. At the same time, experimental data¹³¹ and the theoretical predictions of ref.³⁸ show the opposite trend. The scaling arguments lead to the same behavior (see Eq. (12)). Earlier, for branched polymers constrained to have n branch points, it has been suggested^{131,132,133,134}, that the mean radius of gyration is reduced from the unbranched value: $R_g \sim N^\nu n^{-\beta}$, at least at low densities n/N . For the models without volume exclusion and with a fixed branching functionality, a mean-field value of $\beta = 1/4$ independent of space dimensionality has been found. For our present calculations, one has $n \sim m^{-1} \sim \sigma$. Thus, taking $\nu = 0.588$, we have computed the relative value of R_g/N^ν for the overall structure. This ratio is presented in **Figure 17b** as function of m^{-1} . It is seen from the figure that the size of branched polymer is smaller than that for the linear macromolecule with the same monomer number N and decreases with an increase in grafting density. Thus, we conclude that the statistical-mechanical results and the scaling treatment of the relative contraction properties are correct. Again, an induction region is observed at relatively low values of σ . For the

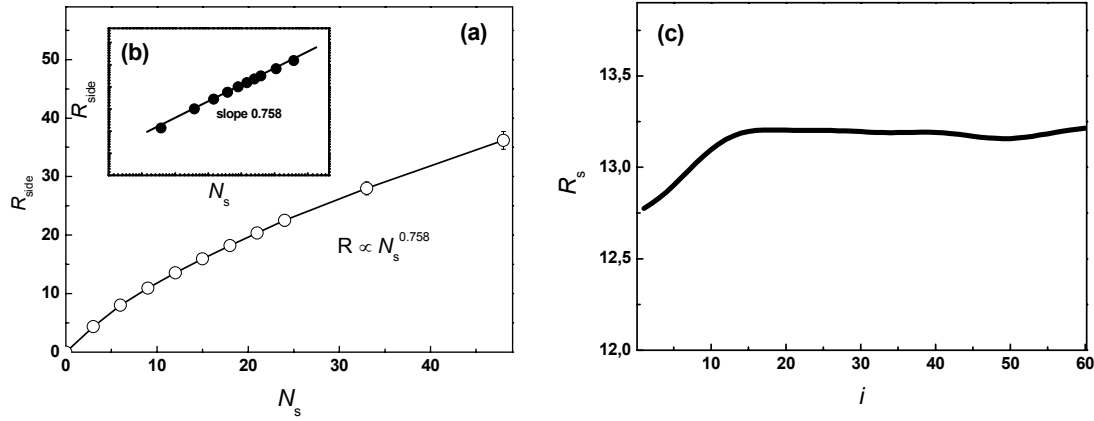


Figure 18. (a) end-to-end distance of the side chains R_{side} vs. N_s for $N_b = 60$ and $m = 1$. The inset (b): plot of $\log_2 R_{\text{side}}$ vs. $\log_2 N_s$. (c) radius of gyration of side chain R_s as a function of index number, i , for $N_b = 120$, $N_s = 48$, and $m = 1$.

postinduction R_g data we have $R_g \sim \varpi^{-(0.23 \pm 0.01)}$. The exponent of -0.23 is slightly larger than that obtained in ref. ³⁸ ($R_g \sim \varpi^{-0.3}$) and is in excellent agreement with the value of -0.24 predicted by Birshtein et al. ⁴² and Fredrickson ⁴³.

2.2.2.4. The conformational properties of side chains

Let us consider the behavior of the side chains in the highly branched regime. The side chain dimensions calculated for chains containing from 3 to 48 units are presented in Figure 18 for $N_b = 60$ and $m = 1$ (plot of $\log_{10} R$ vs. $\log_{10} N_s$ is given in the inset (b) of Figure 18). The least squares fit yields $R \sim N_s^{0.758 \pm 0.013}$. Actually, this corresponds to the statistics of two-dimensional self-avoiding walk, i.e., $R \sim N_s^\nu$ with $\nu = 3/4$. Since the exponent ν obtained in our calculation is considerably larger than the 3d-SAW value of 0.588, it is clear that the excluded-volume interactions are much more pronounced for the systems under study as compared to free (ungrafted) chains. Of course, in the $\varpi \rightarrow 0$ limit, one must be $\nu = 0.588$.

It should be noted that, in principle, chain end effects should be taken into account ⁴⁹. Such effects are due to the fact that the side chains situated at both ends of the main chain are nonequivalent to the strongly overlapping side chains which are placed in the middle part of the backbone. That is the reason that in refs. ⁴⁹ only a certain number of inner side chains were considered.

However, it turns out to be that for the lattice model studied in this work the chain end effect is rather weak, as it can be seen from Figure 18c, where we show

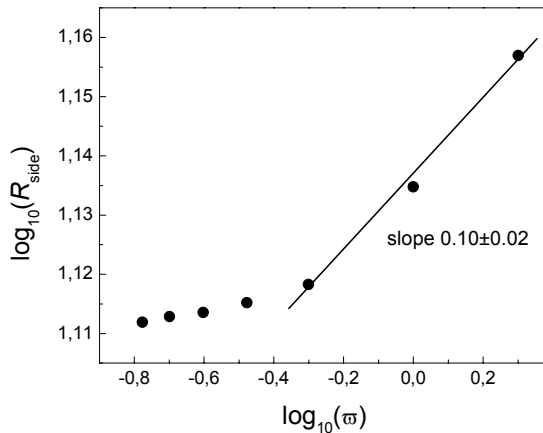


Figure 19. End-to-end distance of the side chains R_{side} vs. grafting density ϖ at $N_b = 60$ and $N_s = 12$.

side-chain size R_g as a function of index number i ($=1, \dots, n_s$), for $N_b = 120$, $N_s = 48$, and $m = 1$. Near the main-chain end (at $i \lesssim 12$), the i -dependence of R_g exhibits an induction region as the index number i is increased. Nevertheless the ratio $R_g^{\min} / R_g^{\max}$ is very close to 1 ($R_g^{\min} / R_g^{\max} = 0.96$). What is more, rejecting a certain number of end side chains (12 or even more) we obtain almost the same value of ν ($=0.751 \pm 0.081$). Of course, the chain end effect becomes more pronounced as the length of side chains is increased. This is why we consider relatively small values of N_s (≤ 48). In any case, the exponent obtained here is even slightly larger than the known limiting $2d$ scaling exponent of $3/4$. Broadly speaking, this is not surprising in view of the fact that in the present simulation the relatively short side chains have been studied. It seems evident that the exponent ν will decrease with increased N_s . Clearly, an extension of the simulations to much larger systems would be very desirable, as well as systematic studies for various grafting densities and backbone lengths. However, all these studies would require substantial efforts of computing time and hence are not easily feasible at the moment.

Now, we shall try to determine the dependence of side-chain end-to-end distance R on grafting density ϖ . The data shown in **Figure 19** demonstrate a steadily increasing mean end-to-end distance as a function of ϖ . Again, we observe a density-dependent induction region in the behavior of R at small ϖ . For the postinduction regime, a power dependence of R can be postulated. Although the exact scaling analysis of R as a function of σ cannot be performed on the basis of these results, the data suggest that in this regime the value of R behaves like $R \sim \varpi^{0.1}$. This happens to be

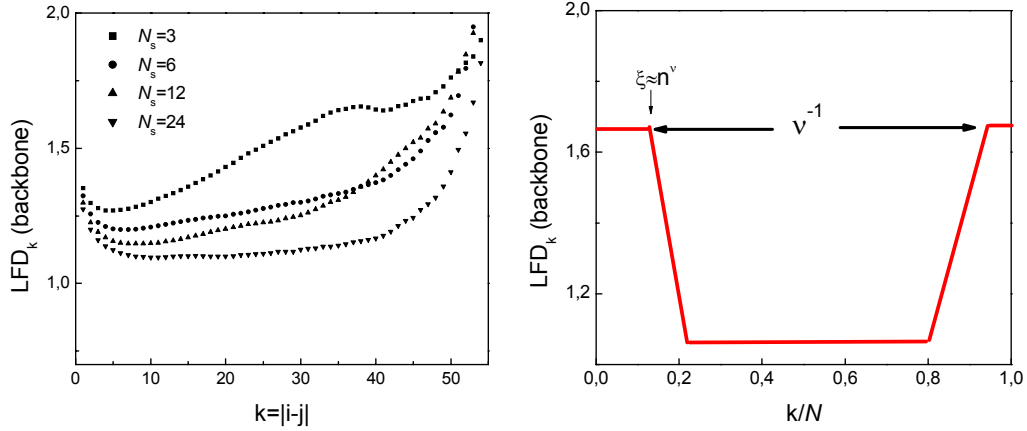


Figure 20. The LFD function of the 60-unit main chain vs. $k = |i-j|$ at $m = 1$ and different side-chain lengths N_s . The inset: schematic representation of LFD as a function of k/N for the “superblob” model⁴².

close to the prediction of Birshtein and co-workers⁴² for the strongly overlapping side chains, $R \sim \varpi^{0.12}$ (see Eq. (2)).

2.2.2.5. The local structure

Birshtein and co-workers⁴² have suggested that the conformation of molecular bottle-brushes can be treated from local point of view as a linear sequence of “superblobs”. In fact, this blob model provides a conceptual framework to describe the features of comblike polymers in ref.⁴². Following the blob model, the overall structure of N monomers is viewed as made up of N/N_s subchains or blobs of size ξ , so that the overall size of polymer is given by $R \sim \xi(N/N_s)^{3/5}$. At small scales ($r < \xi$) each blob retains the statistics of a three-dimensional self-avoiding walk of size $\xi \sim N_s^{3/5}$. Inside a blob, i.e., for short internal sequences of k monomer units at $k \lesssim \xi$, the backbone is flexible and behaves like a usual swollen chain. At intermediate length scales, it becomes extended, that is, the corresponding linear sequences are predicted to be mainly a linear string. Finally, at large length scales the macromolecule as a whole behaves as a self-avoiding walk consisting of blobs. This picture has been partially supported in ref.⁴⁹ using computer simulation; in particular, it has been shown that the main chain is rather flexible at small length scales and becomes extended on larger length scales.

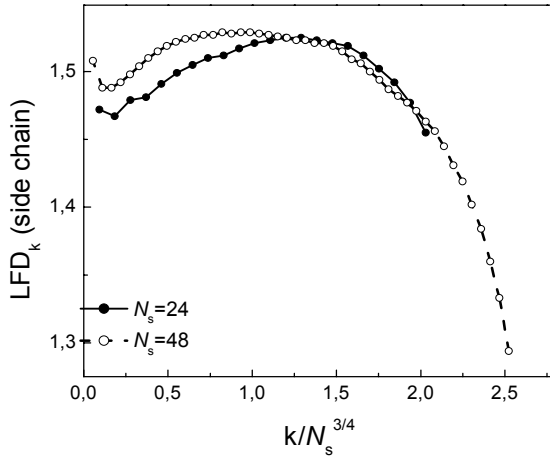


Figure 21. The LFD function of the side chains vs. $k/N_s^{3/4}$ for $N_s = 24$, $N_s = 48$, at $N_b = 60$ and $m = 1$.

The validity of the blob model can be established from analysis of the internal chain conformation. In order to study it, we define the so-called local fractal dimensionality (LFD)

$$\text{LFD}_k = \frac{\ln[k / (k-1)]}{\ln(\langle R^2 \rangle / \langle R_{k-1}^2 \rangle)^{1/2}} \quad \text{Equation 14}$$

where $\langle R_k^2 \rangle$ is the mean-square distance between and points of a chain sequence consisting of k monomer units along the chain. The LFD represents the extent to which the chain is winding. If the chain is straight line, then $\text{LFD}_k = 1$, whereas for a freely jointed noninteracting chain $\text{LFD}_k = 2$ for all k . In the intermediate regime, where the chain with excluded-volume interactions behaves as a 3d self-avoiding walk, $\text{LFD}_k = \nu^{-1} (\approx 5/3)$. Following the blob model considered above, for short internal sequences with $k \lesssim \xi$ it should be $\text{LFD}_k = \nu^{-1}$. Larger sequences with $k > \xi$ are predicted to be mainly a stretched string of blobs and this simply corresponds to $\text{LFD}_k \approx 1$. For $k \gg \xi$, one can expect that again $\text{LFD}_k = \nu^{-1}$. These contrasting regimes are illustrated schematically (Figure 20b).

As should be clear from Figure 20, the calculated k -dependence of LFD_k appears to be more or less similar to that predicted on the basis of "superblob" model⁴² for large N_s . For $N_s \gtrsim 6$ we do observe a non-monotonous behavior shape of LFD as a function of k . Nevertheless, although the "superblob" model seems to provide a reasonably good description of local conformational structure, the computer simulation results exhibit somewhat different behavior than expected. Indeed, the short chain sequences (for small values of k) are more expanded than would be predicted on the basis of simple blob theory. This extra expansion appears to be due to the neglect in

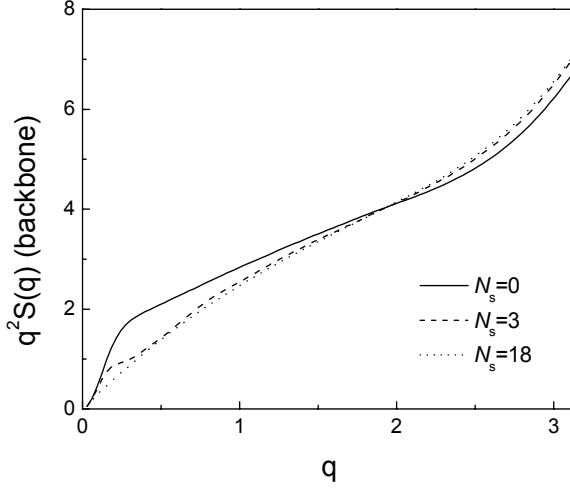


Figure 22. The intrachain static structure factor of the 60-unit main chain vs. wave number q at $m = 1$.

the blob model of interactions between monomer units inside one blob with the units inside other blobs. From Figure 20 we can see that the induced backbone extension is more pronounced for the structures with longer side chains. Note that support for this conclusion comes from the observation of Saariaho et al.²²⁾ that the persistence length of the main chain becomes larger as the side-chain length is increased, at least for not too large values of N_s . In addition, our results confirm the assertion of the same authors that for molecular bottle-brushes the possibility of more than one characteristic length should be considered. As has been mentioned above, they showed that the backbone is rather flexible at small length scales and becomes extended on a larger length scale.

Figure 21 presents the value of LFD_k as a function of $k N_s^{-3/4}$ for the side chains of some selected lengths ($N_s = 24$ and 48). We see that for sufficiently large N_s the dependence of LFD_k appears to be more or less universal function of scaling argument $k N_s^{-3/4}$. This indicates that the strongly overlapping side chains can be viewed as a fractal object on all length scales. There are clear differences with the previous results describing the backbone. We can speculate that at large values of N_s each side chain behaves as a string consisting of successively increasing blobs inserted into a cone with the top being the grafting point.

Figure 22 shows some typical results for the intrachain scattering function $S(q)$ plotted in the standard Kratky form. It is seen that at high grafting density the influence of the side chains on local backbone conformation is appreciable even for very short side chains. As N_s is increased, the behavior of $q^2 S(q)$ becomes to resemble that characteristic for a stretched line of scattering centers. Thus we conclude again that

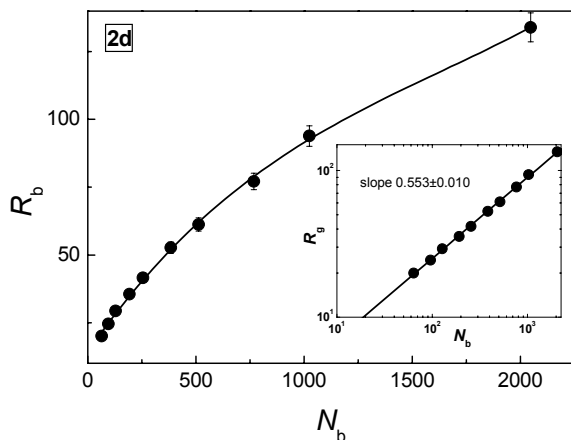


Figure 23. Radius of gyration of the main chain of the $2d$ bottle-brush structure as a function of main chain length, at $N_s = 1$ and $m = 1$.

densely grafted side chains induce the strong stretching of the main chain. However, as we will see below, a directly opposite effect is possible.

2.2.2.6. Exotic behavior of the $2d$ bottle-brushes

Let us consider the conformational properties of bottle-brush structures strongly adsorbed on a flat surface. It is clear that the limit of strong adsorption simply corresponds to a two-dimensional system. For this case we have performed very extensive calculations including main-chain lengths up to $N_b = 2048$. For the $2d$ bottle-brushes with the side chains situated on the one side of the backbone, we found an extremely unusual behavior of chain dimensions as a function of backbone length. It turns out that the $2d$ bottle-brush SAW (i.e., the chain with repulsive interactions between monomer units) behaves like a typical globular structure in a bad solvent (!). As an example of this we present in Figure 23 the root-mean-square radius of gyration R_g of the backbone with smallest side chains, $N_s = 1$, grafted at maximum one-sided density, $m = 1$. From these data, it follows that the value of R_g scales with N_b as $R_g \sim N_b^{0.553 \pm 0.010}$. The obtained exponent is much smaller than the value of $3/4$ known for $2d$ SAW's. On the other hand, this exponent is very close to $1/2$, the value which is characteristic for the unperturbed chains without excluded volume interactions or for the $2d$ chains in collapsed (globular) state. The same findings are correct for any other N_s and m .

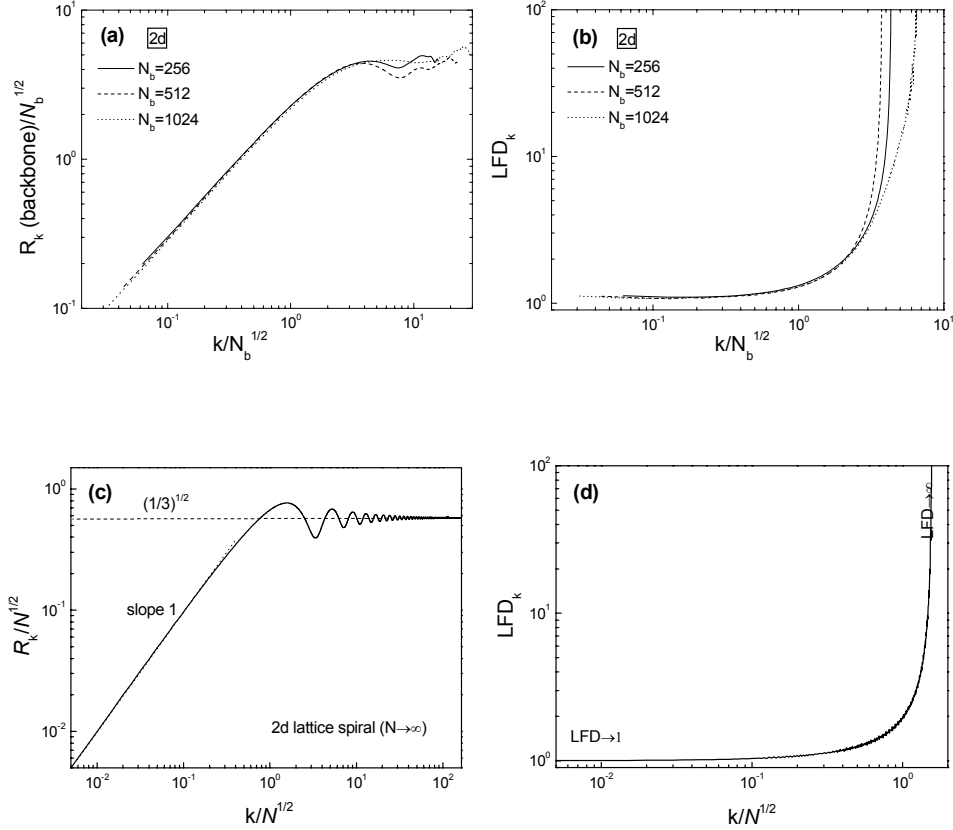


Figure 24. (a) The value of $R_k/N^{1/2}$ and (b) the LFD function vs. $k/N_b^{1/2}$ for the main chain of the 2d bottle-brush structure for different values of N_b , at $N_s = 1$ and $m = 1$. (c) The value of $R_k/N^{1/2}$ and (d) the LFD function vs. $k/N_b^{1/2}$ for the 2d regular lattice helix of infinite length.

Figure 24a shows a plot of R_k , the root-mean-square distance between end monomer units i and j of a section of $k = |i-j|$ units along the main chain, as a function of k for three different values of N_b . We find that the ratio $R_k/N_b^{1/2}$ is a universal function of scaling argument $k/N_b^{1/2}$, that is, $R_k = N_b^{1/2}f(k/N_b^{1/2})$. For the local fractal dimensionality (Figure 24b), one has $LFD_k = 1$ at small $k/N_b^{1/2}$ and $LFD_k \rightarrow \infty$ at large $k/N_b^{1/2}$. This means that the backbone chain behaves as a straight line on a small length scales and becomes tightly twisted on large length scales. Such a behavior corresponds to a fractal object having helical shape. To illustrate this in a little more detail, we show in Figure 24c,d the same dependencies but obtained for the perfect two-dimensional helix constructed from the infinite number of sites, N , of a square lattice with unit spacing. In this case, there is the following exact result for the scaling function $f(k/N^{1/2})$: $df(x)/dx = 1$ at $x \rightarrow 0$ and $f(x) \rightarrow 3^{-1/2}$ for large x . When the value of x grows, $f(x)$ exhibits a damped oscillatory behavior. Since by definition $LFD_k = d \ln k / d \ln R_k$, the LFD function shows the corresponding features. In general, we ob-

serve the same properties for the backbone chain of the $2d$ bottle-brushes. It is also useful to note that the square radius of gyration of the perfect lattice spiral is given by $R_g^2 = (N-1)/6$.

Thus we conclude that the equilibrium conformation of $2d$ bottle-brushes is nothing but the tightly winding helix. Snapshots presented in **Figure 25a**, where we can observe the kinetics of winding, illustrate this statement. In addition, in **Figure 25b** we show the partially adsorbed $3d$ chain. One sees that the chain section adsorbed on a surface forms a helical-shaped conformation.

The explanation of the formation of such exotic structures is trivial. The excluded volume of the side chains induces the spontaneous bending of the chain (i.e. the conformation corresponding to the minimum bending energy is not rectilinear).

Snapshots in **Figure 25c** illustrates the kinetics of the winding process of a brush molecules containing 40 % of the side chains at one side and 60% at the other side of the backbone, i.e. $\varphi = 0.4$ (see below). The initially stretched brush molecule starts to wind at both ends, while at later stages one of the ends prevails and results in either left-hand or right-hand helix.

This behavior depends on the relative number of the side chains located on the opposite sides of the backbone. We can use parameter $\varphi = n_i/n$ to characterize the asymmetry of the side chain distribution, where n_i –number of the side chains segregated at one of the sides of the main chain and consequently $n-n_i$ – number of the side chains at the opposite side. The value of φ is varied between 0 and 0.5. At $\varphi = 0$, all side chains are at one side of the backbone. This case was considered above. The other limiting case $\varphi = 0.5$ corresponds to random orientation of the side chains with respect to the backbone, with an equal number of the side chains at either of sides. At $\varphi > 0$, the conformational properties were averaged over different side-chain distributions ($\sim 10^2$). We have found that the mean backbone size R_b is an increasing function of φ , as it can be seen from **Figure 26**. However, our simulation shows that sufficiently long $2d$ comblike polymers form the helical conformation at any $\varphi < 0.5$, though the time needed for equilibration increases with increasing φ .

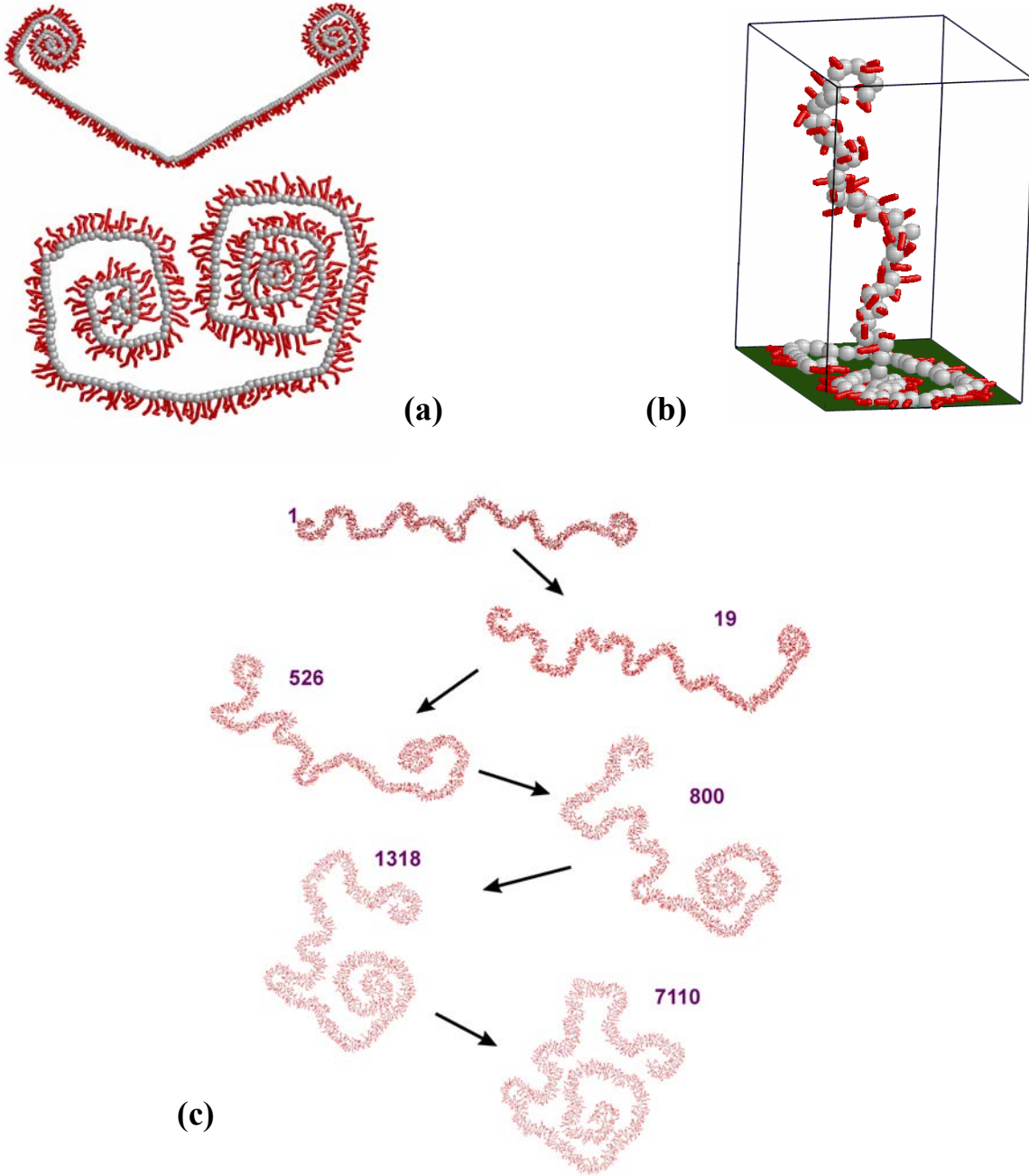


Figure 25. Snapshot pictures of bottle-brush structures: **(a)** completely adsorbed ($2d$) bottle-brush structure consisting of the 256-unit main chain and the 4-unit side chains grafted at $m=1$, *top*: configuration arising from fully extended state after 10000 time steps, *bottom*: configuration after 300000 time steps; **(b)** partially adsorbed $3d$ bottle-brush structure with the 102-unit main chain and the $n = 2$ side chains grafted at $m = 1$; **(c)** strongly adsorbed ($2d$) bottle-brush structure consisting of the 256-unit main chain and the 10-unit side chains grafted at $\varpi = 1$ and $\varphi = 0.4$, configuration arising from fully extended state to a helical configuration after 1318000 time steps, the corresponding time steps ($\times 1000$) are indicated next to the snapshot pictures.

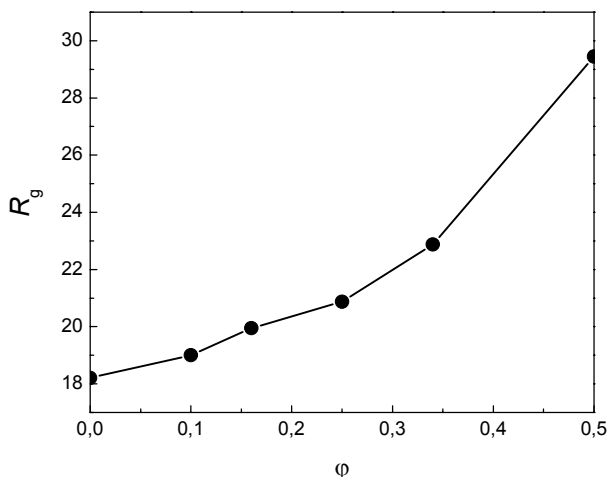


Figure 26. R_b as a function of ϕ , at $N_b = 60$, $N_s = 4$ and $\varpi = 1$.

It should be noted, that the $\sqrt{8}$ forbidden bond vector in 3d bond fluctuation model leads to an alternation of the excluded volume interaction that is no more correctly screened¹³⁵. For highly grafted chains this can have some effect. While this problem does not appear in two dimensions, it must be kept in mind for three dimensional systems.

2.2.2.7. *Scanning force microscopy*

Unlike $\phi = 0$, the case of $\phi \approx 0.5$ is quite realistic and might occur upon random sequential adsorption of cylindrical brushes on a flat surface. Scanning force microscopy was employed in group of M. Möller¹³⁶ to verify the hypothesis regarding plausibility of the helical conformation of cylindrical brushes in a 2d state. Molecular brushes were prepared by polymerization of poly(methyl metacrylate) (PMMA) macromonomers with a methacrylate end group by group transfer polymerization as described elsewhere¹³⁷. The degree of polymerization could be as high as $N_D = 10^4$, while the molecular of the macromonomer $M_n = 2410$ g/mol corresponds to $N_s = 25$. Thus, the resulting brushes consist of a long polymethylacrylate main chain and relatively short poly(methylmethacrylate) side chains grafted to each monomer unit of the backbone, i.e. $\varpi = 1$. To obtain macromolecules with a relatively narrow molecular weight distribution, the samples were fractionated by preparative size exclusion chromatography using tetrahydrofuran (THF) as a solvent. The fraction containing the largest molecules with $M_w = 25 \times 10^6$ g/mol and $M_w/M_n = 1.4$ was chosen for the experiment.

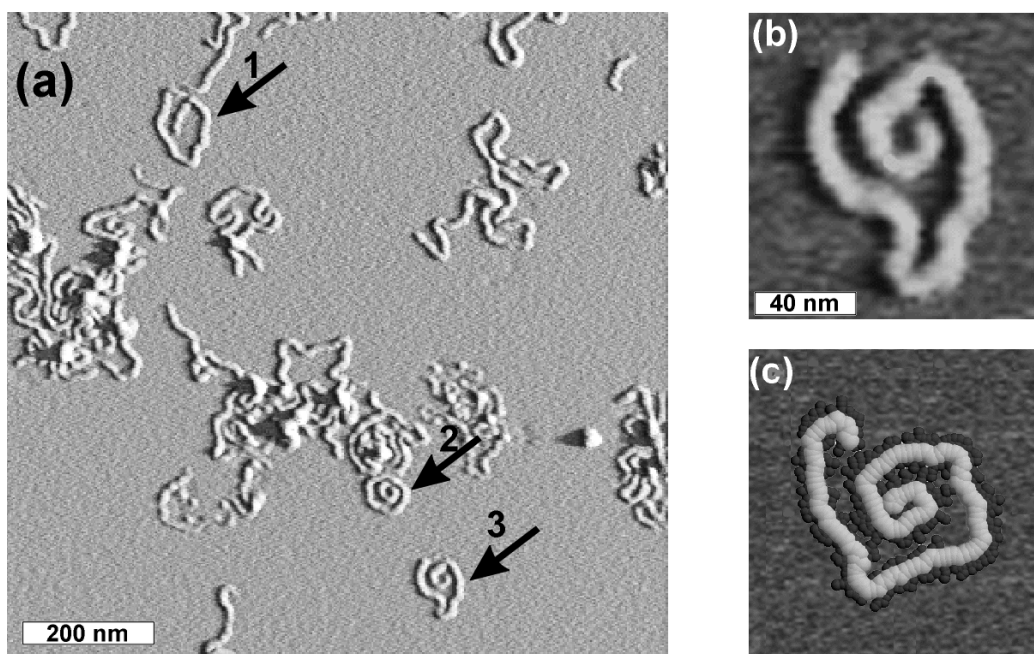


Figure 27. The SFM image of the individual PMMA macromolecules lying flat on the mica surface. (b) Typical snapshot of the simulated $2d$ bottle-brush structure consisting of the 128-segment main chain and the 4-segment side chains grafted at $\sigma = 1$ and $\phi = 0.1$.

The PMMA polymacromers were deposited from a dilute solution in chloroform by spincoating on a freshly cleaved crystal of mica. Chloroform is a good solvent for PMMA, while the polar surface of mica causes strong interaction with the polar methacrylate units. The solvent was evaporated at ambient condition for about 3 hours. Scanning force micrographs were recorded with a Nanoscope IIIa scanning force microscope (Digital Instruments) operated in the tapping mode at a resonance frequency of about 300 kHz. The measurements were performed at ambient conditions (in air, 50% RH, 23°C) using Si probes with a spring constant of 50 N/m.

The resulting SFM image is shown in Fig. 5a where the individual macromolecules are observed lying flat on the mica surface. Due to the strong interaction of PMMA with mica, the molecules are compressed towards the surface so that the width of the molecule $d_{||} = 11 \pm 1$ nm measured parallel to the surface plane was significantly larger than their height of $d = 2.0 \pm 0.1$ nm. The width was estimated by deconvolution of the independently determined radius of the SFM-tip $r_a = 8$ nm from the cross-sectional profile. **Figure 27a** displays different types of macroconformations which were vitrified by rapid evaporation of the solvent. One of the typically observed structures is the compact helix-like structures indicated by arrows. E.g., the molecule indicated by arrow 3 (**Figure 27b**) is remarkably similar to those predicted theoretically

and shown in **Figure 27c**. Also this coincidence is very remarkable, one cannot expect that all of the adsorbed brushes will adopt such conformation. The final conformation is controlled by the adsorption process depending on the molecular structure (degree of polymerization, side-chain length, grafting density), adsorption strength, the solvent quality, and the vapor pressure. Due to the fast evaporation of the solvent, it might take prohibitively long to achieve the equilibrium structure for large molecules strongly adhering to the substrate. Eventually, the helical conformation can be observed if the asymmetry of the side chain distribution relative to the backbone is sufficiently large (small ϕ) and the side chains are sufficiently long to wind the molecules during the short time interval of the adsorption event. The micrograph in **Figure 27a** shows that less than 10 % of the adsorbed molecules were able to form the helix. The ongoing experiments are focused to control the adsorption process and the chemical structure of the brushes to approach the equilibrium state.

The origin of such unusual molecular conformations is rather trivial. The excluded volume of the side chains induces the spontaneous bending of the chain, i.e., the conformation corresponding to the minimum bending energy is not rectilinear. It is also interesting to note that the formation of the helix-like objects is observed in computer simulations for two-sided 2d comblike polymers at $\phi = 0.5$ as well, provided that the chains grafted to each side of the backbone are characterized by different excluded volume interactions. In this case, by varying the quality of solvent (i.e., the interaction between the corresponding side-chain monomers), one can change the direction of winding or unwinding. Actually, such a system represents a "molecular spring" which could act as a molecular nanodevice transforming chemical energy into mechanical.

2.2.2.8. *The dynamical properties*

Among the many dynamical characteristics which can be studied, the chain relaxation is most important. The relaxation process is defined by the decay of the time-dependent autocorrelation function $C(R^2, t)$. This function measures the extent to which a configuration at a given time t_0 influences the configurations at subsequent times $t_0 + t$. The function $C(R^2, t)$ is defined by

$$C(R^2, t) = \frac{\langle R^2(t_0) \cdot R^2(t_0 + t) \rangle - \langle R^4 \rangle}{\langle R^4 \rangle - \langle R^2 \rangle^2} \quad \text{Equation 15}$$

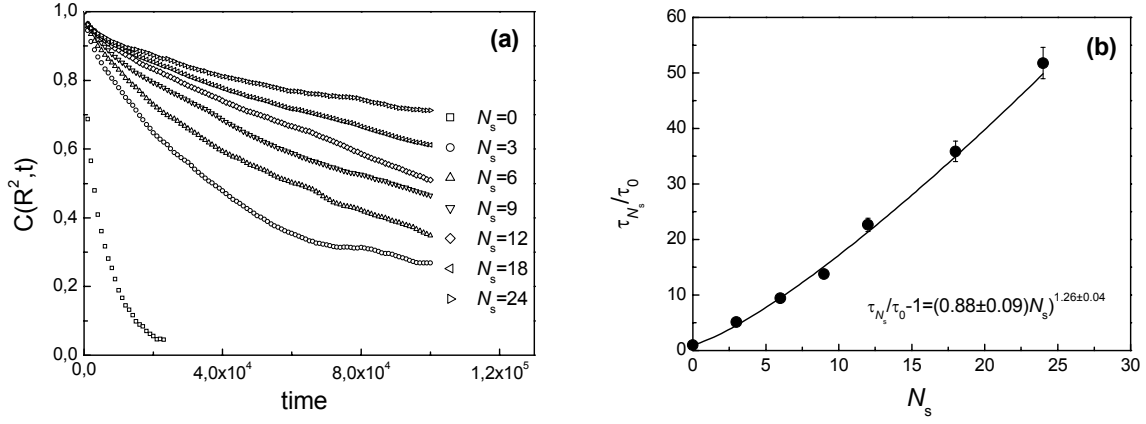


Figure 28. (a) Time autocorrelation functions obtained for end-to-end distance of the 60-unit main chain, at $m = 1$ and different values of N_s . (b) The ratio τ_{N_s}/τ_0 vs. N_s , at $N_b = 60$ and $m = 1$.

where $R^2(t)$ denotes the value of R^2 at time t and ensemble averages $\langle \dots \rangle$ are made with a succession of the time origin t_0 . Clearly, $C(R^2, t) = 1$, and since the correlation weakens as t increases, $C(R^2, t) \rightarrow 0$ for large t .

In **Figure 28a**, the behavior of $C(R^2, t)$ is shown for the 3d structure composed of the 60-unit backbone and the side chains of different lengths grafted at $m = 1$. For comparison, we also present the data obtained for the 60-unit chain without pendant chains. Several observations can be made. First, the excluded volume interaction between the side chains slows down the decay of $C(R^2, t)$. For small n , as in the case of a single linear chain, $C(R^2, t)$ follows roughly a single exponential decay $C(R^2, t) = \exp(-t/\tau)$, where τ is the relaxation time. At $n \geq 12$, $C(R^2, t)$ decays considerably slower and cannot be fitted by a simple exponential decay, but can still be fitted to a stretched exponential form, or the Kohlraush law $C(R^2, t) = \exp[-(t/\tau)^\alpha]$, where $\alpha \approx 1$ and $\tau = \int_0^\infty C(R^2, t) dt = (\tau/\alpha) \Gamma(1/\alpha)$. **Figure 28b** shows the variation of the ratio τ/τ_0 (τ_0

being the value of τ at $n = 0$) as a function of N_s . It is observed that τ increases drastically with n . The apparent divergence of τ at large N_s indicates that the backbone chain is "frozen" or in some kind of "glassy" state. A speculative suggestion for the N_s – dependence of τ is a simple power law, $\tau_n \sim N_s^x$. This type of fitting leads to the following dependence: $\tau_n/\tau_0 \sim N_s^{1.26 \pm 0.04}$. Clearly, a specific theoretical treatment is needed to interpret this dependence in more detail.

2.2.3. Conclusion

In this work extensive computer simulation have been performed using the lattice bond-fluctuation model (BFM) and cellular-automaton-based simulation technique to probe the equilibrium structure and the relaxation of comb-branched polymers in which the flexible side chains of a given length are placed regularly along the backbone and the number of branches increases linearly with total molecular weight.

In many cases, the "lattice molecular dynamics" (LMD) technique proposed in the present study requires about 1 order of magnitude less computer time than the standard MC/BFM method^{122,123,124,125}. Since a lattice structure of the space is used, very effective programming is possible on both scalar and vector computers. Of course, there exist a number of other efficient MC algorithms for single-chain (on-lattice and off-lattice) systems in which the excluded volume effect is relatively weak: the pivot (or wiggle) algorithm¹³⁸ is a typical example. This method has been applied to simulate molecular bottle-brushes^{50,139}. However, it must be kept in mind that such simulations are expected to be much less efficient for polymers with complex nonlinear global architecture and strong excluded-volume interactions or for dense, many-chain systems; in this case, most of the trial conformations will be forbidden (it stands no reason that as the amount of void space, or solvent volume fraction, decreases, the corresponding MC simulations become impossible). On the other hand, for the LMD model, based on the local moves of segments, these problems are not so serious. In addition, this model leads for sufficiently long chains to a correct (both Rouse-like and Zimm-like) dynamics.

By applying LMD, we have been able to investigate the properties of sufficiently large comblike structures (up to 5880 monomer units). Depending on the length of main and side chains as well as on interbranch spacing (grafting density), we have calculated mean chain dimensions, local fractal dimensionalities, particle scattering functions, time autocorrelation functions, etc. The following main conclusions may be drawn from the results presented in our study:

- (i) The scaling properties of three dimensional branched systems are amenable to analysis using the same formalism as is used for linear chains, and the evidence is that the critical exponent, governing the mean size of the main chain as a function of its length, remains unchanged from its value known for a 3d self-avoiding walk. On the other hand, two-dimensional branched macromolecules with one-sided branches

are effectively in a collapsed state even under conditions of a good solvent that is due to the formation of regular spiral-like conformations. It should be noted that the two-dimensional spiral-like structures for comblike copolymers strongly adsorbed on a flat solid surface have been recently observed experimentally using the scanning force microscopy.

(ii) Comparison of the simulated data with the predictions of the scaling model indicates that the latter is valid in describing the mean dimensions of the backbone, R , as a function of side-chain length, N_s , and interbranch spacing, m . In particular, it is found that the value of R scales with N_s and m as $R \sim N_s^{0.398}$ and $R \sim m^{-0.320}$ for sufficiently large N_s and high grafting densities. This supports the scaling relation $R \sim (N_s/m)^{9/25}$ first proposed by Birshtein and coworkers¹⁶⁾. For the dimensions of the overall structure, R_N , we have obtained the following dependencies: $R_N \sim N_s^{-0.26}$ and $R_N \sim m^{0.23}$, which are in reasonable agreement with the scaling relation $R_N \sim (m/N_s)^{6/25}$. These results show that the size of branched polymers is smaller than that observed for linear macromolecules with the same molecular mass and decreases as side-chain length and grafting density are increased. Such a behavior is consistent with numerous experimental data, but it is at variance with the mean-field-type theories. In addition, it is found that the side chains behave like a 2d SAW and their size is a density-dependent function that varies with m as $m^{-0.1}$. These findings happen to be close to those predicted by Birshtein and coworkers⁴²⁾ for the case of strongly overlapping side chains.

(iii) The excluded volume interaction between side chains dramatically slows down the relaxation of the backbone chain. The corresponding relaxation time, τ_n , is found to behave as $\tau_n/\tau_0 \sim N_s^{1.26}$.

(iv) The computer simulation showed that the 2d-macromolecules with asymmetric distribution of the side chains relatively to the backbone are effectively in a collapsed state even under conditions of a good solvent. They formed peculiar helical superstructures which could be observed by scanning force microscopy of cylindrical brushes of polymethylmethacrylate on mica. The origin of such unusual molecular conformations is rather trivial. The excluded volume of the side chains induces the spontaneous bending of the chain, i.e., the conformation corresponding to the minimum bending energy is not rectilinear. It is also interesting to note that the formation of the spiral-like objects is observed for two-sided 2d structures too, provided that the chains grafted to each side of the backbone are characterized by different excluded

volume interactions. In this case, by varying the quality of solvent (i.e., the interaction between the corresponding side-chain monomers), one can change the direction of winding or unwinding. Actually, such a system represents a "molecular spring" which could act as a molecular device transforming chemical energy into mechanical.

Of course, the model considered in this study is only a prototype of realistic comb-branched polymers. One of the main limitations stems from the fact that the simulations presented here are restricted to systems of freely jointed chains without bond-angle and dihedral-angle potential functions. This makes the quantitative comparison with experiment impossible. It is also obvious that the monomeric units should, generally speaking, be regarded as effectively interacting in a dense solvent, rather than in vacuum.

2.3. Comblike copolymers under lateral compression

2.3.1. Model

Here, the computer simulation technique based on the idea of cellular automaton and lattice model of a chain with fluctuating bonds has been applied. The system consisting of $K = 9$ comblike macromolecules with the parameters $N_b = 60$, $n = 30$ and $\varpi = 2$ was studied. The side-chain length N_s was varied from 4 to 16. Correspondingly, the total number of segments N was varied from 1620 to 4320. Initially, all macromolecules were placed into a three-dimensional cell with the lateral dimensions $L_x = 240$, $L_y = 240$ at $N_s = 4$, $L_x = 360$, $L_y = 360$ at $N_s = 8$, $L_x = 480$, $L_y = 420$ at $N_s = 16$. The box dimension along the z axis was varied from $L_z = 15$ to 55 (depending on the side-chain length). All lengths are expressed in lattice units σ . The cell with the initial surface density of monomer units $\rho_0 = 0.01$ was compressed to the maximum density of $\rho_{\max} = 0.71 \pm 0.02$ (reasons for this limitation on the density will be discussed below). The surface density of the system was determined as $\rho = 2^d N_a / S$, where N_a is the average number of adsorbed monomer units, S is the surface area (i.e., the total number of lattice sites in the plane (x, y)), and $d = 2$. The energy $\varepsilon_b = -12kT$ or $\varepsilon_s = -4kT \div -6kT$ was attributed to each main-chain or side-chain unit in contact with the surface $z = 0$, respectively. Therefore, the adsorption of main chains was practically irreversible, whereas side chains could partially desorb from the interface under certain thermodynamic conditions. To estimate the entropic contribution, we performed additional calculations at $\varepsilon = 0$. For convenience, we can describe the system by using the "compression parameter" p , that is, the concentration of the main-chain units on the surface $p = KN_b / S$, and the fraction of adsorbed side-chain units $\gamma_s = N_{as} / N_s$. In the computer experiment, transitions between different states of the system were drawn according to the standard Metropolis scheme. The conditional evolution time of the system was measured in the number of MC-steps per unit, τ / N .

In the initial state, all macromolecules had a regular stretched conformation and were placed in the plane $z = 0$. Depending on the total number of monomer units in the system, the relaxation time varied from $\tau = 3 \times 10^6$ to 6×10^6 . By this time, the equilibrium was attained. After the initial relaxation of the system, the box was

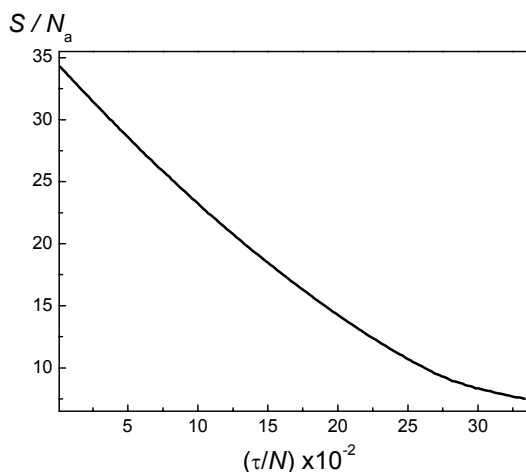


Figure 29. The area per adsorbed unit S/N_a as a function of the evolution time of the system expressed as the number of time steps per unit τ/N .

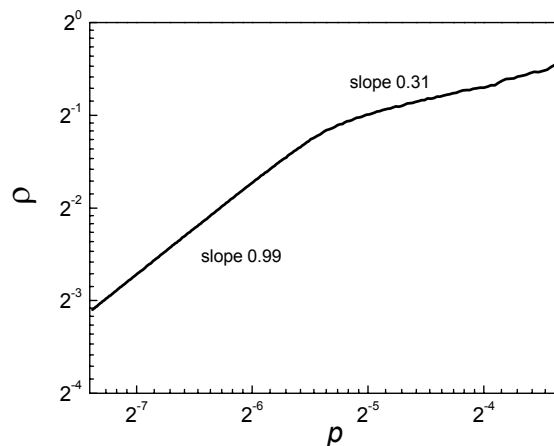


Figure 30. Double logarithmic plot of the number-average density of units in the adsorption layer ρ vs. the compression parameter p at $N_s = 8$.

gradually contracted in the plane (x,y) in both directions simultaneously. After each shift of a virtual angular barrier of the Langmuir trough by $\sigma \times \sigma$, the system was equilibrated and, then, the required characteristics were determined. These characteristics were the root-mean-square gyration radius of a macromolecule as a whole R_g^2 , root-mean-square gyration radius of the main chain R_b^2 , root-mean-square gyration radius of side chains R_s^2 , and the numbers of adsorbed main-chain units N_{ab} and side-chain units N_{as} (the total number of units adsorbed on the surface is $N_a = N_{ab} + N_{as}$).

Figure 29 presents a typical example of the kinetic of a monolayer contraction. The area per adsorbed unit S/N_a is plotted versus simulation time τ .

Theoretically, the minimum box dimension (at which zero adsorption of side chains $\gamma_s = 0$ and unit surface density of main chains (excluded volume is taken into account) $\rho = 1$ are attained) is 47×47 . However, in the computer simulation, we managed to achieve only $\rho_{\max} = 0.71 \pm 0.02$ at all side-chain lengths examined. Note that, for the linear chains (without side chains) also simulated in this work, we attained $\rho_{\max} = 0.74$. It should be pointed out that the liquid-crystalline ordering of main chains of molecules as a whole was absent in the system for all model parameters tried. Therefore, the corresponding orientation characteristics will not be further discussed.

2.3.2. Results and discussion

Three systems differing in the side-chain length of macromolecules $N_s = 4, 8$, and 16 were studied. Under the initial conditions at $\rho = 0.01$, the initial degree of adsorption of main chains is 100% and that of side chains is 95%. As the box sizes decrease, the density of units in the adsorbed layer ρ increases. As it can be seen, two regimes can be distinguished in the plot of ρ versus the compression parameter p . With monolayer compression, first, ρ increases rapidly and proportionally to increase of p : $\rho \sim p^{0.99}$. Next, the rate of increase in ρ decelerates drastically (as $\rho \sim p^{0.31}$). Below, we will discuss this data in more detail.

Figure 31 presents typical structures observed under different conditions of the computer experiment.

Figure 31d-f illustrates the deposition of side chains from the surface to the subphase at three values of the surface density.

As it can be seen, under the initial conditions ($\rho_0 = 0.01$), macromolecules are almost completely adsorbed on the surface and their sizes are close to the two-dimensional ones. At intermediate densities, side chains desorb partially from the surface and transfer to the subphase volume. In other words, both two-dimensional (adsorbed) and three-dimensional (desorbed) chains are present in the system in this case. The maximum density corresponds to the most complete desorption of side chains, when they are oriented parallel to each other in the direction normal to the adsorbing surface (similar to Langmuir fencing of surfactant molecules). In this case, in addition to a small residue of adsorbed two-dimensional units, strongly stretched side chains behaving almost like one-dimensional chains are present in the system. Therefore, with contraction of the system, side chains undergo consecutive transitions between spaces of different dimensionality $2d \rightarrow 3d \rightarrow 1d$.

2.3.2.1. The side-chain size

Figure 32 illustrates a drastic variation in the size of side chains upon their desorption from the surface. Three regions are distinguished in Figure 32a: the region corresponding to strong adsorption, where contraction of side chains without their detachment from the surface occurs with decreasing S ($d = 2$); the region of desorption, that is, of transfer of side chains to the volume ($d = 3$); and the region characterized by stretching and ordering of desorbed chains ($d = 1$).

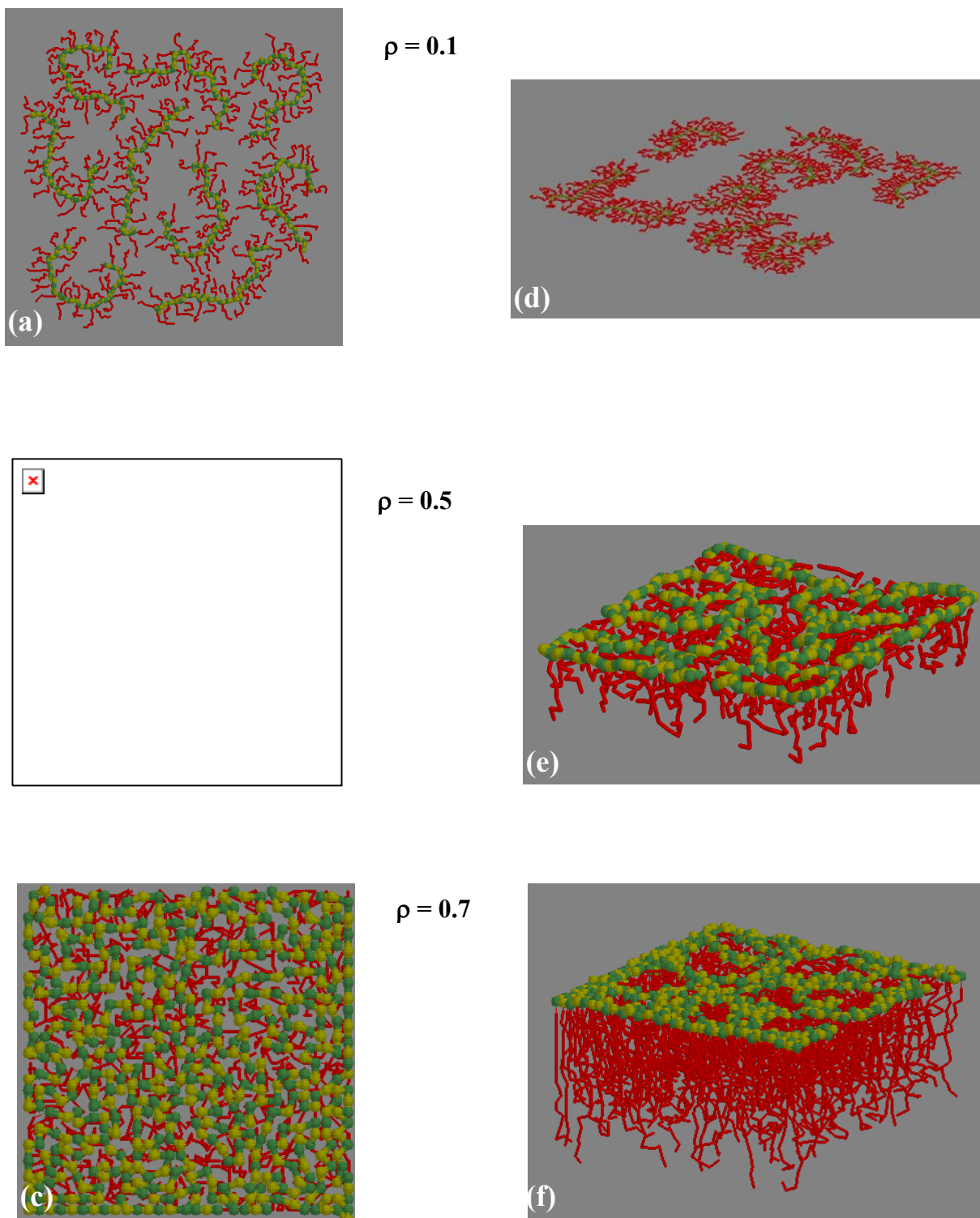


Figure 31. Typical structures of a molecular monolayer at different densities ρ and side-chain lengths $N_s = 8$ and 16 ; the main-chain length is $N_b = 60$. Main and side chains are shown in white and black, respectively; free sites at the surface are given in gray. The systems are imaged (a-c) in the XY plane of the surface and (d-f) in the solvent phase. The surface density of monomeric units ρ is (a, d) 0.1 , (b, e) 0.5 , (c, f) 0.7 .

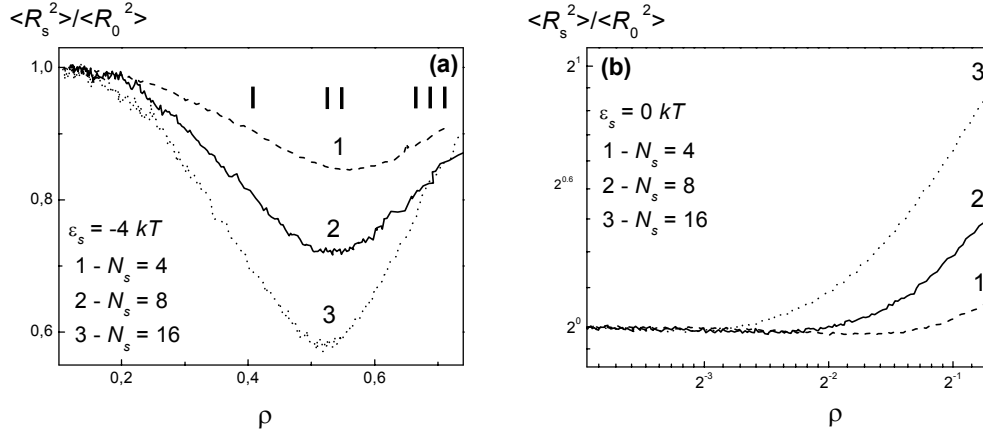


Figure 32. The average side-chain size R_s^2 reduced by the initial values R_0^2 (at $\rho = 0.1$) plotted vs. the adsorption layer density ρ at $\epsilon_s = -4kT$ (a) and 0 (b) and $N_s = 4, 8$ and 16. The log-log plot is presented in fig. b.

Figure 32b shows the variation in the average interaction with the surface ($\epsilon = 0$). In this case, detachment of the side chains from the surface occurs due to purely steric (entropic) reasons. In this case, in contrast to adsorbed chains, no considerable changes occur at not very high densities ρ . With a further increase in ρ , linear growth of R_s^2 is observed, which is accompanied by stretching of the chains normally to the surface.

As can be seen from Figure 32a, as N_s increases, more drastic variation of R_s^2 occurs. The minimum of the curves lie in a narrow density range ($0.52 < \rho < 0.56$). Therefore, stretching and ordering of the side chains parallel to each other strongly depend on the two-dimensional density of the system (or, in other words, on the grafting density of the side chains to the surface). The calculations show that the position of the minimum is weakly dependent on N_s . Nevertheless, this dependence is still observed: the larger is N_s , the smaller the onset density of chain stretching. This is due to the enhancement of the excluded-volume effect.

2.3.2.2. *Scaling dependences on side-chain size*

To determine the scaling dependences, we considered the behavior of R_s^2 as a function of the number of side chains per unit surface area $\sigma = Kn/S = 1/2p$ (at different values of $N_s = 4, 8$, and 16). The corresponding calculations were performed for the previously defined region 3 (see also Figure 32a). We obtained that double logarithmic plots of chain sizes versus the density of grafting to the adsorption surface are

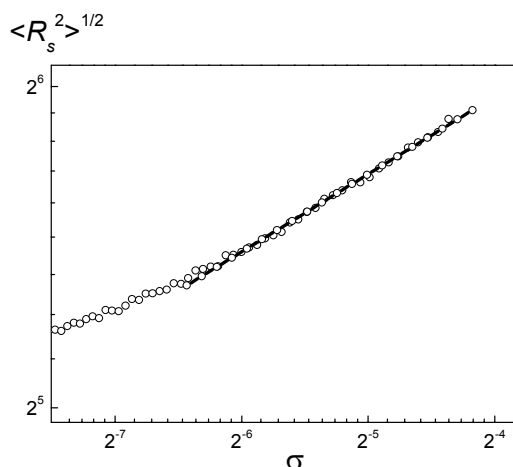


Figure 33. Log–log plot of the average side-chain size vs. the parameter $\sigma = Kn/S$ at $N_s = 16$.

linear (Figure 33). The calculated values of the exponent ν in the relationship $\sqrt{R_s^2} \propto \sigma^\nu$ are 0.073 ± 0.005 (at $N_s = 4$), 0.154 ± 0.000 (at $N_s = 8$), and 0.242 ± 0.000 (at $N_s = 16$) (table 1).

With increasing N_s (Table 2), these results approach the theoretically calculated relationships obtained in the framework of the theory of a uniform brushlike layer^{140, 141, 60} and the parabolic distribution of the polymer segments in the layer^{142,62,143}. In both cases, it was shown that the average layer thickness h is related to the density of grafting of side chains to the surface σ (i.e., the number of grafted tails per unit surface area) by $h \propto \sigma^{1/3}$. It is clear that the value N_s must be sufficiently large ($N_s \gg 1$) to obey scaling laws.

Table 2. Scaling exponent ν at different side-chain lengths N_s . The values of the exponent ν in the relationship $\sqrt{R_s^2} \propto x^\nu$ are presented, where R_s^2 is the mean square gyration radius of side chains and the argument x is the side-chain grafting density σ , the surface density of the molecular brushes ρ , and the side-chain surface density ρ_s ; $\rho_{\min}$ is the minimum (final) density of side chains on the surface attained in the computer experiment.

N_s	$\rho_{\min}$	Values of ν		
		σ^ν	ρ^ν	ρ_s^ν
4	0.282	0.073	0.200	0.187
8	0.344	0.154	0.350	0.801
16	0.341	0.242	0.769	0.833

Moreover, the computer simulation results fit to the theoretical data only for region III, where $\sqrt{R_s^2} \propto h$. Note that the observed values of the critical parameters are formed through superposition of the contributions of the side chains adsorbed on the surface and those stretched into the solvent medium. This results in decreasing the values of these parameter, as compared to the case when adsorption of chains on the surface is absent. We believe that it is this situation that is responsible for the discrepancy between the scaling theory^{140,141} and the computer simulation data. In addition, it should be kept in mind that the side-chain lengths studied here are too small to exhibit the scaling behavior.

The results of our calculation can be compared with the experimental data obtained by Miller *et al.*¹⁴⁴ in a neutron diffraction study of the organization at the water–air interface of comblike copolymers with the hydrocarbon [poly(norbornene)] main chain and poly(ethylene oxide) side chains grafted to each mainchain monomer unit. The neutron diffraction data were analyzed by the optical-matrix method and the kinematic approximation (which give partial structure factors for PEO layers and the aqueous layer at the interface). It was found¹⁴⁴ that the density of the PEO segments of the upper layer was constant at a low surface concentration. As the surface concentration increases, PEO chains begin to penetrate into the subphase. These observations are consistent with the computer simulation results presented above. From the scattering data obtained for each layer, Miller *et al.*¹⁴⁴ concluded that the hydrophobic main chains primarily occur in the air phase and comprise the main portion of the upper layer, where the PEO content and the air content are small. A more detailed analysis of the neutron reflection coefficient of the PEO layers formed by hydrophilic side chains penetrating into the aqueous subphase shows that these layers consist of two sublayers. One of the sublayers is characterized by a uniform density of ethylene oxide segments, and the other sublayer exhibits a parabolic density profile in the direction normal to the surface. The layer containing the main chains has the same thickness (~ 5 Å) over the entire range of the surface concentrations studied, whereas the side-chain layer thickness increases from 15 to 45 Å in the range of sufficiently large surface concentrations. As the surface concentration increases, the contraction of the separation region between PEO side chains is accompanied by exclusion of water from the PEO-containing layer and deeper stretching of the side chains into the subphase. The results show that the thickness of the PEO-containing layer increases linearly with the grafting density to the water–air interface.

Therefore, the computer simulation and physical experiment exhibit qualitatively the same general picture of compression and desorption of side chains. However, the experimental value of the scaling exponent ν determining the dependence of the PEO layer thickness h on the side-chain density at the aqueous surface is equal to $2/3$ ¹⁴⁴, which differs considerably from the theoretical predictions [28–33] and computer simulation data ($\nu \sim 1/4$). According to Miller *et al.*¹⁴⁴, this noticeable discrepancy with the theory^{140,141,143} is due to a relatively small molecular mass of the synthesized PEO side chains (27 ± 2 monomer units). It should be borne in mind that, in the considered model of a chain with fluctuating bonds, each chain unit actually corresponds to a statistical segment of a real molecule. Therefore, in view of the finite rigidity of a PEO chain, the number of statistical units is substantially smaller than in the model chains at $N_s = 16$. Moreover, in the theories of wet brush layers, it is assumed that the sites of grafting to the surface are fixed, which is not fully consistent with the experimental situation. Next, to obtain scaling dependences, Miller *et al.*¹⁴⁴ assumed that all side chains are immersed into the solvent in the region of sufficiently large concentrations (when formation of an ordered layer of side chains begins). However, as is indicated in the discussion of the results¹⁴⁴, an insignificant portion of side chains remains on the surface. The computer experiment also shows that part of the side-chain units lies on the surface even at rather large surface concentrations. Consideration of these chains leads to a noticeable change in the dependence of the monolayer thickness $\sqrt{R_s^2} \propto h$ on its density. Actually, when considering R_s^2 as a function of ρ ($=2dna/S$), we obtain that the corresponding power index is close to $2/3$ (at $N_s = 8$). Nearly the same value was found in the experimental study¹⁴⁴.

2.3.2.3. *The main-chain size*

Figure 34 presents the average size of main chains R_b^2 plotted versus surface density. As can be seen, R_b^2 decreases with increasing ρ . In the absence of adsorption of side chains (at $\varepsilon = 0$), R_b^2 decreases proportionally to ρ^{-1} and the curves corresponding to different N_s coincide (see Figure 34b). At $R_b^2 = -4kT$, the dependence is slightly different: at small R_b^2 , the average size of the main chain depends on the side-chain length. The larger is N_s , the larger is R_b^2 .

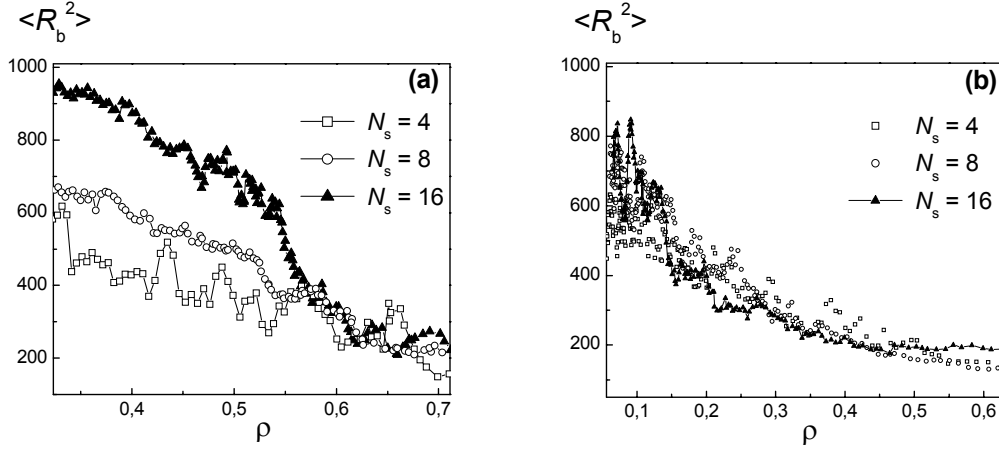


Figure 34. The average main-chain size R_b^2 plotted vs. the adsorption layer density ρ at $\Sigma = -4kT$ (a) and 0 (b) at $N_s = (1) 4$, (2) 8, and (3) 16.

2.3.2.4. *Scaling dependencies on the side-chain length*

Figure 35 presents the plots of R_b and R_s versus N_s at a fixed density $\rho = 0.1$ (at this density, an additional calculation run was performed at $N_s = 32$). It was found that $R_s \propto N_s^{0.818}$ and $R_b \propto N_s^{0.818}$. As can be seen, the dependence of the main-chain size on N_s is substantially weaker than that of the side-chain size. The obtained critical index for R_s as a function of N_s can be compared with the value 0.75 known for 2d chains with excluded volume. However, the obtained index is noticeably higher than 0.75. We should take into account that, in the system studied, the dependence of R_s on N_s is governed by two main factors: steric intramolecular interactions favoring stretching of side and main chains and intermolecular interactions leading to contraction of chains with increasing ρ . As in the case of side chains, the behavior of main chains is determined by the superposition of intra- and intermolecular interactions, which noticeably affects the scaling index. As the density of the system increases, the effect of side chains on levels off; at $\rho \geq 0.55$, the average size of main chains becomes almost independent of N_s and R_b is determined by the total density of the monolayer alone (Figure 34a).

We carried out an additional computer experiment to calculate the size of a single two-dimensional linear chain with $N = 60$ bearing no side chains and the size of an ensemble of 9 linear chains with $N = 60$ at $p = 0.15$, which corresponds to $\rho \sim 0.55$ for a system of grafted copolymers. The results show that the average sizes of both the single chain and ensemble are close to the corresponding value R_b^2 of for a

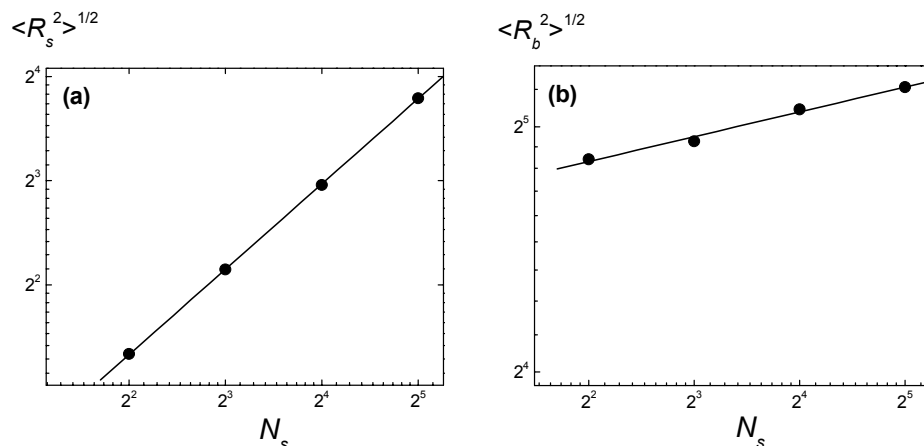


Figure 35. Log-log plots of (a) the average side-chain size R_s and (b) the average main-chain size R_b vs. the number of segments in a side chain N_s at the number-average density $\rho = 0.1$.

monolayer of comblike copolymers at a high degree of compression (at $\rho \geq 0.55$). Therefore, at $\rho \geq 0.55$, the main chains of a comblike copolymer behave like linear two-dimensional macromolecules. It is interesting that the minimums of curves in Figure 32 corresponding to the smallest (under the conditions of the calculation) sizes of side chains lie in the same density range ($\rho = 0.52 \div 0.56$). Moreover, comparison of the dependences of R_s^2 on N_s in Figure 32b and Figure 34b at $\varepsilon = 0$ shows that, at the surface density $\rho = 0.15\text{--}0.25$, R_s^2 begins to increase; that is, the side chains begin to stretch into the volume phase.

Therefore, we can conclude that there is a certain critical monolayer density ρ^* above which the side chains begin to stretch normally to the surface and the main chains behave like linear macromolecules independently of the length of grafted side chains.

We should note that the experimental study performed in ¹⁴⁴ revealed an increase in the volume fraction of air in the surface monolayer with compression of the cell with adsorbed macromolecules. According to Miller *et al.* ¹⁴⁴, this is due to bending of the main chains in the plane of the interface.

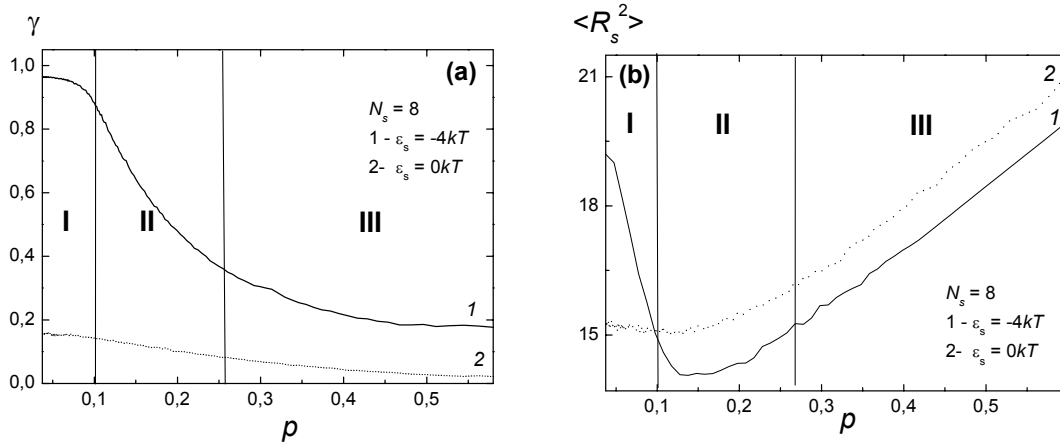


Figure 36. (a) Plots of the adsorption of side chains γ and (b) the average side-chain size R_s^2 as functions of the compression parameter p at $N_s = 8$ and $\epsilon_s = -4kT$ (1) and 0 (2).

2.3.2.5. Dependences on the compression parameter

Figure 36 presents the plots of the adsorption of side chains γ versus the compression parameter p at $N_s = 8$. The curves in Figure 36b correspond to $\epsilon = 0$ and $-4kT$. At $\epsilon = 0$, the initial adsorption γ is small ($\gamma = 0.15$) (Figure 36a) and, therefore, the average size of side chains is close to that of three-dimensional chains (Figure 36b). As the density of the system increases, the adsorption drops almost to zero and the average size drastically increases. At $\epsilon = -4kT$, the dependence is slightly different. Initially, the side chains are adsorbed almost completely ($\gamma = 0.95$) and have “two-dimensional” sizes (region I in Figure 36). For compression parameter $p \geq 0.1$, they begin to intensely desorb (Figure 36a). The intersection point of the curves in Figure 36b corresponds to the same density. This coincidence of the densities allows us to make the following conclusion. When the size of the side chains adsorbed on the surface becomes comparable with the three-dimensional size of desorbed chains of the same length, they begin to detach from the surface and escape into the bulk of the solvent. In region II corresponding to intense desorption (Figure 36), the average size R_s^2 exhibits an additional decrease due to the increasing fraction of desorbed (three-dimensional) units and further contraction of the side chains that still lie on the surface (Figure 36b). In region III, desorption noticeably decreases and the curve saturates (Figure 36a). This process is accompanied by a symbatic run of the curves in Figure 36b. This behavior is typical for all the values of N_s examined.

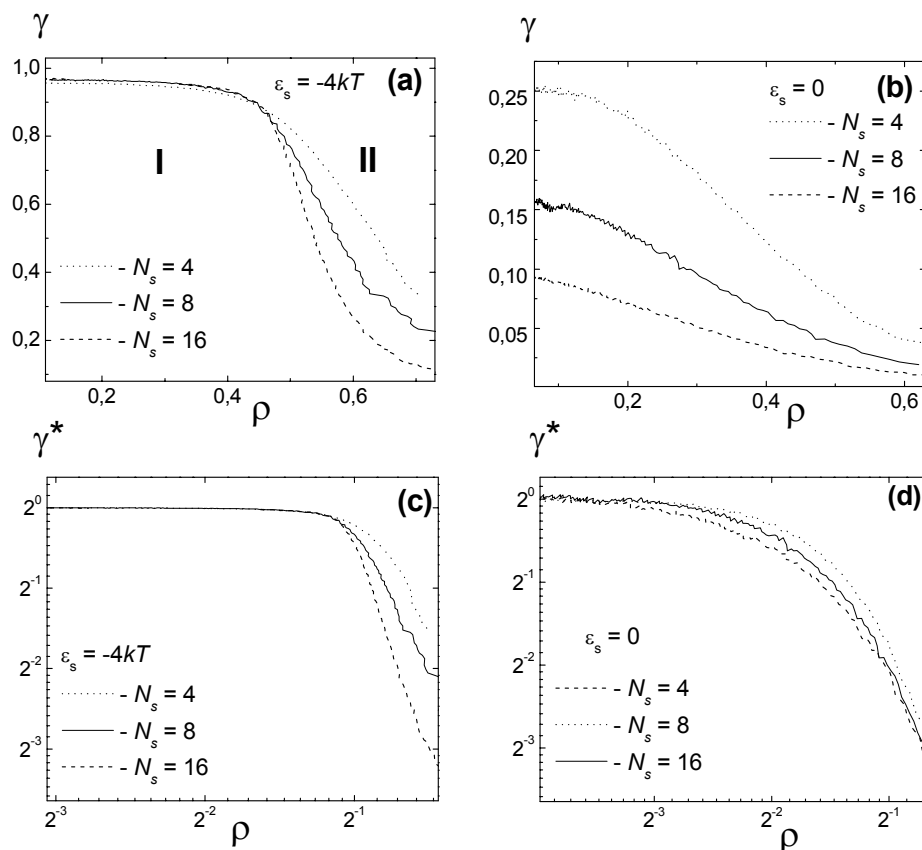


Figure 37. Plot of the adsorption of side chains γ (a,b) and the log–log plot of the reduced value γ^* (c,d) vs. the adsorption-layer density ρ at $\varepsilon_s = -4kT$ (a,c) and 0 (b,d) and $N_s = (1)$ 4, (2) 8, and (3) 16.

2.3.2.6. Adsorption properties

Figure 37 presents the reduced values of adsorption γ^* at $N_s = 4, 8$, and 16. The γ^* value is defined as the ratio of adsorption at a given density ρ to the initial adsorption γ_0 , $\gamma^* = \gamma/\gamma_0$ corresponding to $\rho = 0.01$. At $\varepsilon = 0$, the initial adsorption γ_0 is inversely proportional to N_s ; that is, the larger is N_s , the smaller is γ_0 (Figure 37b). When the adsorption process is operative, γ_0 is almost the same for all N_s (Figure 37a, inset); however, at $\rho \geq 0.45$, γ and γ^* become strongly dependent on N_s . Intense desorption of side-chain units from the surface also begins at a surface density close to 0.45. Discussion of Figure 36 and Figure 37 allows us to conclude that there is a critical surface density ρ^* at which the size of side chains adsorbed on the surface is close to that of grafted chains of the same length immersed into the bulk solvent and desorption of side chains from the surface begins.

Turning back to the previous considerations, let us make some comments on the arbitrary subdivision into the regions of data presented in Figure 32a. In the region

of $0.1 \leq \rho \leq 0.45$, compression of the side chains to the “pseudo-three-dimensional” size without the desorption of side chains from the interface is observed. In the range $0.45 \leq \rho \leq 0.55$, the intense desorption of side chains to the solvent medium occurs and the side-chain size varies insignificantly. In the region $0.55 \leq \rho \leq 0.74$, the desorption of side chains is accompanied by a drastic increase in their size and exhibition of the linear behavior of the main chains on the surface.

2.3.3. Conclusions

The results of the performed calculations show that three stages characterizing the desorption of side chains can be distinguished in the case of lateral compression of a monolayer.

At small degrees of monolayer compression (stage I), the desorption of side chains is almost absent; the sizes of the main and side chains considerably decrease. This stage is controlled mostly by steric factors, and the potential energy of the system remains almost constant. When the critical surface density ρ^* is attained, the side chains begin to intensely desorb from the surface. The intensity of the process increases with increasing N_s . Stage II is realized in a narrow density range and determined by both steric and energetic factors. A typical feature of this intermediate stage is that both two-dimensional (anchored to the surface) and three-dimensional (excluded from the surface) side chains are simultaneously present in the system. However, in this case, the side-chain density in the volume is comparably small. Thus, steric restrictions are manifested mostly for the chains attached to the surface. At this stage, the main chains remaining on the surface contract and, after the critical surface density ρ^* is attained, take sizes typical of two-dimensional linear chains (without side chains) with the same number of units. The third, final stage is characterized by stretching of the side chains normally to the surface, which is due to their overlapping in the layer adjacent to the surface. In this case, steric effects play the dominant role. In fact, the transitions between stages I, II, and III can be considered as consecutive transitions of the side chains from the two-dimensional (2d) to three-dimensional (3d) and one-dimensional (1d) states: $2d \rightarrow 3d \rightarrow 1d$.

Chapter 3

Conformation-dependent sequence design of linear copolymers near the surface

3.1. Introduction

Initially, the general idea connected with conformation-dependent sequence design was realized in computer simulations⁸⁹⁻⁹³ and developed theoretically^{145,146} for the simplest model of a two-letter copolymer, i.e., a copolymer consisting of only two comonomers. In the model, an initial homopolymer in its original dense globular state corresponding to the bare conformation is modified into two different (A and B) units by assigning (insoluble) A type to the units in the core of the globule, and (soluble) B type to those on its surface. The heteropolymer obtained as a result of such simple one-step procedure can self-assemble into a segregated core-shell microstructure thus resembling some of the basic properties of globular proteins, in particular, their solubility in water.

In the present chapter the computer-aided synthesis of amphiphilic quasirandom copolymers with quenched primary structure near a macroscopic planar substrate has been investigated. The following two routes are used. (i) On the basis of an MC simulation technique, the chemical modification ("coloring") of a partially adsorbed homopolymer chain has been imitated. This surface-induced conformation-dependent sequence design is similar to that described above for bare polymer globules dissolved in a bulk solution and has been earlier realized for obtaining "adsorption-turned copolymers". Here, main aim is to analyze in detail the statistics of arising copolymers for sufficiently long chains. (ii) The second approach is aimed at computer

synthesis of copolymers from two types of selectively adsorbed monomers A and B distributed near a planar substrate with given gradients. The irreversible growth process is simulated in the dilute regime for polymerizing monomers with different affinity to the surface. The polymerization is modeled as step-by-step chemical reaction of addition of A and B monomer units to the growing copolymer chain, assuming that depolymerization reaction is not allowed in the simulation. Then, the adsorption and statistical properties of prepared sequences are investigated to compare with those known for other types of copolymers (random, random-block, etc.).

3.2. “Colouring” of adsorbed copolymer chains

3.2.1 Computational Technique and Model

For the sake of computational efficiency, the chemical details of simulated polymer chains are not taken into account here, but only the generic features of surface-induced sequence are used. Thus, all simulations are performed with the standard bond-fluctuation model, which is described in detail in Ref. 147. This is a fast lattice algorithm that in three dimensions (3d) offers a set of 108 bond vectors with five different lengths. These are chosen such that the local self-avoidance prevents chains from crossing each other during their motion. The fluctuating bond length permits the implementation of random, local monomer displacements such that the dynamics of an isolated chain can be well-described by the Rouse model. In contrast to usual lattice algorithms, one monomer does not occupy one lattice site but eight sites in three dimensions. The motion of monomer units is generated by the Monte Carlo (MC) technique: A monomer unit and a lattice direction are chosen at random, and a move is attempted in the proposed direction. The move is successful, if the targeted sites are empty (excluded volume interaction), if it allows to be compatible with chain connectivity, and if it lowers the potential energy. On the other hand, if the energy difference, ΔU , between the final and the initial state is positive, the move is only accepted with probability $\exp[-\Delta U/T]$ according to the standard Metropolis algorithm¹⁴⁸, where T denotes the temperature (Boltzmann's constant $k_B = 1$). By means of this probability, temperature is introduced into the simulation. The chains are placed in a three-dimensional cubic lattice, which is infinite in the x and y directions and limited in the z direction by the two planes. In this computer experiment only excluded volume interactions between monomer units were taken into account. Thus, thermodynamically good solvent conditions were modeled for all the units.

The results are expressed in internal units: lengths are measured in units of the lattice spacing, σ , and time, τ , is in units of MC steps (MCS) per monomer (on the average each monomer attempts to jump once within a Monte Carlo step, successfully or unsuccessfully). In the simulations, temperature was set to $T = 1$.

The homopolymer chain of a fixed length N was placed inside b^3 box ($b_x = b_y = b_z = 240$, in lattice units, σ) with periodic boundary conditions applied in the x and y

directions. In the z direction, the system is limited by the two planes at $z = 0$ and $z = b_z$. The $z = 0$ plane is considered as an adsorbing surface, and the $z = b_z$ plane was assumed to be a reflecting wall. The distance between planes is sufficiently large so that the chain cannot interact simultaneously with both planes. To simulate adsorption, we applied a short-range potential, $\varepsilon(z)$, modeling the attraction of monomer units to the surface. The (negative) energy ε (measured in the units of $k_B T$) was attributed to any monomer unit located in the layers $z = 1$ and 2 . Thus, to obtain 2δ -height adsorbed layer, we used first two lattice layers. Note that " 2δ -adsorption" makes adsorption process more effective and, at the same time, excludes bilayer adsorption. Unadsorbed chain segments were described by a usual three-dimensional self-avoiding walk on a cubic lattice above the surface, while the adsorbed segments were modeled as two-dimensional self-avoiding chains on a square lattice located in the plane $z = 0$. Because the excluded-volume interactions are taken into account for our lattice bond-fluctuation model, each monomer unit occupies one lattice site and prevents other units to invade its nearest environment (i.e., 26 and 8 adjacent sites in $3d$ space and in $2d$ space, respectively). Unoccupied lattice sites are regarded as solvent particles. In this work, the parameter ε was varied from 0 to 6. Note that ε corresponds to the net enthalpy change upon replacement of an adsorbed polymer segment by solvent.

As an initial state, a system with zero adsorption potential was prepared. When the adsorption potential is switched on, one has to relax the system a long time, since chains need to diffuse from the bulk of the box to the adsorbing wall. Depending on the total number of monomer units in the chain (up to $N = 1024$ in this work), between 10^6 and 10^7 MC time steps per monomer unit were necessary to obtain completely equilibrated configurations. After equilibration at a given segment-surface attraction energy ε , different configurations of a single homopolymer chain were generated. This chain contains N segments (all of type A) and interact with a flat surface with this value of ε . The total number of generated configurations was ranged from 10^7 to 10^8 and each 10^4 th of them was recorded by assigning unity to each adsorbed segment ($z \leq 2$) and zero to each unadsorbed segment ($z > 2$). In subsequent studies, these records were treated as copolymer primary structures, where unity indicates a type A segment and zero corresponds to a type B segment. It is evident that at small ε some of the obtained primary structures can consist of only type B segments. The

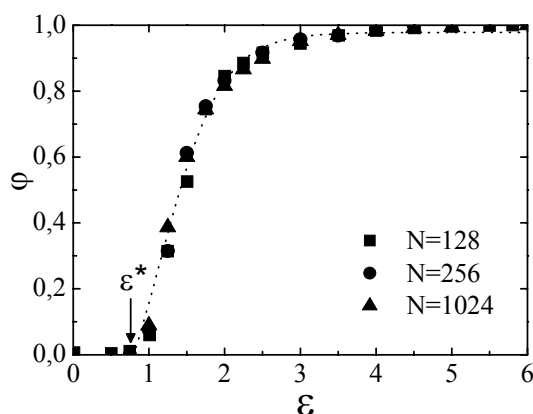


Figure 38. The average fraction of adsorbed (A-type) monomer units against the attraction energy ε (in the units of $k_B T$) for the chains of length $N = 128, 256$, and 1024 .

frequency of appearance of these latter primary structures of $N = N_B$ type B segments depends on the parameter of the simulation box b_z . So, in order for the ensemble averages to be independent of such an artificial parameter as the simulation box size, and to reflect the pure effect of the attraction energy at which the ensemble of AB copolymers was generated, these primary structures were excluded from subsequent consideration.

It is clear that the resulting AB composition of the generated copolymers, ϕ_{AB} , is determined by the average fraction of adsorbed chain segments, ϕ . One can anticipate that the 1:1 composition will be obtained in the vicinity of the critical adsorption energy of a single homopolymer chain, ε^* . To estimate this energy, the ϕ value as a function of ε was calculated. Results are shown in Figure 38.

Interception of the ε axis with the straight line tangential to a sigmoidal approximation of the dependence $\phi(\varepsilon)$ at the inflection point gives an estimate of the critical adsorption energy of the chain of length $N^{149, 150}$. It was found that ε^* is practically independent of N for $N \geq 128$ and is estimated as $\varepsilon^* = 0.8 \pm 0.1$. This value is close to that obtained for the same model of a polymer chain in Ref. 92. However, as seen from Figure 38, at $\varepsilon = \varepsilon^*$ only ca. 5% of segments are in adsorbed state. The conclusion from the data presented in Figure 38 is that the AB composition approximately corresponding to $\phi = 1/2$ is attained at $\varepsilon \approx 1.5$. Below, the adsorption and statistical properties obtained only for these copolymers will be discussed.

3.2.2. Results and discussions

3.2.2.1. The structure of adsorbed copolymers

Several equilibrium characteristics of the adsorbed copolymer chains were calculated. They include the average numbers of monomer units in train sections, N_{tr} , in loop sections, N_{lp} , and in tail sections, N_{tl} ; the average numbers of trains, n_{tr} , loops, n_{lp} , and tails, n_{tl} , in a chain. By a train section of a chain we mean its adsorbed section; a loop is an unadsorbed section between two trains, and a tail is the unadsorbed end section of a chain. Note that $n_{tr} \times N_{tr} + n_{lp} \times N_{lp} + n_{tl} \times N_{tl} = N$. These quantities were calculated as a function of the adsorption energy ε , which is gained when a monomer A is in contact with the adsorbing surface. The average numbers of chemically uniform A and B segments in the designed copolymers, m_A and m_B , as well as the average lengths of these segments, L_A and L_B , were found. For both copolymers, the length of the segment composed by the units of a given type is a random quantity. First, a thermodynamic average of each of these values was found for a chain with a certain primary structure, and, then, the thermodynamic average was averaged over the sample of the sufficiently large number of primary structures of the corresponding subensemble in which the AB composition φ_{AB} is close to 1:1.

Some of the results obtained for 1024-unit "colored" chains are shown in **Figure 39**. It is seen that at small values of ε the average number of loops ($n_{lp} = n_{tr} - 1$) is close to zero and increases with ε . In the vicinity of $\varepsilon = 1.5$, the $n_{lp}(\varepsilon)$ function attains a maximum and then slowly decreases with increasing ε [**Figure 39(a)**]. Note that in the strong adsorption regime, nearly all type A segments and some portion of type B segments lie on the surface. So, loops can be formed only from type B segments. It is interesting that the maximum of $n_{lp}(\varepsilon)$ is located practically at the same value of ε at which the "coloring" of the bare homopolymer chain was performed. The average tail length quickly decreases with ε and becomes virtually zero in the region $\varepsilon \gtrsim 1.5$ [**Figure 39 (b)**]. The average train length N_{tr} is a slowly increasing function of ε . This is quite understandable, because in the strong adsorption regime all type A segments and some portion of type B segments lie on the adsorbing surface. On the other hand, similar to the $n_{lp}(\varepsilon)$ function, the average loop length N_{lp} goes through the maximum [**Figure 39 (c)**]. In this case, however, the maximum is shifted toward smaller ε . Note that the curves $N_{tr}(\varepsilon)$ and $N_{lp}(\varepsilon)$ cross each other at $\varepsilon \approx 1.5$.

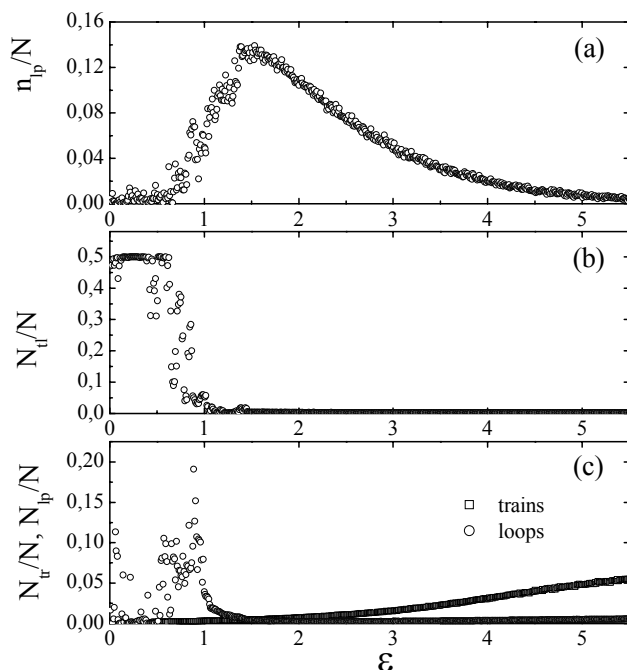


Figure 39. (a) The average number of loops, n_{lp} ; (b) the average number of monomer units in tails, N_{tl} ; and (c) the average number of monomer units in trains, N_{tr} , and loops, N_{lp} , of an adsorbed 1024-unit copolymer as a function of ϵ . The results correspond to copolymer chain obtained via the "coloring" procedure.

The results presented above allow to assert that the adsorbed copolymer "remembers" the preparation conditions and displays this memory in some adsorption properties discussed here. In addition, as has been mentioned in the Introduction, such a copolymer demonstrates "adsorption-tuned" properties⁹².

3.2.2.2. Analysis of designed sequences

Let us now turn to the question of long-range correlations in the copolymer sequences obtained in the present work. In Ref. 107 it has been shown that already single "coloring" of a homopolymer globule leads to long-range correlations of the Levy-flight type 108. The question is: whether these correlations are present in the polymers obtained via the "coloring" near an adsorbing surface?

The statistical analysis of the designed sequences was carried out according to the method similar to that used by Stanley and co-workers^{151, 152, 153} in their search for long-range correlations in DNA sequences. In this approach, each AB sequence is transformed into a sequence of symbols 0 and 1. Each 0 is interpreted as a downward step and 1 as an upward step of one-dimensional random walk. Shifting the sliding window of length λ step by step along the sequence, the number of A and B monomer units inside the window is counted at each step. This number, which we write as $\gamma(\lambda) = \sum_{i=j}^{j+\lambda} \xi_i$ is a random variable, depending on the position j of the window along the sequence; here ξ_i is the variable associated with every monomer i , such that $\xi_i = 0$

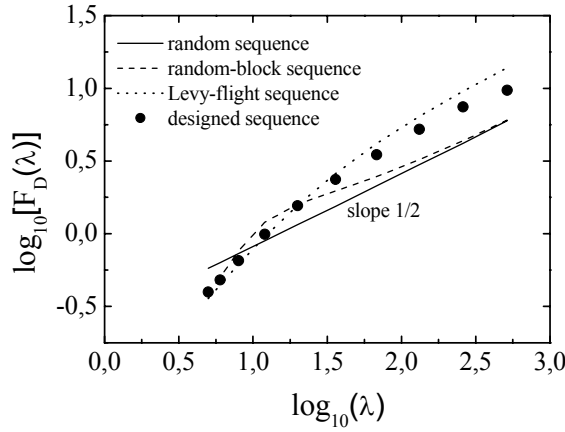


Figure 40. Detrended fluctuation function for random, random-block, Levy-flight, and designed by “colouring” sequences of length $N = 1024$.

if monomer i is B and $\xi_i = 1$ if it is A. This random variable has certain distribution. Its average is determined by the overall sequence composition (the total numbers of A and B monomers), and its dispersion is given by $D_\lambda^2 = \sum_{i,j=k}^{k+\lambda} (\langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle)$. If the string sequence is uncorrelated (normal random walk) or there are only local correlations extending up to a characteristic range (Markov chain) then the value of D_λ scales as $\lambda^{1/2}$ with the window of sufficiently large λ . A power law $D_\lambda \propto \lambda^\alpha$ with $\alpha > 1/2$ would then manifest the existence of long-range (scale-invariant) correlations. However, due to large fluctuations, conventional scaling analyses of the dispersion D_λ cannot be applied reliably to the entire short sequence. To avoid this problem, we use the detrended fluctuation analysis (DFA), the method specifically adapted to handle problems associated with nonstationary sequences^{152,153}.

In brief, DFA involves the following steps: (i) Divide the entire N -symbol string into N/λ nonoverlapping substrings, each consisting λ symbols, and then define the local trend in each substring to be the ordinate of a linear least-squares fit for the random walk displacement within this substring. (ii) Find the difference $\Delta(\lambda)$ between the original random walk $\gamma(\lambda)$ and the corresponding local trend. (iii) Calculate the variance about the detrended walk for each substring. The average of these variances over all the substrings of size λ , denoted $F_D^2(\lambda)$, characterizes the detrended local fluctuations within the sliding window of length λ . Generally, the $F_D(\lambda)$ function shows the same behavior as D_λ .

Figure 40 presents the results of the statistical analysis performed as described above for 1000 sequences obtained via the “coloring” procedure. On average, these sequences have 1:1 AB composition and block lengths $L_A \approx L_B = 4.4$.

For comparison, the data obtained for a purely random 1:1 sequence and a random-block 1:1 sequence (both with $N = 1024$) are shown in the same figure. Note that a random sequence here is the sequence for which the probability p_A of each unit to be of type A is constant throughout the whole sequence. This means, for example, that the conditional probability $p_A(i+1, i)$ that the $(i+1)^{\text{th}}$ unit is of type A when the i^{th} unit is also of type A is equal to p_A . The average fraction of type A units in a random sequence is equal to the probability p_A , which in our case is set to $p_A = 1/2$. It is clear that for such sequence $L_A = L_B = 2$. By definition, a random-block sequence is characterized by the Poisson distribution of the type A and B block lengths, $f(x) = e^{-L} L^x / x!$, where L is the average block length (L_A for type A blocks and L_B for type B blocks). Systematic consideration and comparison of the properties of the ensembles implies that L_A and L_B must be determined for the ensemble of designed sequences, the random-block ensemble can be created using these parameters in the corresponding Poisson distribution. Thus, the Poisson distribution is generated. This distribution adjusted to achieve the same 1:1 composition and the same "degree of blockiness" as for a designed copolymer obtained by "colouring". Also, in **Figure 40** the $F_D(\lambda)$ function is presented. This function found for a model Levy-flight sequence¹⁰⁷ of length $N = 1024$.

It is seen from **Figure 40** that the data obtained for a purely random sequence demonstrates $F_D(\lambda) \propto \lambda^{1/2}$ scaling throughout the interval of λ examined, as expected. For a random-block sequence having the same composition and average block length as designed sequences, there are well-pronounced correlations in the region corresponding to small λ 's, which are close to the average block length. However, as λ increases, dumping of the correlations is observed, and for sufficiently large λ the behavior demonstrated by the random and random-block sequences is almost identical. Comparing these curves with the simulation results it can be seen immediately that designed sequences do not correspond to random and random-block statistics, and strong correlations do exist in these sequences. Although the simulation results do not fit accurately to any power law $F_D(\lambda) \propto \lambda^\alpha$ throughout the interval of λ considered, the slope α observed for the dependence of $\log[F_D(\lambda)]$ on $\log \lambda$ corresponds to a value significantly larger than $1/2$, up to about 1 at small values of λ , thus indicating pronounced long-range correlations in these designed sequences. Of course, when λ becomes comparable to the total chain length N , the long-range correlations fade and α

$\rightarrow 1/2$. A similar behavior with a wide crossover region between $\alpha \rightarrow 1$ and $\alpha \rightarrow 1/2$ is seen for a model sequence with the Levy-flight statistics (**Figure 40**). Thus, the conclusion is that the "coloring" of adsorbed chains leads to the sequences, which distinctly demonstrate the presence of long-range correlations and these correlations are of the Levy-flight type. In this respect the properties of the copolymers obtained by "coloring" of partially adsorbed homopolymer chains are similar to those known for proteinlike copolymers¹⁰⁷.

3.3. Copolymerization near a selectively adsorbing surface

Here, the computer simulation results are compared with the *probabilistic model* of copolymerization, proposed by Dr. Yury Kriksin¹⁵⁴ (see also **Appendix A**).

3.3.1. Simulation technique and model assumptions

All simulations are performed with the standard lattice bond-fluctuation model, which is described in detail in Refs.¹⁵⁵ and ¹⁵⁶. In this model, each monomer unit corresponds to a chain segment consisting of several (about 10) chemical groups of a typical flexible-chain polymer. The motion of particles (polymerizing monomers and chain segments) is generated by the Monte Carlo (MC) technique: A particle and a lattice direction are chosen at random, and a move is attempted in the proposed direction. The move is successful, if the targeted lattice sites are empty (excluded volume interaction), if it allows to be compatible with chain connectivity, and if it lowers the potential energy. On the other hand, if the energy difference, Δu , between the final and the initial state is positive, the move is only accepted with probability $\exp[-\Delta u/T]$ according to the standard Metropolis algorithm,¹⁵⁷ where T denotes the temperature (Boltzmann's constant $k_B = 1$).

The results are expressed in internal units: lengths are measured in units of the lattice spacing, σ , and time, τ , is in units of MC steps (MCS) per particle (on the average each particle attempts to jump once within a Monte Carlo step, successfully or unsuccessfully). Temperature was set to $T = 1$.

A total of N monomers A and B were placed in a self-closed slab (with periodic boundary conditions in the x and y directions) of size $b_x = b_y = 400$ and $b_z = 120$, in units of σ . The planes at $z = 0$ and $z = b_z$ are considered as reflecting boundaries. The $z = 1$ plane was chosen as an adsorbing surface. To model adsorption, the following slowly decaying adsorption potential was used: $u(z) = \varepsilon_a/z^3$ (where ε_a is the characteristic adsorption energy at $z = 1$) that acts only on the polymerizing A monomers and the corresponding chain segments. Therefore, selective adsorption with a fixed adsorption energy ($\varepsilon_A < 0$) was simulated, while the B monomers had no attraction to the surface, $\varepsilon_B = 0$. In this study, the value of ε_A was set to $\varepsilon_A = -2.08$. With this choice, the density of A monomers far from the attractive surface was negligibly small, and

thus the precise location of the repulsive walls had a negligible influence on the results.

The simulation was performed in two stages. First, in order to calculate equilibrium adsorption profiles, free (nonreacting) monomers inside the reaction box were considered. Among the monomers, N_A were the monomers of type A and N_B were the monomers of type B. A fixed number of A monomers were placed into the simulation box, while the number of B monomers was a variable parameter. The values of N_A and ε_A were chosen such that about 95% of all the polymerizing A monomers were in strongly adsorbed state for each N_B . The bulk number density of unadsorbed B monomers, $\rho_B = N_B/(b_x \times b_y \times b_z)$, was much larger than the number density of A monomers in the system, $\rho_B \gg \rho_A$. Due to the strong adsorption, however, the equilibrium number density of A monomers within a narrow-width adsorption layer near the surface was always much larger than ρ_B . The ρ_B value was varied from 0.01 to 0.25. After equilibration, the simulations were carried out during 3×10^6 MC steps. After each 10^2 MC steps the monomer density profiles $\rho(z)$ normal to the $z = 0$ plane were calculated. To this end, we divided the distance b_z into 120 bins and sampled how many monomers fall into each bin. Then, the average density profiles for A and B monomers, $\rho_A(z) = N_A(z)/S$ and $\rho_B(z) = N_B(z)/S$ were found, where $S = b_x \times b_y$ is the surface area and $N(z)$ denotes the average number of the corresponding monomers in the z layer. Thus, choosing the number density of B monomers in the bulk, ρ_B , we can obtain various density profiles $\rho_B(z)$. Note that $\rho_A(z)$ depends on ρ_B very weakly.

During the second phase of the simulation, we studied the irreversible polymerization process, which was considered as a step-by-step chemical reaction of addition of monomer units to the growing polymer chain. In our polymerization model, the presence of low-molecular-weight species (both solvent molecules and free monomers) was taken into account only implicitly through the density profiles of A and B monomers obtained at the first stage. In the implicit-monomer model these profiles define the probabilities of addition of monomer units to the growing macroradical. Note that in reality correlations in the density of reactive species are only weakly perturbed by the reactions for low monomeric reaction probability. It is assumed that the reactants are ideally mixed and that diffusion is not important. In principle, such conditions can be realized if typical diffusive time, τ_d , and the characteristic time of adsorption equilibrium are essentially less than the reaction time τ_r . It is clear that this assumption corresponds to the kinetically controlled regime.

Usual radical polymerization process consists of the following three parts: initiation, chain propagation, and termination. In this study, the initiator of polymerization process was modeled as a fixed point of type A with co-ordinates $x = b_x/2$, $y = b_y/2$, and $z = 1$ and was fixed on the attractive surface. Since only one radical initiator was put into reaction mixture, spontaneous chain terminating reactions, such as radical combination and disproportionation, were excluded. This situation takes place in reality for the case when the concentration of radical species in a polymerization reaction is very small compared to other reagents, the rate at which the radical-radical termination reactions occur is also very small, and most growing chains achieve moderate length before termination. In the present study, the growing chain was automatically terminated at the number of monomer units $N = 1024$. Notice that since in our model the concentration of monomers in solution does not depend on their conversion and, therefore, always remains constant, we in fact consider an infinitely diluted polymer solution.

The implicit-monomer model involves two characteristic time scales. First, the reaction time scale is set by the time between two reaction trials, τ_r . Second, the equilibrium motion time, τ_{rel} , includes conformation relaxation of growing chain. Internal motion of the chain mainly depends on the current chain length, N_τ ; that is, the length of growing chain corresponding to a given time τ . It should be noted here that the Rouse relaxation time $\tau_{rel} \sim N^2$ for an ideal chain. For simplicity, we take the following fixed relaxation time $\tau_{rel} = 1024 \times N_\tau$ in the present study. Any bias introduced by the growing method towards a certain distribution of configurations should become unimportant as the chain has enough time to relax from the nonequilibrium state between two successive reactions.

In copolymerization mechanism, the rate of addition of a monomer to a growing free radical depends only on the nature of the end-group on the chain. There are four possible ways in which a monomer can be added:

Reaction	Rate
$A\bullet + A \rightarrow AA\bullet$	$k_{AA}[A\bullet][A]$
$A\bullet + B \rightarrow AB\bullet$	$k_{AB}[A\bullet][B]$
$B\bullet + A \rightarrow BA\bullet$	$k_{BA}[B\bullet][A]$
$B\bullet + B \rightarrow BB\bullet$	$k_{BB}[B\bullet][B]$

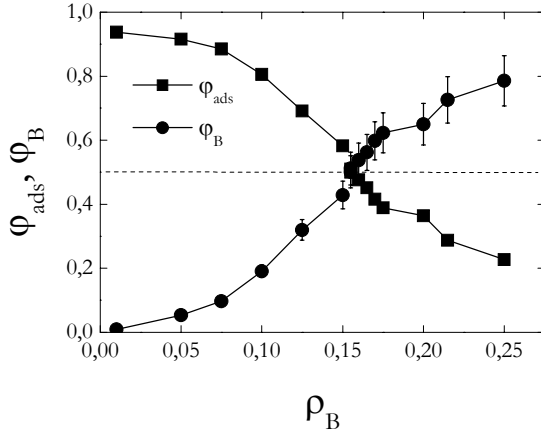


Figure 41. (■) Average fraction of adsorbed segments, ϕ_{ads} , and (●) average fraction of B segments in the resulting copolymer, ϕ_B , as a function of the number density of monomers B in the bulk, ρ_B . Chain length $N = 1024$. Dashed line corresponds to $\phi_{ads} = \phi_B = 1/2$.

An "ideally polymerizing" system is modeled in which the rate constants are equal to each other, $k_{AA} = k_{AB} = k_{BA} = k_{BB}$. In this case, the end group on the growing chain has no influence on the rate of monomer addition, and the two types of monomer units are arranged along the chain in relative amounts determined by the local concentrations of A and B monomers near the end radical of the chain. Thus, the time of addition of monomer to the chain and probabilities of A or B monomer additions are determined by combination of the equilibrium density profiles, $\rho_A(z)$ and $\rho_B(z)$, and by the growing chain end location.

During the simulation, the current position of free ("active") end of the chain along the z direction, $z_p(\tau)$ was found, and the new monomer was added to it, according to relative probabilities to occur the monomer A or monomer B in the z layer: $p_A \equiv \tilde{\rho}_A(z_p)$ and $p_B \equiv \tilde{\rho}_B(z_p)$, where $\tilde{\rho}_A(z_p)$ and $\tilde{\rho}_B(z_p)$ are the normalized density profiles and $p_A + p_B = 1$. Thus, in the model used here, we have only one variable parameter of the copolymerization process, viz., the number density of monomers B in the bulk, ρ_B .

The algorithm used for modeling of chain growth was as follows. A random number uniformly distributed between 0 and 1 was generated and then compared to the probability p_A of having an addition of the monomer unit to the growing chain. If the random number occurred to be less than the value of p_A , monomer A was linked with the "active" end of the N_τ -unit macroradical; otherwise, monomer B was taken. After each such step, chain relaxation during the time τ_{rel} was performed. After termination of the growing chains at $N = 1024$, their statistical analysis was carried out. To gain better statistics, 10^3 fixed-length copolymers for each density ρ_B were generated and then required average characteristics were found.

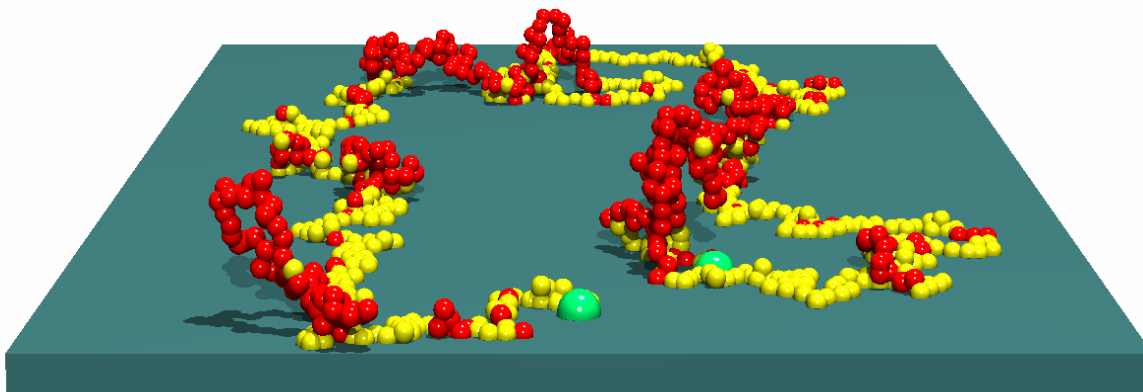


Figure 42. Snapshot of the copolymer chain with $N = 1024$ obtained from copolymerizing monomers at $\rho_B = 0.155$. The yellow and red spheres show adsorbed (A) and unadsorbed (B) monomer units, respectively. The place of connection of the chain with the surface ("initiator") and the chain end are depicted as larger green spheres.

Depending on ρ_B , the following characteristics were calculated for the ensemble of the generated copolymers: the average fraction of adsorbed segments, φ_{ads} ; the average fractions of A and B segments in the chain, φ_A and φ_B ($\varphi_A + \varphi_B = 1$); the average numbers of chemically uniform A and B sections (blocks), n_A and n_B , as well as the average lengths of these sections, L_A and L_B ; and the distributions of segments along the chain. Note that, first, an average of each of these quantities is found for a chain with a certain primary structure and then, the quantities are averaged over the sample of the sufficiently large number of independently generated primary structures.

Intuitively, one may expect that the average fraction of B units φ_B in the resulting copolymer should increase with their bulk concentration ρ_B , thereby leading to a decrease in the number of strongly adsorbed segments. As seen from Figure 41, where the values of φ_{ads} and φ_B vs. ρ_B are plotted, this is indeed the case. At some point $\rho_B^* \approx 0.155$ the curves φ_{ads} and φ_B cross each other. It was found that in this case, about half of chain segments is in adsorbed state ($\varphi_{ads} \approx 1/2$), and the AB composition of synthesized copolymer is close to equimolar ($\varphi_A = 0.512$ and $\varphi_B = 0.488$). At $\rho_B < \rho_B^*$, the growing chain is enriched with A monomers; when $\rho_B > \rho_B^*$ the growing chain end deeply penetrates into the bulk, and the B segments prevail in the resulting copolymer. Thus the change in the solution concentration of unadsorbed (or weakly adsorbed) reactive monomer allows varying the chemical composition in a wide range. Due to a one-to-one correspondence between φ_A (or φ_B) and ρ_B (Figure 41), this model

can operate only with one parameter governing the chain properties at a fixed degree of polymerization N , specifically with average chemical composition φ_A .

For the sake of simplicity, the discussion presented in this paper will be focused mainly on the systems where the chemical AB composition of resulting copolymers is close to 1:1. As a matter of fact, the equimolar composition is of special interest.

Throughout the simulation, snapshots of the system were collected. To give a visual impression of the simulated system, **Figure 42** presents a typical snapshot picture of an 1024-unit copolymer chain synthesized at $\rho_B = 0.155$.

3.3.2. Results and discussion

In this section the factors controlling the formation of copolymers near a selectively adsorbing surface are investigated and some sequence characteristics are described. the computer simulation results are compared with the *probabilistic model* of copolymerization, proposed by *Dr. Yury Kriksin*¹⁵⁸ (see also **Appendix A**).

3.3.2.1. Block Lengths

The average lengths of A and B blocks, L_A and L_B , are shown in **Figure 43** as a function of copolymer composition φ_A . As expected, when φ_A is increased the A blocks become longer while the B blocks shorten. Probabilistic model¹⁵⁴ predicts qualitatively similar behavior. At $\varphi_A = 0.57$ the values L_A and L_B become approximately equal to each other, $L_A \approx L_B \approx 8.5$ (in this case, $n_A \approx n_B \approx 60$ so that $2nL \approx N$). Surprisingly, the equality $L_A = L_B$ is observed in PM for almost the same composition ($\varphi_A = 0.60$), although the length of A and B blocks predicted for 1024-unit sequence is considerably larger as compared to that from MC simulations. For $\varphi_A = 0.512$ (the value which is closest to equimolar composition in the simulations performed in this study) we find $L_A = 8.4$, $L_B = 9.3$, and $L = (L_A + L_B)/2 \approx 9$.

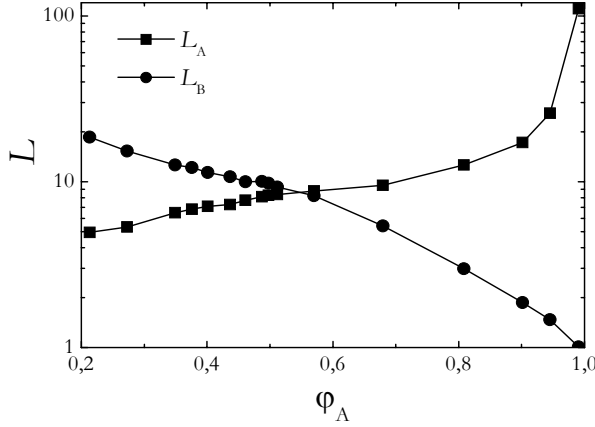


Figure 43. Average lengths of (■) A and (●) B blocks, L_A and L_B , as a function of copolymer composition ϕ_A . Chain length $N = 1024$.

3.3.2.2. Detrended Fluctuation Analysis

Let us now turn to the question of long-range correlations in the copolymer sequences obtained in the present work. For statistical analysis of copolymer sequences, different mathematical techniques have been used. Here, the method developed by Stanley and co-workers^{151,159,160} in their search for LRC in DNA sequences will be used. In this approach, each AB copolymer sequence is transformed into a sequence of symbols +1 and -1 which are considered as steps of a one-dimensional random walk. Shifting the sliding window of length λ along this sequence step by step, the number of symbols +1 and -1 inside the window is counted at each step.

This number $\gamma_k(\lambda) = \sum_{i=k}^{k+\lambda-1} \eta_i$ is a new random variable, depending on the position k of

the window along the sequence; here η_i is associated with every symbol i , such that $\eta_i = +1$ if chain segment i is A and $\eta_i = -1$ if it is B. This random variable has certain distribution. Its average is determined by the overall sequence composition, and its dispersion is given by $D_\lambda^2 = \langle \gamma^2(\lambda) \rangle - \langle \gamma(\lambda) \rangle^2$, where $\langle \dots \rangle$ stands for the average over all windows of size λ .

If the sequence is uncorrelated (normal random walk) or there are only local correlations extending up to a characteristic range (Markov chain) then the value of D_λ scales as $\lambda^{1/2}$ with the window of sufficiently large λ . A power law $D_\lambda \propto \lambda^\alpha$ with $\alpha > 1/2$ would then manifest the existence of LRC. However, due to large fluctuations, conventional scaling analysis cannot be applied reliably to the relatively short sequences generated in typical simulations. To avoid this problem, the so-called detrended fluc-

tuation analysis (DFA) is employed. This method is specifically adapted to handle problems associated with nonstationary sequences.^{159,160} In brief, DFA involves the following steps. The entire N -symbol sequence is divided into N/λ subsequences, each consisting of λ symbols. The best linear trend for each subsequence is then defined. The difference between the original random walk $\gamma(\lambda)$ and the corresponding local trend is found. Finally, the variance about the detrended walk for each subsequence is calculated. The average of these variances over all the subsequences of size λ , denoted $F_D^2(\lambda)$, characterizes the detrended local fluctuations within the window of length λ . Generally, the $F_D(\lambda)$ function shows the same behavior as D_λ .

Figure 44a presents the results of the statistical analysis performed as described above for 10^3 generated sequences. On average, these sequences have approximately 1:1 AB composition ($\phi_A = 0.512$). For comparison, we show in the same figure the data obtained for a purely random 1:1 sequence and a random-block 1:1 sequence, both with $N = 1024$. By definition, a random-block sequence is characterized by the Poisson distribution of the type A and B block lengths, $f(x) = e^{-L} L^x / x!$, where L is the average block length. Systematic consideration and comparison of the properties of the ensembles implies that we must determine L_A and L_B for the ensemble of simulated sequences and then create the random-block ensemble using these parameters in the corresponding Poisson distribution. Thus, we generated the Poisson distribution adjusted to achieve 1:1 composition and the same "degree of blockiness" as for a simulated copolymer. Also, in Figure 44a the $F_D(\lambda)$ function predicted by probabilistic model for $N = 1024$ and $\phi_A = 1/2$ is presented.

It is seen from Figure 44a that the data obtained for a purely random sequence demonstrates $F_D(\lambda) \propto \lambda^{1/2}$ scaling throughout the interval of λ examined, as expected. For a random-block sequence having nearly the same composition and average block length as simulated sequences, there are well-pronounced correlations in the region corresponding to small λ 's, which are close to the average block length. However, as λ increases, dumping of the correlations are observed, and for sufficiently large λ the behavior demonstrated by the random and random-block sequences is almost identical.

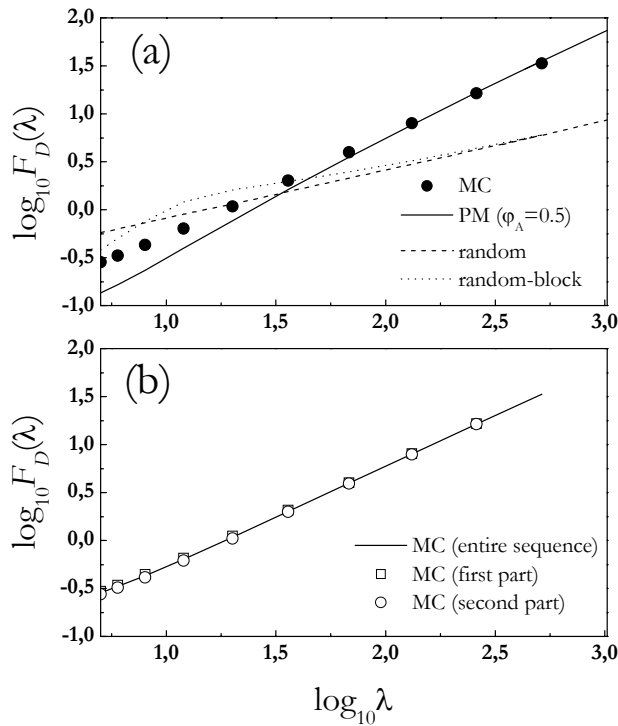


Figure 44. (a) Detrended fluctuation functions for (●) designed, (---) random, and (.....) random-block sequences of length $N = 1024$. Solid line shows the PM results at $\varphi_A = 0.5$.

(b) Detrended fluctuation functions for the generated copolymers: (—) the entire 1024-unit sequence, (□) the first 512-unit half, (○) the second 512-unit half.

Comparing these curves with the simulation results we see immediately that designed sequences do not correspond to random and random-block statistics, and strong correlations do exist in these sequences. For sufficiently large λ very good agreement between the MC simulation and the analytical PM result is observed. In both cases, the long-range correlations persist up to the windows with length close to N . Moreover, the correlations turn out to be more pronounced as λ is increased: the dependence of $\log[F_D(\lambda)]$ on $\log \lambda$ becomes a nearly linear function whose slope approaches unity with increasing λ . These sequences do not show dumping of the correlations and a wide crossover region with varying slope, the behavior that was found for "proteinlike" copolymers obtained via "coloring" of a homopolymer globule.¹⁴⁵ On the other hand, our findings are surprisingly similar to those known for DNA sequences, which appeared as a mosaic of coding and noncoding patches¹⁶⁰. Indeed, similar to DNA chains containing coding and noncoding regions, the copolymer under consideration also contains two types of alternating sections forming a certain pattern. It is known that the noncoding regions in DNA do not interrupt the correlation between the coding regions (and *visa versa*), and the DNA chain is fully correlated throughout its whole length. As a result, the D_λ^2 curve does not contain the linear portion $D_\lambda^2 \propto \lambda$. In a sense, such a behavior reflects the statistical properties of nonsta-

tionary fragments of a fixed length. In principle, the same behavior is observed in the present study.

From the facts presented above, it is evident that the sequences discussed here are correlated throughout their whole length. Also, this implies that if the averaged sequence is cut into a number of short fragments and then randomly shuffled, the $F_D(\lambda)$ dependence obtained in this way would not correspond to that observed in Figure 44a. On the other hand, it was found that any sufficiently large part of the averaged sequence has practically the same correlation properties as the entire sequence. Figure 44b demonstrates the fluctuation functions $F_D(\lambda)$ calculated separately for the first and second 512-unit parts of the 1024-unit sequences. One sees that the $F_D(\lambda)$ functions for these sections and for the entire sequence are nearly the same. This means that the generated sequences show scale invariance, a feature typical of fractal structures. Thus, the question is: what kind of statistics corresponds to the generated copolymer?

3.3.2.3. Distribution Functions

To gain some insight into the discussed problem, we present in Figure 45 the block length distribution functions $\mathcal{P}_A(\ell)$ (plotted on a semi-log scale) and $\mathcal{P}_B(\ell)$ (plotted on a log-log scale) obtained from simulations at $\phi_A = 0.512$. It is seen that the $\mathcal{P}_A(\ell)$ function decays exponentially with increasing block length ℓ while the $\mathcal{P}_B(\ell)$ function exhibits a power-law decay $\mathcal{P}_B(\ell) \propto \ell^{-\alpha}$. As has been noted, the same behavior follows from the probabilistic model. Moreover, the exponent α estimated from the simulation data ($\alpha \approx 1.6$) is, up to the "experimental" uncertainty, quite close to that predicted by our analytical model ($\alpha = 3/2$). Such power-law decay is a characteristic of Lévy probabilistic processes.¹⁰⁹ For these processes an observable stochastic variable x exhibits large jumps ("flights"), termed "Lévy flights", characterized by power-law (rather than exponential) probability distribution function, $\mathcal{P}(x) \propto x^{-\mu}$ ($1 < \mu < 3$). In this case, the variance D_ℓ^2 is a nonlinear function of ℓ , in contrast to Markovian processes for which D_ℓ^2 is linearly dependent upon ℓ for large ℓ . In this context, one may mention that statistical properties of many two-letter copolymers can adequately be described by the ergodic n -step Markov process. Markovian statistics have often been utilized to fit polymer sequence distribution data. For Markovian binary copoly-

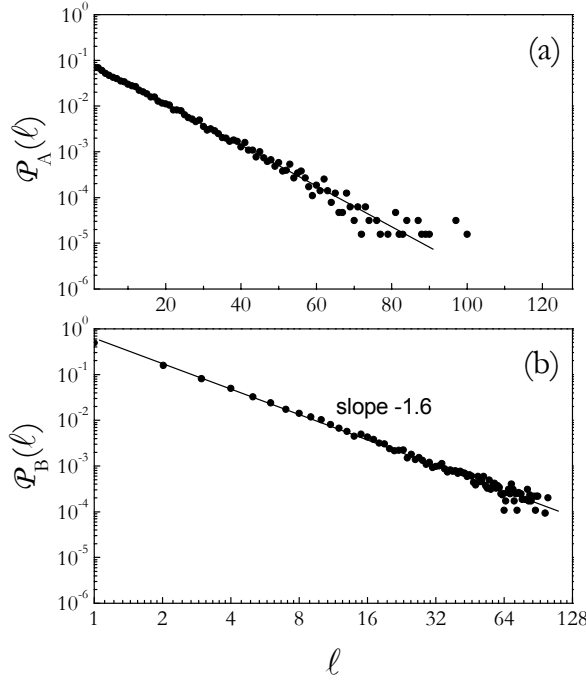


Figure 45. Block length distribution functions obtained from simulations: (a) $P_A(\ell)$ (plotted on a semi-log scale) and (b) $P_B(\ell)$ (plotted on a log-log scale) at $\phi_A = 0.512$. Solid lines show the best fits on the simulation data.

mers there is a characteristic length ("memory length") of the order of n , which defines the scale of correlations between segments in a copolymer sequence. For $\ell \gg n$, however, such correlations are washed out, and it is expected that $D_\ell^2 \propto \ell$ (or $F_D(\lambda) \propto \lambda^{1/2}$) and $\ln P(\ell) \propto -\ell$.

As seen from Figure 44 and Figure 45b, this is definitely not the case for the copolymers generated in the present study. Therefore, one cannot define the finite value of "memory length" which is analogous to n , and the statistics of these copolymers cannot be described by a Markov process. Of course, it is possible to interpret any sequence of length N in terms of an $(N-1)$ Markov process, but the definition of this maximum order model is nothing but a rephrasing of the original sequence and one has no guarantee that the model will work for longer sequences.

3.3.2.4. Intrachain Correlations

Another useful quantity that can be defined is the normalized correlation function

$$C_\eta^{(i)} = \frac{(N-i) \sum_{j=1}^{N-i} \eta_j \eta_{j+i} - \sum_{j=1}^{N-i} \eta_j \sum_{j=1}^{N-i} \eta_{j+i}}{\left\{ (N-i) \sum_{j=1}^{N-i} \eta_j^2 - \left[\sum_{j=1}^{N-i} \eta_j \right]^2 \right\}^{1/2} \left\{ (N-i) \sum_{j=1}^{N-i} \eta_{j+i}^2 - \left[\sum_{j=1}^{N-i} \eta_{j+i} \right]^2 \right\}^{1/2}} \quad \text{Equation 16}$$

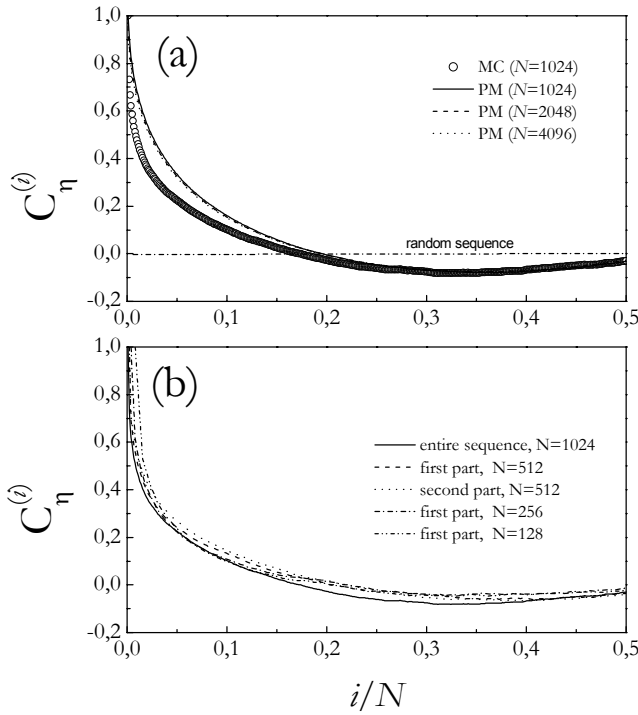


Figure 46. (a) Correlation function (Eq. 27) plotted vs. i/N . (○) Simulation data ($\phi_A = 0.512$ and $N = 1024$); solid, dashed, and dotted lines correspond to the PM results for different N , as marked in the figure. (b) The MC results for sub-

It quantifies how the stochastic variable η at one position i_1 is correlated to its value at some other position i_2 , both separated by a gap of $i = |i_1 - i_2|$ segments along the chain. By definition, $C_{\eta}^{(1)} = 1$. When all η_i are statistically independent (random copolymer), $C_{\eta}^{(i)} = 0$ for $i > 1$. If the $C_{\eta}^{(i)}$ function decreases fast with "chemical distance" i , then faraway positions are relatively uncorrelated and the sequence is dominated by its short-range structure. On the other hand, a slow decrease of $C_{\eta}^{(i)}$ would imply that faraway positions along the chain have a large degree of correlation or influence on each other. The sequence thus becomes organized at a macroscopic level with the possibility of new structure beyond the obvious one dictated by the short-ranged arrangement of different monomer units.

As it can be seen from Figure 46, this possibility does actually occur. Here the $C_{\eta}^{(i)}$ function is presented. This function is averaged over all the sequences generated by MC method for $N = 1024$ and $\phi_A = 0.512$ as well as the analogous PM results for a few values of N . It is evident from the PM data that $C_{\eta}^{(i)}$, when plotted against scaling variable i/N , is a universal function of "chemical distance" for any sufficiently long sequence. The fact that no effect of sequence length is seen here reflects the strict fractal structure of the sequence. There is good agreement between the MC and PM data;

moreover, at $i/N > 0.25$ they practically coincide. In both cases, no simple exponential decay of $C_{\eta}^{(i)}$ is observed. One sees that there are two regimes. On short scales, there is a fast decay. On longer scales, however, there is a long negative tail, which is determined by the overall structure of the whole sequence. The presence of negative correlations in $C_{\eta}^{(i)}$ bears some similarities with the behavior of a regularly alternating multiblock copolymer for which $C_{\eta}^{(i)}$ has an oscillatory structure with persistent period corresponding to block length. However, the sequences under consideration have rather randomly alternating statistical pattern than regularly alternating one.

In addition, in Figure 46b the correlation functions are shown. These functions are calculated separately for different subsequences of the generated 1024-unit sequences. It is seen that the statistical properties of the subsequences are close to each other and to those of the entire sequence. Again, such a behavior mirrors fractal properties of this two-letter sequence and is the signature of scale invariance.

3.3.2.5. Compositional Inhomogeneity

The intramolecular composition profile $\varphi_A^{(i)} = 2p_A^{(i)} - 1$ calculated here characterizes intramolecular chemical inhomogeneity along the chain and is related to the probabilities $p_A^{(i)}$ to find a monomer unit A at the i 'th position from the beginning of a growing macromolecule. The present definition of $\varphi_A^{(i)}$ assumes that the A-type segments are coded by symbol +1 while symbol -1 is prescribed to the B-type segments. For an ideal random copolymer in which chemically different segments follow each other in statistically random fashion, the $p_A^{(i)}$ function should coincide with the average fraction φ_A of A segments for any i . For a random-block copolymer, the fraction of one component averaged over many chains should also be uniform along the chain.

Figure 47 demonstrates a typical composition profile calculated as a function of i/N for $\varphi_A = 0.512$. First, rather good (almost quantitative) agreement between MC and PM results is observed. Second, both profiles show a monotonous decrease with the segment position. Therefore we deal with a specific copolymer whose primary structure is similar to that known for so-called "tapered" or *gradient* copolymers exhibiting strong composition inhomogeneity along their chain.^{161,162,163} The tapered nature of such copolymers, usually formed in the course of living anionic polymerization, is

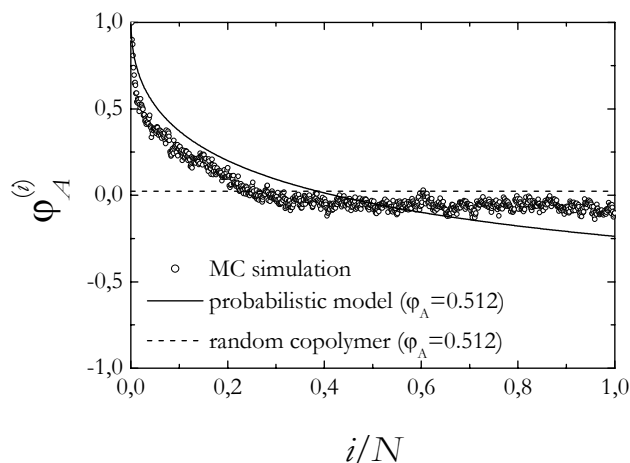


Figure 47. Composition profiles calculated as function of i/N for $\phi_A = 0.512$ and $N = 1024$: ($\circ$) simulation data, (—) probabilistic model, (---) random copolymer

due to a drift in free monomer composition during solution polymerization. The drift in free monomer composition in turn is caused by the different reactivities of the macroions towards the different monomers.¹⁶³ Such copolymers can be considered as a special type of block copolymers in which composition of one component varies along the chain.

With a decreasing difference in the monomer reactivity ratios, the formation of gradient statistical copolymers rather than tapered block copolymers occurs¹⁶³. In the model polymerization process, however, all the polymerizing species have the same reactivities, and the monomer concentrations remain unchanged during synthesis. Therefore, the changes in the probabilities of addition of components to the growing macroradical are due to the evolution of its chemical composition.

3.3.2.6. Conversion Dependencies

To further explore the origin of the gradient-like primary structure observed in the simulation and PM calculations, the variation of AB composition during copolymerization have been monitored. To this end, the "degree of conversion" N_τ/N is defined. This value varies from N^{-1} to 1. Analysis of the MC data shows that at the very beginning of copolymerization ($N_\tau/N \lesssim 0.05$), the growing chain radical gathers mainly monomers A strongly adsorbed at the surface. Then, as the chain becomes longer and the number of connected B units increases, the probability to find growing

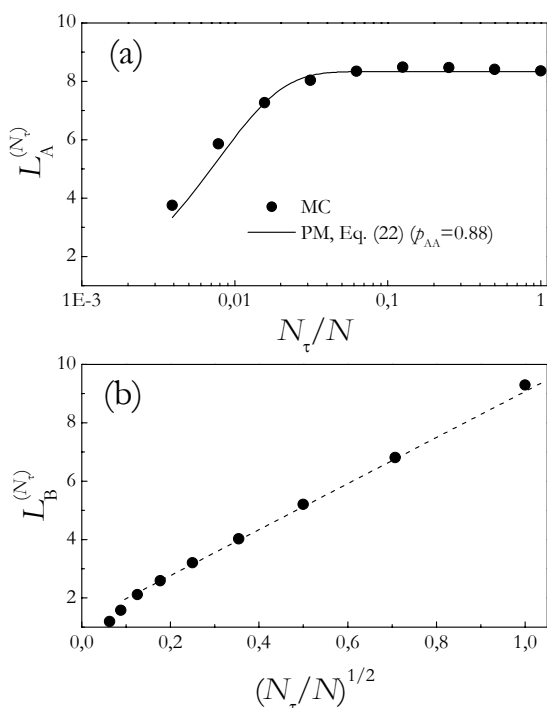


Figure 48. Current average block lengths, (a) $L_A^{(N_\tau)}$ and (b) $L_B^{(N_\tau)}$, vs. the length of growing copolymer fragment, for 1024-unit chains: (●) simulation data, (—) probabilistic model ($p_{AA} = 0.88$), (---) the best fit on the simulation data.

end-radical in B environment rises (reactions with the participation of unadsorbed B monomers dominate in the bulk). This causes the changes both in the current AB composition and in the average block lengths in growing chains of the current length N_τ . **Figure 48** illustrates these trends. Here, the current average block lengths, $L_A^{(N_\tau)}$ and $L_B^{(N_\tau)}$, vs. N_τ/N are presented. Note that the data in **Figure 48a** are given on a semi-log scale while **Figure 48b** shows the dependence of $L_B^{(N_\tau)}$ on $(N_\tau/N)^{1/2}$. In **Figure 48a** the data of MC simulations are compared with the theoretical model. In **Figure 48b**, the best fit on the simulation data is presented.

First of all, again qualitative agreement between MC and PM results is emphasized. In particular, as follows from Eqs. 18-20 for truncated probability distribution, the $L_B^{(N)}$ value scales with N as $L_B^{(N)} \propto N^{1/2}$. It is evident from **Figure 48a**, that the $L_A^{(N_\tau)}$ value reaches its limiting level L_A rather quickly (at $N_\tau \gtrsim 10^2$). On the other hand, the current average length of blocks B increases with N_τ up to $N_\tau = N$ (**Figure 48b**). As a result, for copolymer which was adjusted to achieve approximately 1:1 composition and required length of $N = 1024$, the primary structure of gradient-like type is obtained. In this copolymer, the content of B monomer units and the corresponding block length gradually increase from the beginning of chain to its end, while the same

quantities observed for A monomer units remain practically unchanged along the chain, except its very beginning.

It is clear that the behavior discussed above can take place only if both the total chain length and AB composition are constrained simultaneously. Without these constraints we would have: $L_B \rightarrow \infty$ and $L_A \rightarrow \text{constant}$ for the $N \rightarrow \infty$ limit. However, it should be stressed that if average copolymer composition is fixed, then both L_A and L_B scale with N as $N^{1/2}$, as directly follows from the PM prediction. This is due to the fact that the probability p_{AA} entering Eqs. 12 and 18 itself depends upon N via the constraint equation 22 so that increasingly large values of p_{AA} must be used to achieve desired AB composition for each given N . Such a composition constraint is precisely the major reason behind the specific chain growth and affects the global statistical nature of sequences on large scales.

3.4. Conclusion

Two different approaches have been employed: (i) a "coloring" (i.e., chemical modification) of partially adsorbed homopolymer chains and (ii) a copolymerization near a surface. In the former case, AB copolymers were prepared by adsorbing a bare homopolymer chain onto a flat substrate, after which its adsorbed segments were converted to type A ones, and its unadsorbed segments to type B ones. The second approach represents an irreversible radical copolymerization of selectively adsorbed A and B monomers with different affinity to a surface. It have been shown that the statistical properties of the copolymer sequences obtained in these two ways exhibit well-pronounced long-range correlations in distribution of different monomer units along the chain. In particular, the primary structure of copolymers generated via the "coloring" procedure is similar to that known for proteinlike copolymers. On the other hand, the copolymers obtained from polymerizing monomers selectively adsorbed onto a flat substrate demonstrate a specific quasi-gradient primary structure under the preparation conditions studied in this work. In addition, some characteristics of the adsorbed single chains (statistics of trains, loops, and tails) have been also investigated.

Second approach represents an irreversible radical copolymerization (chain growth) of selectively adsorbed A and B monomers with different affinity to a surface. In the computer simulation model, one of the types of monomers and chain segments were preferentially distributed near the adsorbing surface while other monomers and chain segments were preferentially located in the solution. As a result, the primary sequence and conformation of growing macroradical become mutually dependent. The growth of polymer chains during the addition copolymerization produced a monodispersed system. Despite the relatively simple formulation of this model, its predictions are in good qualitative (in some cases, semi-quantitative) agreement with the probabilistic model, proposed by A. Kriksin¹⁵⁴. The differences between the analytical and simulation results may be mainly due to the fact that our probabilistic model does not include intrachain excluded volume effects.

It was shown that copolymerization near the adsorbing surface can lead to a copolymer with a specific quasi-gradient primary structure and power-law long-range correlations in distribution of different monomer units along the chain. The gradient extends along the entire chain for any chain length. Inhomogeneous spatial distribution of polymerizing monomers and composition constraints in the resulting copolymer are major reasons behind the specific chain growth and the global statistical nature of sequences on large scales. These numerical results are all consistent with our theoretical predictions¹⁵⁴.

Actually, the polymerization procedure discussed in this Chapter can be considered as a prototype of template polymerization (also connected with molecular imprinting) that is one of the most productive and promising approaches to the synthesis of various polymeric materials. The main idea of this technique is to form the desired (inhomogeneous) spatial distribution of monomers, e.g., via binding them to a template, and then to fix this distribution by polymerization. In the present study concentration inhomogeneities in the reaction bicomponent system had been marked. Therefore, by varying the average copolymer composition, defined by the effective monomer-substrate interaction and surface coverage, the copolymers with different primary sequences can be designed and synthesized in a controlled fashion. Moreover, just by radical copolymerization of two monomers with different affinity to a certain plane surface it is possible to obtain copolymers with a gradient primary structure.

Chapter 4

Molecular Motor Based on Two-State Model of Block Copolymer

4.1. Introduction

Nowadays, molecular motors became one of the intensively exploring objects in modern molecular biology and nanotechnology because of their ability to convert chemical or light energy into mechanical work (rotational or translational motion). By means of various biomolecular motors different vital functions of biological organisms are realized, such as muscle contraction, cell division, cell crawling, targeted vesicle transport, synthesis of ATP, RNA, and DNA. Most of molecular motor proteins cannot be considered as motors by themselves: some specific tracks along which they move are required (e.g., myosin on actin filament, kinesin on microtubules, polymerase on DNA, etc.)¹⁶⁴. A number of theoretical approaches for the description of molecular motors have been developed recently^{165,166}. Both detailed models considering microscopic properties of specific molecular motors¹⁶⁷ and very simple ideal models taking into account only some basic principles of phenomena¹⁶⁸ have been discussed.

The present study is dedicated to the computer simulation of a simple model of artificial molecular motor. The model realizes, for the first time, long-range directional motion (reptation) of single block AB copolymer chain strongly adsorbed on a molecularly structured, stripe-patterned surface which is a source of "molecular friction". We have also visualized such translational motion explicitly by using molecular graphics. The driving force for the motion is a variation of the stickiness (adhesive contact) of different polymer segments to the surface under applied external periodic field. Our simulation is based on the molecular dynamics (MD) approach.

4.2. Model and Simulation Method

For the sake of computational efficiency, we do not focus here on chemical details of the simulated copolymers addressing the generic features of the model system. We consider a continuum space (bead-rod) model of a flexible copolymer chain that contains two parts: A- and B-blocks consisting of monomer units A and B type, respectively. The time evolution of the system is determined by Newton's equations of motion. Monomer units (chain beads) are linked by rigid bonds of a fixed length to form a chain of $N = N_A + N_B$ beads, where N_A and N_B are the lengths of the corresponding blocks. No additional restrictions are imposed on bond angles (i.e., the angles between two successive bond vectors) other than those naturally arising from the interaction of beads separated by two successive bonds.

The potential energy of the system is given by

$$U = \sum_i^N \sum_{j \neq i}^N [u_{ev}(r_{ij}) + u_{AA}(r_{ij}) + u_{BB}(r_{ij}) + u_{AB}(r_{ij})] + \sum_{i=1}^N u_a(r_i) \quad \text{Equation 17}$$

where r_{ij} is the distance between beads i and j , u_{ev} takes into account excluded volume interactions, u_{AA} , u_{BB} and u_{AB} characterize short-range attractive interactions between monomer units, and u_a is the adsorption potential describing polymer-surface interaction. Excluded volume is included via a repulsive Lennard-Jones (LJ) potential with parameters $\sigma = \varepsilon = 1$ (σ is the diameter of the beads having unit masses and ε controls the energy scale). Intrachain attractive interactions are modeled by a Yukawa-type potential for which we use the following simple form

$$u_{\alpha\beta}(r_{ij}) = \begin{cases} \frac{-\varepsilon_{\alpha\beta}\sigma}{r_{ij}} \left[1 - \left(\frac{r_{ij}}{r_c} \right)^2 \right]^2, & r_0 < r_{ij} \leq r_c \\ 0, & r_{ij} > r_c \end{cases}, \quad \text{Equation 18}$$

where the (positive) parameters $\varepsilon_{\alpha\beta}$ ($= \varepsilon_{AA}, \varepsilon_{BB}, \varepsilon_{AB}$) set the amplitude of the intrachain attraction, $r_0 = 2^{1/6}\sigma$, and $r_c = 4\sigma$ is the cutoff distance. At $\varepsilon_{\alpha\beta} = 0$, there is no attraction between monomer units.

The molecularly structured surface is represented by a plane (at $z = 0$) with discrete interaction sites having infinite masses. The distribution of the interaction sites on the surface corresponds to a simple square lattice with spacing σ . Adsorp-

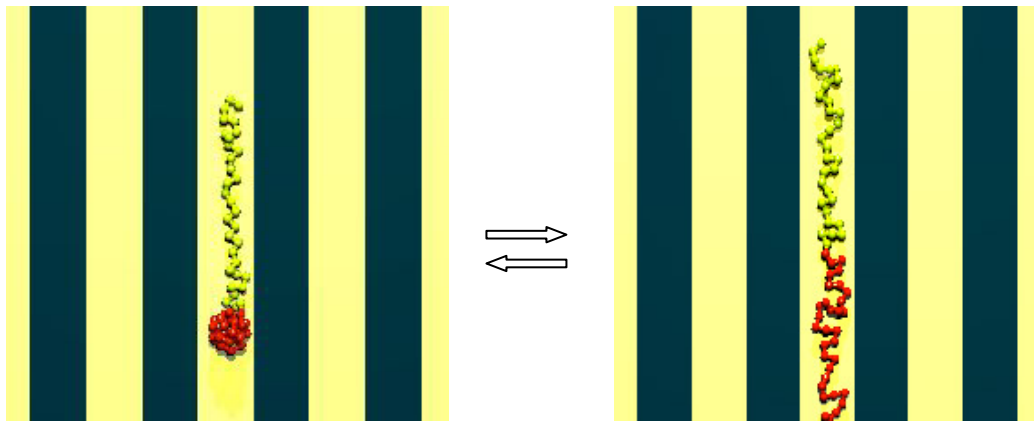


Figure 49. Stripe-patterned surface with adsorbed diblock copolymer. The two different types of interaction sites are colored white and black. In the state I, the block A collapses while the block B swells; in the state II both blocks swell and are stretched along the stripe.

tion potential is a sum of the repulsive part of LJ potential and attractive Yukawa-type potential

$$u_a(r_i) = \begin{cases} -\frac{\varepsilon_a \sigma}{r_i} \left[1 - \left(\frac{r_i}{r_c} \right)^2 \right]^2, & r_0 < r_i \leq r_c \\ 0, & r_i > r_c \end{cases}, \quad \text{Equation 19}$$

where r_i is the distance between chain bead i and the corresponding interaction sites localized on the surface, ε_a ($= \varepsilon_{AS}, \varepsilon_{BS}$) is the (positive) energy parameter, and $r_c = 4\sigma$ is the cutoff distance. The surface is patterned with alternating parallel stripes of two types, S_1 and S_2 ("white" and "black"), which have the same width L . The "white" sites of type S_1 attract chain beads ($\varepsilon_{AS1}, \varepsilon_{BS1} > 0$) while the interaction between S_2 type sites ("black" sites) and chain beads is purely repulsive ($\varepsilon_{AS2}, \varepsilon_{BS2} = 0$), so that the chain is adsorbed on "white" stripes and usually confined in one of these narrow stripes (see **Figure 49**).

We restrict attention to the regime of sufficiently strong segment-surface attraction and study the long-time dynamic behavior of the copolymer in the vicinity of the surface where each monomer unit can interact with many adsorption sites. These adhesive interactions provide "molecular friction" forces in our model. Note that friction is proportional to the actual area of polymer-surface adhesive contact and thus depends on the chain conformation.

Explicitly, no solvent particles are included in the simulations. In order to simulate solvent effects and the time evolution of the system in contact with a heat bath of

temperature T , we augment the equations of motion by Langevin terms related to solvent viscosity and energy dissipation (see also **Appendix B**). The corresponding parameter Γ , which takes into account the viscosity of solvent, is set to $\Gamma = 1$. The reference temperature is fixed at $T = \varepsilon/k_B$.

The equations of motion are solved iteratively using the time step $\Delta t = 0.01$.

In order to realize the directional long-range molecular motion, we need an external source providing periodic changes in internal states of the system. Light, chemical reactions, temperature, quality of the solvent, etc. can be considered as such a source. Acting on the adsorbed copolymer, it can lead to the changes in potential energy of the system thereby controlling the chain conformation. One of the simplest mechanisms for inducing directional motion is a periodic switching of the system between two conformational states, say I and II (see **Figure 49**). In other words, in this two-state model, the system is subjected to an external periodic field that induces sudden switches (transitions) from state I to state II and back, $I \rightleftharpoons II$. This is necessary condition for our model to work. In the simulation, the transitions between the states are modeled as sudden switches of the energy parameters (see below). During the time τ^* , the system is staying in the first state and then passes in the second one, i.e., τ^* is the lifetime of the states I and II.

4.3. Results and discussion

The following characteristics were varied: the number of chain beads ($N = 8 \div 64$), the ratio N_A/N_B (number of A beads / number of B beads) from 3:1 to 1:3 the energy parameters ($\varepsilon_{AA} = 0 \div 4$, $\varepsilon_{BB} = 0 \div 1.5$, $\varepsilon_{AB} = 0 \div 1.5$, $\varepsilon_{AS1} = \varepsilon_{BS1} = 0.5 \div 5.0$; all the energies are measured in units of $k_B T$), and the interval between switches ($\tau^* = 10^2 \div 10^5$ MD time steps). Also, we varied the block lengths. The stripe width was fixed at $L = 5\sigma$. Most of the results discussed in this work were obtained at $\varepsilon_{AA} = 0$ or 4 (states I or II, respectively), $\varepsilon_{BB} = \varepsilon_{AB} = 0$, and $\varepsilon_{AS1} = \varepsilon_{BS1} = 1$. Note that at $\varepsilon_{AA} = 4$ the block A is in a strongly collapsed (globular) conformation and swells at $\varepsilon_{AA} = 0$. Block B always has stretched conformation.

Simulation was started with the deposition of the copolymer onto the surface and then equilibration run for a long time was performed. Then we traced the displacement, d , of the center of mass of the chain along the stripe, where the chain is confined, as a function of the number of switches, n , from $\varepsilon_{AA} = 4$ to $\varepsilon_{AA} = 0$ and back (see **Figure 50**). Between the switches, the chain relaxes for the time τ^* . Using computer graphics, it was observed rather distinctly that the chain can move directionally along the stripe by means of alternating "contraction-stretching" mechanism observed for block A which drags swollen block B. The velocity of molecular motion along the stripe as $v = d/n$ was defined. The value of v is shown in **Figure 51** as a function of τ^*/N^2 . It is seen that v goes through the maximum at $\tau^*/N^2 \approx 2$ and tends to be zero for small and large τ^*/N^2 .

For sufficiently large n , when the system achieves a stationary nonequilibrium state, it was found that the quantity d follows the power law: $d^2 \propto n^\alpha$. The exponent α can be used as an additional measure of the intensity of the directional molecular motion.

At $N = 64$, the ratio N_A/N_B from 3:1 to 1:3 was varied. **Figure 53** shows that under conditions considered, the maximum intensity of the directional drift is reached for 1:1 composition. When adsorption energy is increased ($\varepsilon_{AS1} = \varepsilon_{BS1} = 3$), this leads to an increase in v and α . On the other hand, the dependence of v and α on the ratio

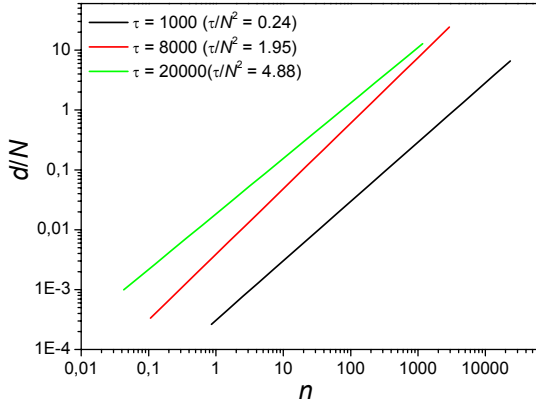


Figure 50. Displacement per unit d/N vs. the number of switches, n .

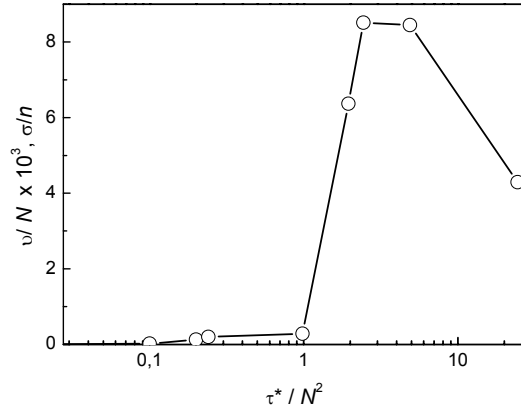


Figure 51. Velocity v vs. the ratio τ^*/N^2 for symmetric diblock copolymer at $N = 64$.

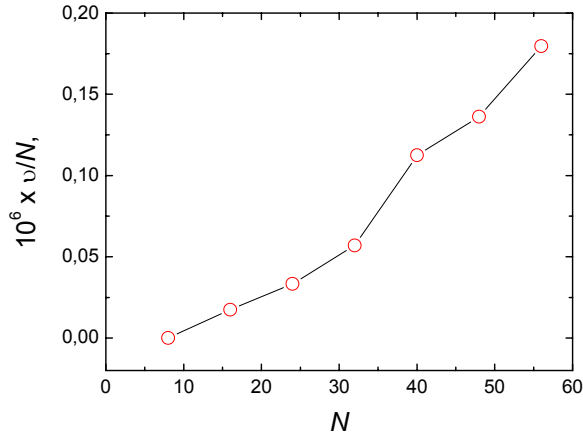


Figure 52. Velocity v vs. the number of units in polymer chain N

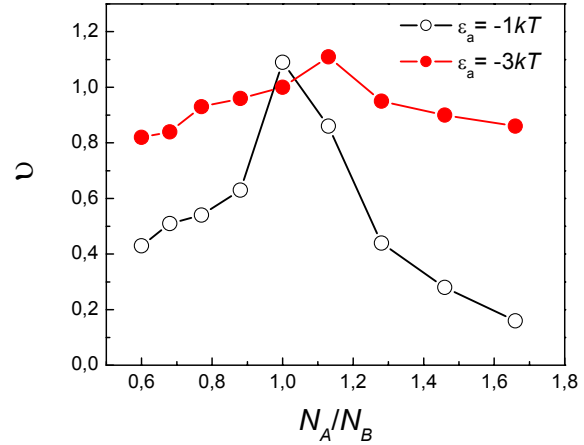


Figure 53. Velocity v vs. the ratio N_A/N_B

N_A/N_B weakens. However, for very large adsorption energies, exceeding ϵ_{AA} , translational motion of the chain is strongly suppressed. It is found that the values of v and α decrease with decreasing N : at small values of N comparable with L , the motion becomes shuttle-like, i.e., the chain shows periodic short-time oscillations along the stripe although it moves directionally on larger time scales.

It is clear that the occurrence of the long-range directional motion requires the presence of a nonzero steady average force acting on the chain and inducing its drift at a constant average velocity. In our two-state model, the origin of this force is a difference between the friction coefficients experienced by the block A in the two internal states (extended and collapsed).

It seems logical to assume that friction forces should be inversely proportional to the distance of polymer segments from the surface. In other words, friction is proportional to the actual area of contact between adsorbed polymer segments and the surface. In the model, the block A is stretched in the state II and, therefore, its monomer units are strongly adsorbed and have the maximum area of contact. In state I, when the block A collapses, some fraction of the A units does not interact with the surface and this leads to a decrease in the friction forces as compared to state II. Owing to the different friction coefficients of the block A in the two states, the average friction force does not vanish. When the system transits from state I to state II, the bulk polymer droplet (globule) formed by the block A spreads on the surface. However, the presence of the permanently adsorbed block B prevents the spreading of A segments in the direction occupied by the one-bead-thick layer B. As a result, we observe a preferential spreading of A segments in the opposite direction leading to a reptation-like directed motion of the chain.

4.4. Conclusion

Using molecular dynamics computer simulation, we have realized the idea of a copolymer-based molecular device. We can conclude that for our two-state model to behave as a molecular motor the following conditions are necessary and sufficient: (i) asymmetric structure of the object achieved by asymmetric interactions with the surface and resulted in "anisotropic molecular friction"; (ii) particular patterning of the surface to specify direction of motion; (iii) external periodic field applied to the system.

For this simple model, adsorption energy, rate of periodic changes, τ^* , copolymer chain composition, N_A/N_B , and chain length, N , were varied in the simulations. Directional motion of the adsorbed copolymer chain was observed for large range of the system parameters.

Appendix A

The probabilistic model of copolymerization¹⁵⁴

This model has been proposed by A. Kriksin¹⁵⁴.

One of the ways to get a correct insight into the nature of correlations in a complex polymerizing system consists in an ability of constructing a simple mathematical (probabilistic) object (e.g., a correlated sequence of symbols) possessing the same statistical properties as the initial system. To this end, in this subsection the model of an ideal, self-intersecting linear polymer chain consisting of two types of segments, A and B is considered. In the model, there is no excluded-volume interaction of chain segments between themselves. The ideal structure of this polymer chain ensures the presence of spatial correlation only between the neighboring segments.

To describe radical copolymerization near a surface, two discrete stochastic processes, $\xi^{(A)}$ and $\xi^{(B)}$ are introduced. They form a compound process ξ , which corresponds to a path associated with the primary sequence of an AB copolymer chain. Let us characterize the sequence of steps (monomer units) by $\sigma_i \in \{A, B\}$ with $i = 0, 1, 2, \dots$ labeling the steps along the sequence so that the random variable ξ_i is the realization of the process ξ at i 'th step. The origin of the path is taken as the origin of coordinates. There is a starting point $i = 0$ which is associated with the initiator of polymerization (monomer A); that is, $\xi_0 = 0$ or $\sigma_0 = A$ in all realizations of the process ξ . This will not affect the asymptotic scaling behavior.

In the model describing a polymer chain growth by reaction of monomers A and B with a reactive end-group on the growing chain, the discrete-state process $\xi^{(A)}$ characterizes attachment of strongly adsorbed monomers A. This process has two outcomes: success, with probability p_A , and failure, with probability $1-p_A$. In other words, with probability p_A , the polymer chain is lengthened by addition of the next monomer unit of the type A to a terminal free-radical reactive site. If the process $\xi^{(A)}$ is terminated, then the process $\xi^{(B)}$, associated with attachment of monomers B in the bulk solution, starts. In our probabilistic polymer growth model, it is convenient to treat the process $\xi^{(B)}$ as an asymmetric random walk on the 1D half-line with an absorbing boundary at the origin. The random walk is defined as follows. At each i 'th step, the path goes further from the origin ($\Delta_i^{(B)} = \xi_i^{(B)} - \xi_{i-1}^{(B)} = +1$) with probability p_B , and goes closer to the origin ($\Delta_i^{(B)} = -1$) with probability $1-p_B$. When the random walk

reaches the origin ($\sum_i \Delta_i^{(B)} = 0$ or $\xi_0^{(B)} = -1$), it is terminated (absorbed). After that the process $\xi^{(A)}$ starts again. Thus, the processes $\xi^{(A)}$ and $\xi^{(B)}$ change each other and continue until the path reaches a desired total length; that is, we deal with a randomly alternating growth. Hence, the random variable ξ_i , obeying specific probability distribution function, takes value $\xi_i = 0$ if $\sigma_i = A$ and $\xi_i = k$ if $\sigma_i = B$, where $k = 0, 1, \dots$

If the step i in the infinite path ξ is of the type A, then the conditional probabilities p_{AA} and p_{AB} for the next step $i + 1$ to be of the type A or B are defined as

$$p_{AA} = p_A + (1 - p_A)(1 - p_B)p_A + (1 - p_A)(1 - p_B)(1 - p_A)(1 - p_B)p_A + \dots = \frac{p_A}{1 - (1 - p_A)(1 - p_B)} \quad (1)$$

$$p_{AB} = (1 - p_A)p_B + (1 - p_A)(1 - p_B)(1 - p_A)p_B + \dots = \frac{(1 - p_A)p_B}{1 - (1 - p_A)(1 - p_B)} \quad (2)$$

with $p_{AA} + p_{AB} = 1$. Below, we restrict ourselves to the simplest (symmetric) case: $p_B = 1/2$ when each first step of the process B is absorbed by the boundary with probability $1/2$.

The probability to find an uninterrupted succession (block) of some length ℓ of A steps in the infinite path ξ is given by the well-known geometric distribution $\mathcal{P}_A^0(\ell) = (1 - p_{AA})p_{AA}^\ell$. However, taking into account that the very first step in the path should always be of the type A ($\sigma_0 = A$), we have the following conditional probability distribution

$$\mathcal{P}_A(\ell) \equiv \mathcal{P}_A^0(\ell | i > 0) = \mathcal{P}_A^0(\ell) / \mathcal{P}_A^0(i > 0) = [(1 - p_{AA})p_{AA}^\ell] / p_{AA} = (1 - p_{AA})p_{AA}^{\ell-1} \quad (3)$$

where $\ell = 1, 2, \dots$ and p_{AA} is defined by Eq. 1. Therefore, the average length of blocks A for the infinite total path length is given by

$$L_A = \sum_{\ell=1}^{\infty} \ell (1 - p_{AA}) p_{AA}^{\ell-1} = (1 - p_{AA})^{-1} \quad (4)$$

One may say that the conditional probability p_{AA} defines the strength of persistent correlations in the sequence. If the persistent correlations are extremely strong ($p_{AA} \rightarrow 1$), then $L_A \rightarrow \infty$. In the polymerization process, such a situation is realized when the bulk concentration of B monomers approaches zero. If $p_{AA} = p_{AB} = 1/2$, one arrives at the known trivial result for the Bernoullian statistics without correlations that corresponds to a random copolymer. In this case, the probability p_A of each segment to be of type A is constant throughout the whole sequence. This means, for example, that the conditional probability p_{AA} that the $(i+1)$ 'th segment is of type A when the i 'th segment is also of type A is equal to p_A . The average fraction of type A segments φ_A in a purely random sequence is equal to the probability p_A . In particular, for a purely random sequence with $p_A = 1/2$ we have $L_A = L_B = 2$. Such a copolymer is obtained in the course of solution copolymerization of A and B monomers having identical solubility and reactivity. Finally, at $p_{AA} = 0$ ($p_{AB} = 1$) we deal with a regular sequence with alternating distribution of A and B segments in the sequence for which $L_A = L_B = 1$ (Eq. 4).

The probability distribution over the length of blocks B is related to the well-known ballot problem or to a classical probabilistic "first return" problem.¹⁶⁹ Here it is not have an underlying analytical process like the geometrical one. In the present context, the ballot problem can be solved by using a conditional probability argument leading to a recurrence relation.

In our formulation, $\xi_i^{(B)}$ is the result of the i 'th step on the half-line: $\xi_i^{(B)} = \xi_{i-1}^{(B)} + 1$ for a step that jumps further from the origin and $\xi_i^{(B)} = \xi_{i-1}^{(B)} - 1$ for a step that jumps closer to the origin. One may then use standard techniques for one-dimensional random walks. It is clear that each block of the type B should contain the even number of steps. Therefore, the one-dimensional walks is considered. This walks start at origin and take $2m$ steps ($m = 1, 2, \dots$). The total number of random walks with the positive first step is thus 2^{2m-1} and we consider that all these walks to be equally probable (since $p_B = 1/2$). Let us collect the fraction of random walks that visit origin for the last time at the step $2n$ and have the non-negative first term. The fraction of such walks of length $2m$ can be written as

$$\phi_m = 2^{1-2m} \sum_{n=1}^m \frac{n}{m} \binom{2m}{n+m}, \quad m = 1, 2, \dots \quad (5)$$

with $\phi_0 = 1$. The function ϕ_m , given above, is related to the probability distribution over the length of process $\xi^{(B)}$. This distribution is similar to the so-called discrete arc-sine distribution of order m .¹⁶⁹ It can be calculated using the following relation

$$\mathcal{P}_{\xi^{(B)}}(k) \equiv \mathcal{P}_{\xi^{(B)}}(k = n \mid k > 0) = \begin{cases} 0, & n = 2m - 1 \\ \phi_{m-1} - \phi_m, & n = 2m \end{cases} \quad m = 1, 2, \dots \quad (6)$$

with

$$\phi_m = \sum_{j=1}^m b_{j,m}, \quad m = 1, 2, \dots \quad (7)$$

where

$$b_{j,m} = \frac{j}{j-1} \frac{m-j+1}{m+j} b_{j-1,m}, \quad j = 2, \dots, m \quad (8)$$

$$b_{1,m} = \frac{a_m}{m+1} \quad (9)$$

$$a_m = \left(1 - \frac{1}{2m}\right) a_{m-1}, \quad m = 2, 3, \dots \quad (10)$$

$$a_1 = 1 \quad (11)$$

The distribution over the length of blocks B, $\mathcal{P}_B(\ell)$, is more complex than $\mathcal{P}_{\xi^{(B)}}(k = n \mid k > 0)$. This is due to the fact that B blocks of some length can be obtained by "gluing together" two or more shorter B sequences, which are neighbors in the total path. This happens when after terminating the process $\xi^{(B)}$, the process $\xi^{(A)}$ is terminated immediately at the first step, and the current B sequence has a chance to be continued. In other words, we take into account the presence of unadsorbed B monomers on the surface.

Let us call the B block of length ℓ "irreducible block", if it is originated from the process $\xi^{(B)}$ that is terminated at the step $2m$. It is clear that any blocks of the type B, including those located at the end of a finite path, can be composed from the irreducible blocks by "gluing" them together. Then the distribution of the B blocks can be written as

$$\mathcal{P}_B(\ell = 2m) = \frac{p_{AA}}{1 - p_{AA}} \sum_{n_j} \prod_{j=1}^m \mathcal{R}_{n_j}, \quad \sum_{j=1}^m n_j = m \quad (12a)$$

$$\mathcal{P}_B(\ell = 2m + 1) = 0, \quad m = 1, 2, \dots \quad (12b)$$

where

$$\mathcal{R}_n = (1 - p_{AA}) \mathcal{P}_{\xi^{(B)}}(k = 2n \mid k > 0), \quad n = 1, 2, \dots, m \quad (13a)$$

$$\mathcal{R}_0 = 1 \quad (13b)$$

Here the function $\mathcal{P}_{\xi^{(B)}}(k = 2n \mid k > 0)$ is given by Eq. 6. To calculate $\mathcal{P}_B(\ell = 2m)$, it is more convenient to use the recurrence relations

$$\mathcal{P}_B(\ell = 2m) = \sum_{j=1}^m q_j^{(m)}, \quad m = 1, 2, \dots \quad (14)$$

$$q_j^{(m)} = \sum_{n=j-1}^{m-1} \mathcal{R}_{m-n} q_{j-1}^{(n)}, \quad j = 2, 3, \dots, m \quad (15)$$

$$q_1^{(n)} = (1 - p_{AA})^{-1} p_{AA} \mathcal{R}_n, \quad n = 1, 2, \dots, m \quad (16)$$

One can show that the block length distribution $\mathcal{P}_B(\ell)$ is characterized for asymptotically large ℓ by the power-law decay of its density $\mathcal{P}_B(\ell) \propto \ell^{-\alpha}$ with the exponent $\alpha = 3/2$.

Formally, the average length of blocks B for the infinite total path length is defined as

$$L_B = \sum_{m=1}^{\infty} 2m \mathcal{P}_B(\ell = 2m) \quad (17)$$

Note that the second moment of $\mathcal{P}_B(\ell)$ diverges for $\ell \rightarrow \infty$, but in a simulation or experiment it should be always finite.

Now we are interested in so-called truncated probability distributions describing a finite path of a given length. A distribution is truncated if observed values must fall within a restricted range, instead of the expected range over all possible values. In our case, the longest path (sequence) can have a length not more than N . If a probability distribution function $\mathcal{P}(\ell)$ is known for an infinite path, then the corresponding truncated distribution $\mathcal{P}(\ell \leq N)$ is given by

$$\mathcal{P}(\ell \leq N) = \begin{cases} \mathcal{P}(\ell), & \ell = 1, 2, \dots, N-1 \\ \mathcal{Q}(\ell), & \ell = N \end{cases} \quad (18)$$

where

$$\mathcal{Q}(\ell) = \sum_{n=\ell}^{\infty} \mathcal{P}(n) = 1 - \sum_{n=1}^{\ell-1} \mathcal{P}(n) \quad (19)$$

and $P(\ell)$ is defined from (3) and (12) for blocks A and B, respectively. The average length of the blocks is

$$L_A^{(N)} = \sum_{\ell=1}^N \ell \mathcal{P}_A(\ell) \quad (20a)$$

$$L_B^{(N)} = \sum_{\ell=1}^{N-1} \ell \mathcal{P}_B(\ell) \quad (20b)$$

Note that in Eq. 20b we take into account that $\sigma_0 = A$, and contribution from the very first step A always takes place. It is easily seen from Eqs. 19 and 3 that for blocks A, the $\mathcal{Q}_A(\ell)$ function reads

$$\mathcal{Q}_A(\ell) = p_{AA}^\ell \quad (21)$$

Therefore, we have

$$L_A^{(N)} = \frac{1 - p_{AA}^N}{1 - p_{AA}} \quad (22)$$

In the $N \rightarrow \infty$ limit, Eq. 22 coincides with Eq. 4a. For $L_B^{(N)}$ there is no simple analytical expression.

As has been noted above, of special interest is a copolymer with a fixed (in particular, equimolar) chemical composition. For the model considered, the corresponding condition can be written as

$$1 + \sum_{i=1}^{N-1} p_A^{(i)} = \varphi_A \quad (23)$$

Here $p_A^{(i)}$ is the probability that the variable σ_i is in the state A at the i 'th step of the finite path ξ of a given length N and $\varphi_A = N_A/N$ is the fraction of the A-type states. By definition, $p_A^{(0)} = 1$. Using the relation for total probability, we arrive at

$$p_A^{(i)} = p(\sigma_i = A | \xi_{i-1} = 0) p(\xi_{i-1} = 0) + p(\sigma_i = A | \xi_{i-1} > 0) p(\xi_{i-1} > 0) \quad (24)$$

Taking into account that $p(\sigma_i = A | \xi_{i-1} = 0) = p_{AA}$ and $p(\sigma_i = A | \xi_{i-1} > 0) = 0$, we rewrite Eq. 24 for $N \geq 4$

$$p_A^{(i)} = p_{AA} p(\xi_{i-1} = 0) \quad (25)$$

where in general case

$$\begin{aligned} p(\xi_i = 0) &= p_{AA} p(\xi_{i-1} = 0) + (1 - p_B) p(\xi_{i-1} = 1) \\ p(\xi_i = 1) &= (1 - p_{AA}) p(\xi_{i-1} = 0) + (1 - p_B) p(\xi_{i-1} = 2) \end{aligned} \quad (26)$$

$$p(\xi_i = k) = p_B p(\xi_{i-1} = k-1) + (1 - p_B) p(\xi_{i-1} = k+1) \quad \text{for } k > 1$$

with $p(\xi_0 = 0) = 1$ and $p(\xi_0 = k) = 0$ for $k > 0$. Due to the composition constraint (23), the conditional probability p_{AA} (and therefore p_A , see Eq. 1) turns out to be a function of N . In this case, it can be shown that the probability p_A converges to unity as $p_A \propto 1 - N^{-1/2}$ for sufficiently large N . Thus, the probability distributions $P(\ell)$ and the corresponding moments, L_A and L_B , become complex functions of two parameters N and φ_A .

Appendix B

Langevin Molecular Dynamics

Explicitly, no solvent particles are included in the simulations; that is, the solvent is represented by a "dielectric continuum". In order to simulate solvation effects and the time evolution of the solution in contact with a heat bath of temperature T , we augment the equations of motion by Langevin uncorrelated noise terms¹⁴⁸. In the MD simulations, the equations of motion of a polymer system in the presence of fixed constraints (the bead-rod model) are

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i [U(\mathbf{r}) - \sum_{s=1}^{n(N-1)} \lambda_s G_s(\mathbf{r}_1, \dots, \mathbf{r}_{nN})] - \Gamma_i \dot{\mathbf{r}}_i + \mathfrak{R}_i, \quad i = 1, 2, \dots, N, \quad (1)$$

with the constraints of fixed bond lengths

$$G_s(\mathbf{r}_1, \dots, \mathbf{r}_{nN}) \equiv \frac{1}{2} [(\mathbf{r}_{s+1} - \mathbf{r}_s)^2 - b^2] = 0, \quad s = 1, 2, \dots, N-1, \dots, n(N-1), \quad (2)$$

where n is the number of chains in the system, $m_i = 1$ is the mass of the chain bead or counterion i , $-\nabla_i U(\mathbf{r})$ represents the total nonbonded forces on the particle i , $b = 1$ is the bond length, λ_s 's are the Lagrange multipliers, $\mathfrak{R}_i$ describes the random force of the heat bath acting on particle i , and Γ takes into account the viscosity of the solvent. The summation in Eq. (10) is performed over all the $n(N-1)$ bonds of the N -unit polymer chains. This term represents the forces, $\nabla_i \sum_{s=1}^{n(N-1)} \lambda_s G_s(\mathbf{r}_1, \dots, \mathbf{r}_{nN})$, which are due to the bond reactions¹⁷⁰. Each of the s^{th} geometrical constraint (bond) is associated with exactly one unknown λ_s . In Eq. (10), $\mathfrak{R}_i$ and Γ_i are connected through the fluctuation-dissipation theorem, $\langle \mathfrak{R}_{\alpha i}(0) \cdot \mathfrak{R}_{\alpha i}(t) \rangle = 2\Gamma_i k_B T \delta(t)$, ($\alpha = x, y, z$; T is the reference temperature) and ensures that the temperature is kept constant. Note that if Γ_i is included without the $\mathfrak{R}_i$ term, the system would simply dissipate and no temperature effects could be addressed.

We take the parameter Γ to be dependent on solvent-accessible surface areas (SASA). To find the values of SASA for a given configuration, we perform an analytical computation of the surface areas A_i for each specified particle¹⁷¹. Having A_i , one can

define Γ_i as $\Gamma_i = \Gamma_0 A_i/A_{max}$, where A_{max} is the maximum solvent-accessible surface area of a particle for the model under study and the reference value of Γ_0 is taken to be equal to unity. The weighting factor A_i/A_{max} represents the degree of exposure of the particle i to the solvent. When the value of SASA for a given particle is zero, the frictional and random forces are zero and the Langevin equation (10) reduces to Newton's equation of motion. For the chain in a globular conformation, this typically happens when the monomer unit is located in the core of a globule. On the contrary, a monomer unit located at the globular surface is strongly solvated; it means that A_i should be close to A_{max} and, as a result, the value of Γ_i is close to its reference value Γ_0 .

The equations of motion (10) in conjunction with Eqs. (11) are solved iteratively using a Newtonian iteration procedure with the time step $\Delta t = 0.01 \sigma \sqrt{m/\varepsilon}$. For this calculation we use the RATTLE algorithm¹⁷⁰. The reference temperature is fixed at $T = 1 \text{ } \varepsilon/k_B$, and $\varepsilon_{\alpha\beta}$ ($= \varepsilon_{HH}, \varepsilon_{PP}, \varepsilon_{HP}$) are considered as only variable parameters.

Summary

At the end of the 20th century, scientific and industrial polymer community started to discuss "smart" or "intellectual" polymer systems (e.g., soft manipulators, polymer systems for controlled drug delivery, field-responsive polymers). This line of research concentrating on polymer systems with more and more complex functions will certainly be in the mainstream of polymer science in the 21st century.

The aim of this thesis is to find the specific properties of certain copolymer systems at an interface, which can provide the special functions of such systems at the nano-scale.

Copolymers have been studied extensively for several decades, partly because of their biological and industrial importance, and partly because of their interesting and sometimes perplexing properties.

The comb copolymers with a high grafting density of side chains ("molecular brushes") display many specific properties, including the formation of highly ordered microstructures. This ordering arises as a result of microphase separation both in solution and in bulk, liquid-crystalline ordering in a dilute good solvent, etc.

The linear copolymers can have different sequences of monomeric units (from alternating to statistical). Although recent years have witnessed an impressive confluence of experiments, simulations, and analytic theories, nowadays there is no comprehensive understanding what role copolymer primary sequences play for the structural and functional properties of copolymer systems.

In this thesis different copolymer systems at an interface have been studied using computer simulation approach. The following problems are discussed: i) conformational behaviour of comblike copolymers with high grafting density of side chains (molecular bottle-brushes) at an interface; ii) primary structure of linear copolymers, synthesized at an interface by different methods; iii) possibility of directed molecular motion of macromolecules at the surfaces by periodic influence of the external field.

The literature review is performed in the first chapter of the thesis. It includes relevant information about comblike copolymers, short description of conformational-dependent sequence design method, etc.

The chapters 2-4 include original results.

In the second chapter of this thesis computer simulation has been performed, using the bond-fluctuation model and cellular-automaton (CA)-based simulation technique to probe the equilibrium structure and dynamical behavior of comb-branched poly-

mers. They have flexible side chains of a given length, which are placed regularly along the backbone. The number of branches increases linearly with total molecular weight. By applying very efficient CA algorithm – the "lattice molecular dynamics" method (LMD) – the properties of sufficiently large structures have been studied both in a bulk and at an interface. Conformational behaviour has been investigated both for the single 2d- and 3d-macromolecules and for the system of 3d-molecular brushes at an interface. The following main conclusions can be drawn from the results presented in this chapter: (i) The critical exponent, governing the mean size of the main chain, remains unchanged compared with its value known for a 3d self-avoiding walk (SAW). (ii) Comparison of the simulated data with the scaling model predictions indicates that the latter is valid in describing the mean dimensions of the backbone as a function of side-chain length and interbranch spacing. (iii) The excluded volume interactions between side chains dramatically slow down the relaxation of the backbone chain. (iv) The strongly adsorbed branched macromolecules with asymmetric distribution of the side chains relatively to the backbone are effectively in a collapsed state even under conditions of a good solvent. These macromolecules form peculiar helical superstructures, which can also be observed by scanning force microscopy for cylindrical brushes of polymethylmethacrylate on mica. (v) A monolayer molecular "brushes" placed in a Langmuir trough has been considered. It has been found that upon the monolayer lateral contraction, side chains first decrease to a size typical to single chains of the same length in a solution. Then they begin to desorb from the surface. With a further increase in the surface concentration of macromolecules, the side chains stretch into the subphase and form an oriented monolayer ("Langmuir fencing"). As the side-chain length increases, desorption becomes stronger. However, the complete desorption of side chains is never reached for steric reasons. The results of computer simulation are consistent with the available experimental data.

In the third chapter the computer-aided sequence design of two-letter (AB) quasirandom copolymers with quenched primary structure near an infinite planar surface has been performed using Monte Carlo simulations and the lattice bond-fluctuation model. To generate the conformation-dependent primary structures, two different approaches have been employed. One of them is a variant of the "coloring" procedure (i.e., the conformation-dependent chemical modification of monomer units), which has been introduced earlier by A.R.Khokhlov and P.G.Khalatur for a solution of polymer globules. This approach is the preparation of AB copolymers by adsorbing a homopolymer chain on a flat substrate: its adsorbed segments are transformed into type A ones, and its unadsorbed segments into type B ones. It has been shown that the statistical properties of the copolymer sequences obtained via the "coloring" procedure exhibit long-range correlations of the Levy-flight type similar to those known for proteinlike copolymers. The second approach is the computer-aided sequence design of a two-letter (AB) copolymer with quenched primary structure near a chemically homogeneous impenetrable surface. An irreversible radical copolymerization process of selectively adsorbed A and B monomers has been simulated. These monomers have different affinity to a surface allowing for a strong short-range monomer (A)-surface attraction. It has been shown that under certain conditions, the chain propagation near the adsorbing surface proceeds as a randomly alternating growth, leading to a copolymer with a specific quasi-gradient primary structure and power-law long-range correlations in distribution of different monomer units along the chain. The

gradient extends along the entire chain for any chain length. Thus, just by radical copolymerization of two monomers with different affinity to a certain plane surface it is possible to obtain copolymers with a gradient primary structure. It has been found that our simulation data provide a close approximation to a simple theoretical model proposed by A.Kriksin for analytical description of chain growth.

In the fourth chapter, both molecular dynamics and Monte-Carlo simulation of a simple model of molecular motor has been performed. The model realizes long-range directional motion (reptation) of a single block AB copolymer chain, which is strongly adsorbed on a molecularly structured stripe-patterned surface. The conclusion is that the following conditions are necessary and sufficient for this two-state model to behave as a molecular motor: (i) asymmetric structure of the object achieved by asymmetric interactions with the surface and resulting in "anisotropic molecular friction"; (ii) particular patterning of the surface to specify the direction of motion; (iii) external periodic field applied to the system.

In this thesis the computer simulation method has been applied to probe the different copolymer systems at an interface. Some unusual and specific features have been found for different macromolecular systems. The main of them are follow:

- Collapse of 2d-molecular brushes in a good solvent and formation of twisted conformation;
- Formation of an oriented monolayer under lateral contraction of the molecular brushes at an interface;
- Long-range correlations in distribution of units for the AB-copolymer chain, which is obtained at an interface;
- Possibility to obtain the gradient structure by copolymerization of monomers at an interface;
- Directional motion of adsorbed blockcopolymer chain along the adsorbing "stripe".

ZUSAMMENFASSUNG

Ende des 20. Jahrhunderts haben wissenschaftliche und industrielle Polymergemeinschaften angefangen über „kluge“ oder „intellektuelle“ Polymersysteme zu diskutieren (z.B. weiche Manipulatoren, Polymersysteme für Transport von Medikamenten, feldsensitive Polymere). Diese Forschungsrichtung, die sich auf Polymersysteme mit immer komplexeren Funktionen konzentriert, wird sicherlich zur Hauptforschungsrichtung der Polymerforschung im 21. Jahrhundert werden.

Das Ziel der vorliegenden Arbeit ist es, die spezifischen Eigenschaften bestimmter Polymersysteme an einer Grenzfläche zu finden, die spezielle Funktionen solcher Systeme auf Nanoskalen liefern.

Copolymere wurden jahrzehntelang ausführlich untersucht, einerseits wegen ihrer biologischen und industriellen Bedeutung, andererseits wegen ihrer interessanten und überraschenden Eigenschaften.

Die Kamm-Polymere mit einer hohen Dichte an Seitenketten („molekulare Bürsten“) zeigen viele spezifische Eigenschaften, einschließlich der Bildung von hoch geordneten Mikrostrukturen. Diese Anordnung ergibt sich aus der Mikrophasenseparation sowohl in der Lösung als auch im Volumen, aus der flüssig-kristallinen Anordnung in verdünntem Lösungsmittel, usw.

Lineare Copolymere können verschiedene Anordnung der Monomereinheiten aufweisen (von alternierend bis statistisch). In den vergangenen Jahren wurden viele Experimente und Simulationen durchgeführt sowie analytische Theorien aufgestellt; trotzdem ist noch nicht vollständig verstanden, welche Rolle die Primärsequenzen von Copolymeren bei den strukturellen und funktionellen Eigenschaften von Copolymersysteme, übernehmen.

In der vorliegenden Arbeit wurden verschiedene Copolymersysteme an einer Grenzfläche mit Hilfe von Computer Simulationen untersucht. Folgende Probleme werden erörtert: i) Konformationsverhalten von kammähnlichen Copolymeren mit hoher Dichte der Seitenketten („molecular bottle-brushes“) an einer Grenzfläche; ii) Primärstrukturen linearer Copolymere, die mit Hilfe verschiedener Methoden an einer Grenzfläche synthetisiert; iii) die Möglichkeit einer gesteuerten Molekularbewegung an der Oberfläche durch periodische Einwirkung eines externen Feldes.

Das erste Kapitel der Arbeit beinhaltet das Literaturverzeichnis. Es enthält relevante Informationen über kammähnliche Copolymere, eine kurze Beschreibung der konformationsabhängigen „sequence design“ Methode, usw.

Die Kapitel 2-4 enthalten eigene Ergebnisse.

Im zweiten Kapitel wurden Computer Simulationen durchgeführt unter Verwendung des „bond-fluctuation“ Modells und der „cellular-automaton“ (CA) Simulationstechnik, um die Gleichgewichtsstruktur und das dynamische Verhalten der Kamm- Polymere zu untersuchen. Sie weisen flexible Seitenketten einer bestimmten Länge auf, die regelmäßig entlang der Hauptkette angeordnet sind. Die Anzahl der Verzweigungen nimmt linear mit der gesamten Molekülmasse zu. Durch die Anwendung der CA-Algorithmen - der „lattice molecular dynamics“ Methode (LMD) - wurden die Eigenschaften von ziemlich großen Strukturen sowohl im Volumen als auch an der Grenzfläche untersucht. Das Konformationsverhalten sowohl von einzelnen 2d- und 3d-Makromolekülen als auch von Systemen von 3d Molekularbürsten an der Grenzfläche, wurde untersucht. Folgende Schlußfolgerungen ergeben sich aus den in diesem Kapitel aufgeführten Ergebnissen: i) der kritische Exponent, der die mittlere Größe der Hauptkette bestimmt, bleibt unverändert verglichen mit dem bekannten Wert für einen „3d self-avoiding walk“ (SAW). (ii) Der Vergleich zwischen den simulierten Daten und den Vorhersagen des Skalenmodell zeigt, dass Letzteres zur Beschreibung der gemittelten Dimensionen der Hauptkette als Funktion der Seitenkettenlänge und des Verzweigungsabstandes gültig ist. (iii) Die ausgeschlossene Volumwechselwirkung zwischen den Seitenketten verringert drastisch die Relaxation der Hauptkette. (iv) Die stark adsorbierten verzweigten Makromoleküle mit asymmetrischer Verteilung der Seitenketten relativ in der Hauptkette, sind effektiv in einem kollabierten Zustand selbst in einem guten Lösungsmittel. Diese Makromoleküle bilden spezielle helikale Superstrukturen, die durch Rasterkraftmikroskopie für zylindrische Bürsten der Polymethylmethacrylate auf Glimmer beobachtet werden können. (v) Es wurde ein monomolekularer Film von „Bürsten“ in einer Langmuir Trog untersucht. Dabei konnte beobachtet werden, dass nach der lateralen Kontraktion des monomolekularen Films die Seitenketten zuerst auf die typische Größe der Einzelketten in einer Lösung schrumpfen. Dann beginnen sie von der Oberfläche zu desorbieren. Nach einer weiteren Vergrößerung der Oberflächenkonzentration der Makromoleküle, strecken sich die Seitenketten in die Subphase hinein und bilden eine orientierte Monoschicht („Langmuir fencing“). Wenn die Länge der Seitenkette vergrößert wird, verstärkt sich die Desorption. Aus sterischen Gründen wird jedoch eine komplette Desorption der Seitenketten nie erreicht. Die Ergebnisse der Computer Simulation sind mit den verfügbaren experimentellen Daten konsistent.

Das dritte Kapitel behandelt das „computer aided sequence design“ quasizufälligen AB Block-Copolymeren mit eingefrorener Primärstruktur an einer unendlichen planaren Oberfläche mit Hilfe von Monte Carlo-Simulationen und des Gitterbindungsfluktuationsmodells. Um die konformationsabhängige Primärstruktur zu erzeugen, wurden zwei verschiedene Zugänge verwendet. Einer davon ist eine Variante der „coloring“ Prozedur (d.h. die konformationsabhängige chemische Veränderung von Monomereinheiten), die früher von A. R. Khokhlov und P. G. Khalatur für eine Lösung von Polymerglobule, eingeführt wurde. Bei dieser Methode werden die AB Copolymere durch Adsorption einer Homopolymerkette an einer ebenen Oberfläche präpariert: die adsorbierten Segmente werden in Typ A und die nicht adsorbierten in Typ B umgewandelt. Es wurde gezeigt, dass die statistischen Eigenschaften der Copolymersequenzen, die durch die „coloring“ Prozedur erhalten werden, eine langreichweitige Korrelation vom Levy-flight-Typ aufweisen, ähnlich wie proteinähnliche Copolymere. Die zweite Methode ist das Computer-unterstützte

Ketten design eines (AB) Block-Copolymers mit eingefrorener Primärstruktur an einer chemisch homogenen, undurchlässigen Oberfläche. Es wurde ein irreversibler Radikal-Copolymerisationsprozess von selektiv adsorbierten A und B Monomeren simuliert. Diese Monomere weisen unterschiedliche Affinitäten zur Oberfläche auf und ermöglichen eine starke kurzreichweitige Oberflächenanziehung von (A) – Monomeren. Unter bestimmten Bedingungen, verhält sich das Wachstum der Kette in der Nähe der adsorbierenden Oberfläche als ein zufällig alternierender Prozeß, der zur Bildung eines Copolymers mit einer spezifischen quasi-Gradienten Primärstruktur führt und einem Potenzgesetz für langreichweitige Korrelationen in der Verteilung verschiedener Monomere entlang der Kette. Der Gradient erstreckt sich entlang der ganzen Kette für alle Kettenlängen. Somit ist es möglich, durch Radikal-Copolymerisation von 2 Monomeren mit unterschiedlicher Affinität zu bestimmten ebenen Oberflächen, Copolymere mit Gradienten- Primärstruktur zu erhalten. Es stellte sich heraus, dass unsere Simulationsergebnisse eine sehr gute Näherung an ein einfaches theoretisches Modell (analytische Beschreibung des Kettenwachstums nach Kriksin), ergaben.

Das vierte Kapitel befasst sich mit Molekulardynamik und Monte Carlo Simulationen eines simplen Modells für einen molekularen Motor. Das Modell führt eine langreichwertig gerichtete Bewegung (Reptation) einer einzigen AB-Block-Copolymerkette durch, die stark auf einer molekular strukturierten Streifenoberfläche adsorbiert wird. Schlußfolgernd kann man sagen, dass folgende Bedingungen notwendig und hinreichend sind, damit sich dieses Zweizustandsmodell wie ein molekularer Motor verhält: (i) unsymmetrische Struktur des Objekts, erzielt durch unsymmetrische Wechselwirkung mit der Oberfläche, die zu anisotroper molekularer Reibung führt; (ii) Spezielle Musterung der Oberfläche, um die Bewegungsrichtung festzulegen; (iii) Einwirkung eines externen periodischen Feldes auf das System.

In dieser Arbeit wurde die Computer Simulations-Methode angewandt um verschiedene Copolymersysteme an Grenzflächen zu untersuchen. Einige ungewöhnliche und spezifische Eigenschaften von verschiedenen makromolekularen Systemen wurden gefunden. Die wichtigsten sind folgende:

- Kollaps von 2d-molekularen Bürsten in einem guten Lösungsmittel und Bildung spiraliser Konformation;
- Bildung einer orientierten Monolage unter lateraler Kontraktion der molekularen Bürsten an einer Grenzfläche;
- Langreichwertige Korrelationen in der Verteilung der Einheiten von AB-Block-Copolymeren an einer Grenzfläche;
- Die Möglichkeit, durch Copolymerisation von Monomeren an Grenzflächen eine Gradientenstruktur zu erhalten;
- Gerichtete Bewegung einer adsorbierten Block-Polymerkette entlang eines adsorbierenden Streifens.

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List of selected publications

1. Khalatur P. G., Khokhlov A. R., Prokhorova S. A., Sheiko S.S., Moller M., Reineker P., Shirvanyanz D. G., Starovoitova N.Yu. Unusual conformation of molecular cylindrical brushes strongly adsorbed on a flat solid surface // *Eur. Phys. J. E* 2000. V.1. PP. 99-103.
2. Khalatur P. G., Shirvanyanz D. G., Starovoitova N.Yu., Khokhlov A. R. Conformational properties and dynamics of molecular bottle-brushes: A cellular-automation-based simulation // *Macromol. Theory and Simul.* 2000. V.9. PP. 141-155.
3. Starovoitova N.Yu., Shirvanyanz D. G., Khalatur P. G., Computer Simulation of Comblike Copolymers at an Interface // *Polymer Science*. 2002. Ser. A. V. 44. No 11. PP. 1175-1184.
4. N. Yu. Starovoitova, P. G. Khalatur, A. R. Khokhlov, "Copolymerization near an Adsorbing Surface: Computer Simulation" // *Doklady Chemistry*. 2003. V. 392. No 4-6 PP. 242-245.
5. N. Yu. Starovoitova, P.G. Khalatur, A.R. Khokhlov, "Copolymers with Long-Range Correlations: Sequence Design near a Surface" // in *Forces, Growth and Form in Soft Condensed Matter: At the Interface between Physics and Biology*, NATO Science Series: II: Mathematics, Physics and Chemistry, Kluwer Academic Publishers, Dordrecht, July 2004, Vol. 160, 253 pp..
6. R. Khokhlov, A. V. Berezkin, N. Yu. Starovoitova, P. G. Khalatur, "Computer-aided sequence design of copolymers with long-range correlations near a solid surface" // in press
7. N.Yu. Starovoitova, A.V. Berezkin, Yu. A. Kriksin, O.V. Gallyamova, P.G. Khalatur, A.R. Khokhlov, "Modeling of radical copolymerization near a selectively adsorbing surface: Design of gradient copolymers with long-range correlations" // *Macromolecules*, in press

List of International Seminars, Schools and Conferences

1. N.Yu. Starovoitova, Behaviour of Molecular Bottle-Brushes at an interface: Computer Simulation Model of Langmuir Experiment. *5 Österreichische Polymertage* (Leoben, Austria, September 12 – 14, 2001).
2. N.Yu. Starovoitova, Computer simulation of comblike copolymers, adsorbed at an interface. *IX International scientific conference of students, PhD students and young scientists "Lomonosov-2002"* (Moscow, Russia, April 9-12, 2002).
3. N.Yu. Starovoitova, Bottle-Brushes at an interface: Computer Simulation Model of Langmuir Experiment. *4th international symposium "Molecular order and mobility in polymer systems"* (Saint-Petersburg, Russia, June 3-7, 2002).
4. N.Yu. Starovoitova, P. G. Khalatur, Molecular Bottle-Brushes Adsorbed at an Interface: Computer Simulation Model of Langmuir Experiment. *NATO-ASI school "Computer simulations of surfaces and interfaces"* (Varna, Bulgaria, September 9-20, 2002).
5. N.Yu. Starovoitova, P.G. Khalatur, I.I. Potemkin, A.R. Khokhlov, Molecular Motor Based on Two-State Model of Block Copolymer: computer simulation. *40th International symposium on Macromolecules "MACRO 2004"* (Paris, France, July 4-9, 2004).

References

- ¹ Kikuchi A., Nose T., Unimolecular-micelle formation of poly(methyl methacrylate)-graft-polystyrene in iso-amyl acetate//Polymer. -1996. -V. 37. -№. 26. -P. 5889-5896.
- ² Kikuchi A., Nose T., Unimolecular-micelle formation of poly(methyl methacrylate)-graft-polystyrene in Mixed Selective Solvents of Acetonitrile/Acetoacetic Acid Ethyl Ether// Macromolecules. -1996. -V. 29. -№. 21. -P. 6770-6777.
- ³ Kikuchi A., Nose T., Multimolecular-Micelle Formation of Poly(methyl methacrylate)-graft-polystyrene in Acetonitrile/Acetoacetic Acid Ethyl Ether// Macromolecules. -1997. -V. 30. -№. 4. -P. 896-902.
- ⁴ Amphiphilic Cylindrical Core-Shell Brushes via a "Grafting From" Process Using ATRP/ Cheng G., Boker A., Zhang M., Krausch G., Muller A.H.E.// Macromolecules. -2001. -V. 34. -№. 20. -P. 6883-6888.
- ⁵ Macromolecular Anisotropic Association in Isotropic Solutions of a Liquid Crystal Side Chain Polymer/ Vietler K., Wewerka A., Stelzer F., Fytas G., Vlassopoulos D.// Macromol. Chem. Phys. -2001. -V. 202. -№. 16. -P. 3174-3179.
- ⁶ The Synthesis of Liquid Crystalline Copolymers with Block Copolymer Grafts/ Hepuzer Y., Serhatli I.E., Yagci Y., Galli G., Chiellini E. // Macromol. Chem. Phys. -2001. -V. 202. -№.11. -P. 2247-2252.
- ⁷ Synthesis of Molecular Brushes with Block Copolymer Side Chains Using Atom Transfer Radical Polymerization / Borner H. G., Beers K., Matyjaszewski K., Sheiko S.S., Moller M., // Macromolecules. -2001. -V. 34. -№. 13. -P. 4375-4383.
- ⁸ Holland N. B., Vacheethasanee Z. Xu, K., Marchant R.E., Structure of Poly(ethylene oxide) Surfactant Polymers at Air-Water and Solid-Water Interfaces// Macromolecules. -2001. -V. 34. -P. 6424-6430.
- ⁹ Miller A.F., Richards R.W., Webster J.R.P. Organization of Well-Defined Amphiphilic Graft Copolymers at the Air-Water Interface // Macromolecules. -2000. -V. 33. -№. 20. -P. 7618-7628.
- ¹⁰ Miller A.F., Richards R. W., Webster J.R.P., Transition in Tethered Layer Thickness Induced by Concentration Changes in a Spread Film of an Amphiphilic Graft Copolymer// Macromolecules. -2001. -V. 34. -№. 23. -P. 8361-8369.
- ¹¹ Davis K.A., Matyjaszewski K., Statistical, gradient, block and graft copolymers by controlled/living radical polymerizations. -Berlin; New York: Springer, 2002, -169 p.
- ¹² Wintermantel, M.; Gerle, M.; Fischer, K.; Schmidt, M.; Wataoka, I.; Urakawa, H.; Kajiwarra, K.; Tsukahara, Y. Molecular BottlebrushesMacromolecules; (Article); 1996; 29(3); 978-983. Molecular Bottle-Brushes/ Wintermantel M., Gerle M., Fischer K., Schmidt M., Wataoka I., Urakawa H., Kajiwarra K., Tsukahara Y. //Macromolecules. -1996. -V.29. -№. 3. -P. 978-983.
- ¹³ Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization //Macromolecules. -1998. -V.31. -№. 26. P.9413-9415.
- ¹⁴ Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. Synthesis of Molecular Brushes with Block Copolymer Side Chains Using Atom Transfer Radical Polymerization //Macromolecules. -2001. -V.34.-№.13. -P.4375-4383.
- ¹⁵ Antonietti M., Conrad J., Thynemann A., Polyelectrolyte-Surfactant Complexes: A New Type of Solid, Mesomorphous Material//Macromolecules -1994. -V.27. -№. 21 -P. 6007- 6011.
- ¹⁶ Markus Antonietti, Stephan Foerster, Mathias Zisenis, Juergen Conrad Solution Viscosity of Polyelectrolyte-Surfactant Complexes: Polyelectrolyte Behavior in Nonaqueous Solvents //Macromolecules. -1995. -V.28. -№. 7. -P.2270-2275.
- ¹⁷ Critical Interaction Strength for Surfactant-Induced Mesomorphic Structures in Polymer-Surfactant Systems/ Ruokolainen J., Trokkeli M., Serimaa R, Vahvaselkä S., Saariaho M., Brinke G. ten //Macromolecules. -1996. -V.29. -№. 20 -P. 6621-6628.
- ¹⁸ Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Komanshek, E.; ten Brinke, G.; Ikkala, O.; Order-Disorder Transition in Comblike Block Copolymers Obtained by Hydrogen Bonding between Homopolymers and End-Functionalized Oligomers: Poly(4-vinylpyridine)-Pentadecylphenol //Macromolecules. -1997. -V.30. -№. 7. -P.2002-2007.

- ¹⁹ Ruokolainen, J.; Tanner, J.; Ikkala, O.; ten Brinke, G.; Thomas, E. L.; Direct Imaging of Self-Organized Comb Copolymer-like Systems Obtained by Hydrogen Bonding: Poly(4-vinylpyridine)-4-Nonadecylphenol //Macromolecules. -1998. -V.31. -№ 11. -P.3532-3536.
- ²⁰ Luyten, M. C.; Alberda van Ekenstein, G. O. R.; ten Brinke, G.; Ruokolainen, J.; Ikkala, O.; Torkkeli, M.; Serimaa, R.; Crystallization and Cocrystallization in Supramolecular Comb Copolymer-like Systems: Blends of Poly(4-vinylpyridine) and Pentadecylphenol //Macromolecules. -1999. -V.32. -№13. P.4404-4410.
- ²¹ Tanaka F.Phase formation of associating polymers: gelation, phase separation and microphase formation//Adv. Colloid & Interface Science -1996. -№.63. -P.23-40.
- ²² Valkama, S.; Ruotsalainen, T.; Kosonen, H.; Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; ten Brinke, G.; Ikkala, O.; Amphiphiles Coordinated to Block Copolymers as a Template for Mesoporous Materials //Macromolecules. -2003. -V.36. -№ 11. -P.3986-3991.
- ²³ Molecular Bottle-Brushes/ Wintermantel M., Gerle M., Fischer K., Schmidt M., Wataoka I., Urakawa H., Kajiwarra K., Tsukahara Y. //Macromolecules. -1996. -V.29. -№ 3. -P. 978-983.
- ²⁴ The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization / Beers K.L., Gaynor S.G, Matyjaszewski K., Sheiko S.S., Möller M. //Macromolecules. -1998. -V.31. -№ 26. -P. 9413-9415.
- ²⁵ Synthesis of Molecular Brushes with Block Copolymer Side Chains Using Atom Transfer Radical Polymerization / Borner H. G., Beers K., Matyjaszewski K., Sheiko S.S., Moller M., // Macromolecules. -2001. -V. 34. -№. 13. -P. 4375-4383.
- ²⁶ Lyotropic phases formed by molecular bottlebrushes/ Wintermantel M., Fisher K., Gerle M., Ries R., Schmidt M., Kajiwarra K., Urakawa H., Wataoka I. // Angew. Chem. -1995. -V. 107. -№ 15. -P. 1606-1611.
- ²⁷ Molecular imaging of monodendron jacketed linear polymers by scanning force microscopy / Prokhorova S.A., Sheiko S.S., Möller M., Ahn C.-H., Percec V. //Macromol. Rapid Comm. -1998. -V.19. -№ .7. -P.359-366.
- ²⁸ Amphiphilic Cylindrical Core-Shell Brushes via a "Grafting From" Process Using ATRP/ Cheng G., Boker A., Zhang M., Krausch G., Muller A.H.E.// Macromolecules. -2001. -V. 34. -№. 20. -P. 6883-6888.
- ²⁹ Djalali R., Li S.-Y., Schmidt M., Amphipolar Core-Shell Cylindrical Brushes as Templates for the Formation of Gold Clusters and Nanowires//Macromolecules. -2002. -V. 35. -№ 11. -P. 4282-4288.
- ³⁰ O.B. Ptitsyn, //J. Chem. Phys. USSR. -1955. -V.29. -P.396.
- ³¹ A.K. Kron, O.B. Ptitsyn, //Vysokomolek. Soedin. -1963. -V.5. -P.397.
- ³² Berry G.C., Orofino T.A. Branched polymers. III. Dimensions of chainswith small excluded volume//J. Chem. Phys. -1964. -V.40. -№ . C.1614- 1621.
- ³³ Conformational properties of macromolecules with side chains/Tsvetkov V.H., Hardy D., Shtennicova I.N., Korneeva E.V., Pyrogova G.F., Nitrai K.// Vysokomolek. Soedin. -1969. -V.11. -№ 2. -P.349-358.
- ³⁴ Decker D. Etude en solution diluée de polymères à structure en "peigne" //Macromol. Chem. -1969. -V.125. -№ .1 -P.136-160.
- ³⁵ Candau F., Rempp P. //Eur. Polym. J. -1972. -V.8. -P. 757.
- ³⁶ Candau F., Rempp P., Benoit H., A New Theoretical Approach to the Problem of Solution Behavior of Branched Polymers // Macromolecules. -1972. -V.5. -№ .5 -P. 627-635.
- ³⁷ Magarik S.Ya., Pavlov G.M., Fomin G.A., Hydrodynamic and Optical Properties of Homologous Series of Styrene-Methyl Methacrylate Graft Copolymers //Macromolecules. -1978 -V.11. -№2. P.294-300.
- ³⁸ Khokhlov A.R., //Polymer. -1987. -V.19. -P.1387.
- ³⁹ Dependence of flexibility of main chain on the structure of crystalpolymers and copolymers with long side branches / Shibaev V.P., Petrukhin B.S., Plate N.A., Kargin V.A.// Vysokomolek. Soedin. -1970. -T. 12. -№ 1. -C. 140-148.
- ⁴⁰ V.N. Tsvetkov., Rumtsev E.I., Shtennikova I.N., Crystal-like polymer chains// Vysokomolek. Soedin. -1971. -T. 13. -№ 2. -C. 506-518.
- ⁴¹ V.N. Tsvetkov, G.A. Andreeva, I.A. Baranovskaya, V.E. Eskin, S.I. Klein, S.Ya. Magaric, J. //Polym. Sci., Part C. -1967. -V.16. -P.239.
- ⁴² Birshtein, O.V. Borisov, Ye.B. Zhulina, A.R. Khokhlov, T.A. Yurasova, Conformations of comblike macromolecules// Polym. Sci. USSR, -1987 -V. 29. -№ 6. -P. 1169-1178.
- ⁴³ Fredrickson G.H., //Macromolecules. -1993. -V.26. -P.2825-. Surfactant-induced lyotropic behavior of flexible polymer solutions Glenn H. Fredrickson //Macromolecules. -1993. V.26. -№11. -P.2825-2831.
- ⁴⁴ Rouault Y., Borisov O.V., Comb-Branched Polymers: Monte Carlo Simulation and Scaling //Macromolecules, -1996. -V.29. -№7. -P.2605-2611.

- ⁴⁵ Gallacher L.V., Windwer S. Monte Carlo Study of Flexible Branched Macromolecules//J. Chem. Phys. –1996. -V.44. No3, PP.1139-1148.
- ⁴⁶ McCrackin F.L., Mazur J., Configuration properties of comb-branched polymers //Macromolecules. – 1981. -V.14. -№5. -P.1214-1220.
- ⁴⁷ Lipson J.E.G., A Monte Carlo simulation study on long-chain combs //Macromolecules. -1991. -V.24. - №6. -P.1327-1333.
- ⁴⁸ On lyotropic behavior of molecular bottle-brushes: A Monte Carlo computer simulation study / Saariaho M., Ikkala O., Szleifer I., Erukhimovich I., Brinke G. J. ten //J. Chem. Phys. –1997. –V.107. -№8. –P.3267 -3276.
- ⁴⁹ M. Saariaho, I. Szleifer, O. Ikkala, G. ten Brinke Extended conformations of isolated molecular bottle-brushes: Influence of side-chain topology //Macromol. Theory Simul. 1998–V.7. -№2. -P.211-216.
- ⁵⁰ Rouault Y., From comb polymers to polysoaps: a Monte Carlo attempt // Macromol. Theory Simul. – 1998. –V.7. -№3. -P.359-365.
- ⁵¹ Potemkin I.I., Khokhlov A.R., Reineker P. Stiffness and conformations of molecular bottle-brushes strongly adsorbed on a flat surface//Eur. Phys. J. E. –2001. –V.4. -P.93-101.
- ⁵² Saariaho M., Ikkala O., Brinke G. ten, Molecular bottle brushes in thin films: An off-lattice Monte Carlo study// J. Chem. Phys. -V.110. -№ 2. -P.1180-1187.
- ⁵³ Khalatur P. G., Khokhlov A. R., Prokhorova S. A., Sheiko S.S., Mouller M., Reineker P., Shirvanyanz D. G., Starovoitova N.Yu. Unusual conformational of molecular cylindrical brushes strongly adsorbed on a flat solid surface// Eur. Phys. J. E. -2000. -V.1. -№1. -P. 99-103.
- ⁵⁴ Single Molecule Rod-Globule Phase Transition for Molecules at a Flat Interface / Sheiko S.S., Prokhorova S.A., Beers K.L., Matyjaszewski K., Potemkin I.I., Khokhlov A.R., Möller M. // Macromolecules. - 2001. -V.34. -№23. -P.8354-8360.
- ⁵⁵ Saariaho M., Ikkala O., Brinke G. ten, Molecular bottle brushes in thin films: An off-lattice Monte Carlo study// J. Chem. Phys. -V.110. -№ 2. -P.1180-1187.
- ⁵⁶ Vliet J. H. van, Luyten M.C., Brinke G. ten, Scaling behavior of dilute polymer solutions confined between parallel plates// Macromolecules. -1992. -V.25. -№14. -P.3802- 3806.
- ⁵⁷ Wittmer J., Johner A., Joanny J.F., Binder K., Chain desorption from semidilute polymer brush: A Monte-Carlo simulation//J. Chem. Phys., v. 101, №5, pp. 4379-4390.
- ⁵⁸ Alexander S. Polymer Adsorption on small spheres. A scaling approach// J. Phys. (Paris). -1977. -V. 38. -P. 977-983.
- ⁵⁹ de Gennes P.G., Scaling Concepts in Polymer Physics. -Cornell: Ithaca, NY, 1985. –385p.
- ⁶⁰ Birshtein T.M., Zhulina E. B. Conformations of polymer chains grafted to flat solid surface//Visokomolec. Soed, USSR. A. -1983. -V. 25. -№ 9. -P. 1862-1869.
- ⁶¹ Semenov A.N.//Sov. Phys. JETP. -1985. -V.61. -P. 733.
- ⁶² Structure of densely grafted macromolecules / Skvortsov A.M., Pavlushkov O.V., Gorbunov A. A., Zhulina E.B., Borisov O.V., Pryamitsyn V.A. // Visokomolec. Soed, USSR. -1988. -T. 30.-№ 8. -C. 1615.
- ⁶³ Milner S.T., Witten T.A., Cates M.E., Theory of the grafted polymer brush // Macromolecules. 1988. V. 21. N. 8. P. 2610 - 2619.
- ⁶⁴ Milner S.T., Witten T.A., Cates M.E., Effects of polydispersity in the end-grafted polymer brush //Macromolecules. -1989. -V. 22. -№. 2. -P. 853-861.
- ⁶⁵ Lai P. Y., Binder K. Structure and dynamics of polymer brushes near the θ point: A Monte Carlo simulation // J. Chem. Phys. 1992. V.97, №1. P. 586-595. P.Y.Lai, K. Binder, J.Chem.Phys., 1991,v. 95, p.9288.
- ⁶⁶ Determination of end-adsorbed polymer density profiles by neutron reflectometry / J. B. Field, C. Toprakcioglu, R. C. Ball, H. B. Stanley, L. Dai, W. Barford, J. Penfold, G. Smith, W. Hamilton // Macromolecules. -1992. -V. 25, -№1. -P. 434-439.
- ⁶⁷ O.V. Borisov, A. Halperin, Polysoaps within the p-Cluster Model: Solutions and Brushes// Macromolecules. -1999. V.32. -№15. P. 5097-5105.
- ⁶⁸ Holland N. B., Vacheethasane Z. Xu, K., Marchant R.E., Structure of Poly(ethylene oxide) Surfactant Polymers at Air-Water and Solid-Water Interfaces// Macromolecules. -2001. -V. 34. -P. 6424-6430.
- ⁶⁹ Miller A.F., Richards R.W., Webster J.R.P. Organization of Well-Defined Amphiphilic Graft Copolymers at the Air-Water Interface // Macromolecules. -2000. -V. 33. -№ 20. -P. 7618-7628.
- ⁷⁰ Miller A.F., Richards R. W., Webster J.R.P., Transition in Tethered Layer Thickness Induced by Concentration Changes in a Spread Film of an Amphiphilic Graft Copolymer// Macromolecules. -2001. -V. 34. -№. 23. -P. 8361-8369.
- ⁷¹ Polymers at Interfaces / Fleer G.J., Cohen Stuart M.A., Scheutjens J.M.H.M., Cosgrove T., Vincent B. - Kluwer Academic Publishers, 1993. – 520 p.

- ⁷² Eisenriegler E., *Polymers near Surfaces: Conformation Properties and Relation to Critical Phenomena*. - Singapore: World Scientific, 1993. -424p.
- ⁷³ Adsorption of linear and star-shaped poly(acrylic acid) to model surfaces formed by amphiphiles at the air/water interface / Schnitter M., Engelking J., Heise A., Miller R. D., Menzel H. // *Macromol. Chem. Phys.* -2000. -V. 201. -№ 13. -P. 1504-1512.
- ⁷⁴ Kim D. Ha, Ho Jo W., *Studies on Polymer-Metal Interfaces*// *Macromol. Chem. Phys.* -2001. -V.202. -№15. -P. 3065-3071.
- ⁷⁵ Omarjee, Espert A., Mondain-Monval O., *Polymer-Induced Repulsive Forces at Solid-Liquid and Liquid-Liquid Interfaces*//*Langmuir*. -2001. -V.17. -№ 18. -P. 5693-5695.
- ⁷⁶ Chi Wu* and Jun Gao, *A Simple Scaling of the Density Profile of Long Linear Polymer Chains Adsorbed on Hydrophobic Surface*// *Macromolecules*. -1999 -V.32. -P.1704-1705.
- ⁷⁷ Carri G. A., Muthukumar M., *Coupling Between Adsorption and the Helix-Coil Transition*// *Phys. Rev. Lett.* -V.82, -№ 26, -P. 5405-5408.
- ⁷⁸ McMullen W. E., Trache M., *Density functionals for polymers near surfaces*//*J. Chem.Phys.* -V.102. -№ 3. -P.1449-1460.
- ⁷⁹ Metzger S., Muller M., Binder K., Baschnagel J., *Adsorption Transition of a Polymer Chain at a Weakly Attractive Surface: Monte Carlo Simulation of Off-Lattice Models*// *Macromol. Theory Simul.* - 2002. -V.11. -№ 11. -P. 985-995.
- ⁸⁰ G. A. Carri, M. Muthukumar, *Coupling Between Adsorption and the Helix-Coil Transition*//*Phys. Rev. Lett.* -1999. -V.26. -P. 5404-5408
- ⁸¹ E. Yu. Kramarenko, R. G. Winkler, P. G. Khalatur, A. R. Khokhlov, P. Reineker, *Molecular dynamics simulation study of adsorption of polymer chains with variable degree of rigidity. I. Static properties*// *J. Chem. Phys.* -1996. -V.104. -№ 12. P. 4806-4813.
- ⁸² Lai P.-Y. *Static and dynamics of a polymer chain adsorbed on a surface: Monte Carlo simulation using bond-fluctuation model*//*Phys. Review E*. -1994. -V. 49. -№ 6. -P. 5420-5430.
- ⁸³ Lai P.-Y., *Statics and dynamics of adsorbed polymer chains: A Monte Carlo simulation* // *J. Chem. Phys.* -1995. -V. 103. -№ 13. -P 5742-5755.
- ⁸⁴ Jianwen Jiang, Honglai Liu, Ying Hu, *Lattice Monte Carlo simulation of polymer adsorption at an interface* // *Macromol. Theory Simul.* -1998. -V. 7. -P.105-111.
- ⁸⁵ Hisao Takeuchi, *Monte Carlo simulations of the exchange kinetics of polymers adsorbed on a solid surface* // *Macromol. Theory Simul.* -1999. -V.8. -№4. -P.391-401.
- ⁸⁶ E. Eisenriegler, K. Kremer, and K. Binder // *J. Chem. Phys.* -1982. -V.77. -P.6296.
- ⁸⁷ H. Meirovitch, S. Livne // *J. Chem. Phys.* -1988. -V.88. -P.4507.
- ⁸⁸ R. Hegger, P. Grassberger // *J. Phys. A: Math. Gen.* -1994. -V.27. -P.1994.
- ⁸⁹ Khokhlov, A.R.; Khalatur, P.G. // *Physica A* -1998. -V.249 -P.253.
- ⁹⁰ Khalatur, P.G.; Ivanov, V.I.; Shusharina, N.P.; Khokhlov, A.R. // *Russ. Chem. Bull.* -1998. -V.47. P.855.
- ⁹¹ Khokhlov, A.R.; Khalatur, P.G. // *Phys. Rew. Lett.* -1999. -V.82 -P.3456.
- ⁹² Zheligovskaya, E.A., Khalatur, P.G., and Khokhlov, A.R. *Properties of AB copolymers with a special adsorption-tuned primary structure* // *Phys. Rev. E*. -1999. -V.59. -P.3071-3078.
- ⁹³ Khalatur, P.G.; Novikov, V.V.; Khokhlov, A.R. // *Phys. Rev. E* -2003 -V.67. -P.051901.
- ⁹⁴ Shakhnovich, E. I.; Gutin, A. M. *Proc. Natl. Acad. Sci. USA* 1993, 90, 7195; Shakhnovich, E.I.; Gutin, A.M. *Protein Eng.* 1993, 6, 793; Abkevich, V. I.; Gutin, A. M.; Shakhnovich, E. I. *Proc. Natl. Acad. Sci. USA* 1996, 93, 839.
- ⁹⁵ Pande, V. S.; Grosberg, A. Yu.; Tanaka, T. *Proc. Natl. Acad. Sci. USA* 1994, 91, 12972; Pande, V. S.; Grosberg, A. Yu.; Tanaka, T. // *Rev. Modern Phys.* -2000. -V.72. -P.259.
- ⁹⁶ Irbäck, A.; Peterson, C.; Potthast, F.; Sandelin, E. *Phys. Rev. E* 1998, 58, R5249; Irbäck, A.; Peterson, C.; Potthast, F.; Sandelin, E. *Structure* 1999, 7, 347.
- ⁹⁷ Gupta, P.; Hall, C.K.; Voegler, A.C. *Protein Sci.* 1998, 7, 2642; Giugliarelli, G.; Micheletti, C.; Banavar, J. R.; Maritan, A. J. // *Chem. Phys.* -2000 -V.113. -P.5072.
- ⁹⁸ Khokhlov, A.R. and Khalatur, P.G. *Proteinlike copolymers: Computer simulation* // *Physica A*. -1998. -V.249. -№.253-261.
- ⁹⁹ Khalatur, P.G., Ivanov, V.I., Shusharina, N.P., and Khokhlov, A.R. "Proteinlike" copolymers: Computer simulations, *Russ. Chem. Bull.* -1998. -V.47. -P.855-860.
- ¹⁰⁰ Khokhlov, A.R., Ivanov, V.A., Shusharina, N.P., and Khalatur, P.G. *Engineering of synthetic copolymers: Proteinlike copolymers*, in: F. Yonezawa, K. Tsuji, K. Kaij, M. Doi, and T. Fujiwara, (eds.), *The Physics of Complex Liquids*, World Scientific, Singapore, 1998, p. 155.

- ¹⁰¹Khokhlov, A.R. and Khalatur, P.G. Conformation-dependent sequence design (engineering) of AB copolymers //Phys. Rev. Lett. -1999. -V.82. -P.3456-3460.
- ¹⁰²Lifshitz, I.M., Grosberg, A.Yu., and Khokhlov, A.R. Some problems of the statistical physics of polymer chains with volume interactions //Rev. Mod. Phys. -1978. -V.50. P.683-713.
- ¹⁰³Grosberg, A.Yu. and Khokhlov, A.R. Statistical Physics of Macromolecules, American Institute of Physics, New York. 1994.
- ¹⁰⁴Khalatur, P.G., Khokhlov, A.R., Mologin, D.A., and Reineker, P. Aggregation and counterion condensation in solution of charged proteinlike copolymers: A molecular dynamics study //J. Chem. Phys. -2003. -V.119. -P.1232-1247.
- ¹⁰⁵Zherenkova, L.V., Khalatur, P.G., and Khokhlov, A.R. Solution properties of charged quasi-random copolymers: Integral equation theory, J. Chem. Phys. -2003. -V.119. -P.6959-6972.
- ¹⁰⁶Ivanov, V.A., Chertovich, A.V., Lazutin, A.A., Shusharina, N.P., Khalatur, P.G., and Khokhlov, A.R. Computer simulation of globules with microstructure //Macromolecular Symposia -1999. -V.146. -P.259-265.
- ¹⁰⁷Govorun, E.N., Ivanov, V.A., Khokhlov, A.R., Khalatur, P.G., Borovinsky, A.L., and Grosberg, A.Yu. Primary sequences of proteinlike copolymers: Levy-flight-type long-range correlations. //Phys Rev E -2001. -V.64. 0409031(R)-4(R).
- ¹⁰⁸Shlesinger, M.F., Zaslavskii, G.M., and Frisch, U. Levy flights and related topics in physics. Lecture Notes in Physics, Springer-Verlag, Berlin, 1996.
- ¹⁰⁹Levy Flights and Related Topics in Physics, edited by M. F. Shlesinger, G. M. Zaslavskii, and U. Frisch, Lecture Notes in Physics, Springer-Verlag: Berlin, 1996.
- ¹¹⁰Virtanen, J., Baron, C., and Tenhu, H. Grafting of poly(N-isopropyl acrylamide) with poly(ethylene oxide) under various reaction conditions //Macromolecules -2000. -V.33. -P.336-431.
- ¹¹¹Virtanen, J., Lemmetyinen, H., and Tenhu, H. Fluorescence and EPR studies on the collapse of poly(N-isopropyl acrylamide)-g-poly(ethylene oxide) in water //Polymer -2001. -V.42. P.9487-9493.
- ¹¹²Lozinsky, V.I., Simenel, I.A., Kurskaya, E.A., Kulakova, V.K., Grinberg, V.Ya., Dubovik, A.S., Galaev, I.Yu., Mattiasson, B., and Khokhlov, A.R. Synthesis and properties of "proteinlike" copolymers //Dokl. Chem. -2000. -V.375. -P.273-276.
- ¹¹³Wahlund, P.-O.; Galaev, I. Y.; Kazakov, S. A.; Lozinsky, V. I.; Mattiasson, B. //Macromol. Biosci. -2002. -V.2. -P.33.
- ¹¹⁴Siu, M. H.; Zhang, G.; Wu, C. //Macromolecules. -2002. -V.35 -P.2723.
- ¹¹⁵Lozinsky, V.I.; Simenel, I.A.; Kulakova, V.K.; Kurskaya, E.A.; Babushkina, T.A.; Klimova, T.P.; Burova, T.V.; Dubovik, A.S.; Grinberg, V.Ya.; Galaev, I.Yu.; Mattiasson, B.; Khokhlov, A.R. //Macromolecules. -2003. -V.36. -P.7308.
- ¹¹⁶Wahlund, P.-O., Galaev, I.Yu., Kazakov, S.A., Lozinsky, V.I., and Mattiasson, B. "Proteinlike" copolymers: Effect of polymer architecture on performance in bioseparation process //Macromol. Biosci. -2002. -P.33-42.
- ¹¹⁷Berezkin, A.V., Khalatur, P.G., and Khokhlov, A.R. Computer modeling of synthesis of proteinlike copolymer via copolymerization with simultaneous globule formation //J. Chem. Phys. -2003. -V.118, -P.8049-8060.
- ¹¹⁸Berezkin, A.V.; Khalatur, P.G.; Khokhlov, A.R.; Reineker P. //New J. Phys. -2004 -V.6 -P.44.
- ¹¹⁹Harwood, H.J. //Macromol. Symp. -1987. -V.10/11. -P.331.
- ¹²⁰Starovoitova, N.Yu.; Khalatur, P.G.; Khokhlov, A.R. Dokl. Chem. 2003, 392, 242; Starovoitova, N.Yu.; Khalatur, P.G.; Khokhlov, A.R. in Forces, Growth and Form in Soft Condensed Matter: At the Interface between Physics and Biology, edited by A.T. Skjeltorp and A.V. Belushkin. NATO Science Series: II: Mathematics, Physics and Chemistry, Kluwer, Dordrecht, -2004. -V. 160. -253 pp.
- ¹²¹Velichko, Yu. S.; Khalatur, P. G.; Khokhlov A. R. //Macromolecules -2003. -V.36. -P.5047.
- ¹²²Carmesin I., Kremer K. The bond fluctuation method: a new effective algorithm for the dynamics of polymers in all spatial dimensions// Macromolecules. -1988. -V. 21. -№ .9 -P. 2819-2823
- ¹²³Kremer K., Computer Simulation of Polymers, in: Computer Simulation in Chemical Physics/ Eds. M.P. Allen and D.J. Tildesley.-New York: Kluwer, 1993. -P. 397-459
- ¹²⁴P.G. Khalatur, Computer Simulations of Polymer Systems, in: Mathematical Methods in Contemporary Chemistry. Ed. S.I. Kuchanov (Gordon & Breach, New York, 1996), pp. 487-556
- ¹²⁵K. Kremer and G.S. Grest, Entanglement Effects in Polymer Melts and Networks, in: Monte-Carlo and Molecular Dynamics Simulations in Polymer Science. Ed. K. Binder (Oxford University Press, New York, 1995), pp.194-270
- ¹²⁶Broadwell J.E. Shock structure in a simple discrete velocity gas// Phys. Fluids. -1964. -V.7. -№ .8 -P.1243-1247.

- ¹²⁷ Frisch U., Hasslacher B., Pomeau Y. Lattice-Gas Automata for the Navier-Stokes Equation//Phys. Rev. Lett. -1986. -V.56. -№.14 -P.1505- 1508.
- ¹²⁸ Colvin M.E., Ladd A.J.C., Alder B.J. Maximally Discretized Molecular Dynamics //Phys. Rev. Lett. – 1988. -V.61. -№.4 -P.381-384.
- ¹²⁹ Vianney A. J. M., Koelman A. //Phys. Rev. –1990. -V.64. -№.16. -P.1915-1918.
- ¹³⁰ Hoogerbrugge P.J., Koelman J.M.V.A. Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics//Europhys. Lett. -1992. -V.19. -№.3. -P.155-160.
- ¹³¹ R.V. Leemput, J. Meunier // Macromol. Chem. -197. -V.191. –P.1147.
- ¹³² B.H. Zimm, W.H. Stockmayer // J.Chem.Phys. -1949. -V.17. –P.1301
- ¹³³ P.-G. de Gennes // Biopolymers -1968. -V.6. –P.715.
- ¹³⁴ T.C. Lubensky J.Isaacson // Phys. Rev. A. -1979. -V.20 –P.2130.
- ¹³⁵ H.-P. Deutsch, R. Dickman, J. chem.. Phys. -1990. –V.93 –P.8983.
- ¹³⁶ Khalatur P. G., Khokhlov A. R., Prokhorova S. A., Sheiko S.S., Moller M., Reineker P., Shirvanyanz D. G., Starovoitova N.Yu. Unusual conformational of molecular cylindrical brushes strongly adsorbed on a flat solid surface // Eur. Phys. J. E -2000. -V.1. -PP. 99-103.
- ¹³⁷ P. Dziezok, S.S. Sheiko, K. Fischer, M. Schmidt, M. Möller //Angew. Chem. Int. Ed. Engl. -1997. -V.36. -P.2812.
- ¹³⁸ B. MacDonald, N. Jan, D.L. Hunter, M.O. Steinitz //J. Phys. A.: Math. Gen. -1985. –V.18. -P.2627
- ¹³⁹ M. Saariaho, O. Ikkala, G. ten Brinke //J. Chem. Phys. -1999. –V.110 –P.1180.
- ¹⁴⁰ de Gennes P.G., Scaling Concepts in Polymer Physics. -Cornell: Ithaca, NY, 1985. -385c.
- ¹⁴¹ Alexander S. Polymer Adsorption on small spheres. A scaling approach.// J. Phys. (Paris). -1977. -V. 38. -P. 977-983.
- ¹⁴² Milner S.T., Witten T.A., Cates M.E., Theory of the grafted polymer brush // Macromolecules. -1988. -V. 21. -N. 8. -P. 2610 - 2619.
- ¹⁴³ Milner S.T., Witten T.A., Cates M.E., Effects of polydispersity in the end-grafted polymer brush //Macromolecules. -1989. -V. 22. -№. 2. -P. 853-861.
- ¹⁴⁴ Miller A.F., Richards R.W., Webster J.R.P. Organization of Well-Defined Amphiphilic Graft Copolymers at the Air-Water Interface // Macromolecules. -2000. -V. 33. -№. 20. -P. 7618-7628.
- ¹⁴⁵ Govorun, E. N.; Ivanov, V. A.; Khokhlov, A. R.; Khalatur, P. G.; Borovinsky, A. L.; Grosberg, A. Yu. //Phys. Rev. E -2001. -V.64. –P.040903.
- ¹⁴⁶ Kuchanov, S.I.; Khokhlov, A.R. //J. Chem. Phys. 2003, 118, 4672.
- ¹⁴⁷ Carmesin, I. and Kremer, K. The bond fluctuation method: A new effective algorithm for the dynamics of polymers in all spatial dimensions //Macromolecules. -1988. -V. 21. –P.2819-2823.
- ¹⁴⁸ Allen, M.P. and Tildesley, D.J. Computer Simulation of Liquids, Claredon Press, Oxford. 1990.
- ¹⁴⁹ Kramarenko, E.Yu., Winkler, R.G., Khalatur, P.G., Khokhlov, A.R., and Reineker, P. Molecular dynamics simulation study of adsorption of polymer chains with variable degree of rigidity: Static properties //J. Chem. Phys. -1996. -V.104. –P.4806-4813.
- ¹⁵⁰ Zheligovskaya, E.A., Khalatur, P.G., and Khokhlov, A.R. Polymer chain binding with a flat adsorbent in the case of selective adsorption of segments: Monte Carlo simulation //J. Chem. Phys. -1997. -V.106. –P.8598-8605.
- ¹⁵¹ Peng, C.K., Buldyrev, S.V., Goldberger, A.L., Havlin, S., Sciortino, F., Simon, M., and Stanley, H.E. Long-range correlations in nucleotide sequences, //Nature (London) -1992. –V.356, -P.168-171.
- ¹⁵² Peng, C.K., Buldyrev, S.V., Goldberger, A.L., Havlin, S., Simons, M. and Stanley, H.E. Finite size effects on long-range correlations: Implications for analyzing DNA sequences //Phys. Rev. E -1993. -V.47. –P.3730-3733.
- ¹⁵³ Buldyrev, S.V., Goldberger, A.L., Havlin, S., Peng, C.-K., Simons, M., and Stanley, H.E. Generalized Levy walk model for DNA nucleotide sequences //Phys. Rev. E -1993. –V.47. –P.4514-4523.
- ¹⁵⁴ N.Yu. Starovoitova, A.V. Berezkin, Yu. A. Kriksin, O.V. Gallyamova, P.G. Khalatur, A.R. Khokhlov, “Modeling of radical copolymerization near a selectively adsorbing surface: Design of gradient copolymers with long-range correlations// Macromolecules, in press
- ¹⁵⁵ Deutsch, H.P.; Binder, K. //J. Chem. Phys. -1991. –V.94. -P.2294.
- ¹⁵⁶ Binder, K. in Monte Carlo Methods in Statistical Physics, edited by K. Binder, Topics in Current Physics, Springer: Berlin, 1977, V. 7.
- ¹⁵⁷ Allen, M. P.; Tildesley, D. J. Computer Simulation of Liquids, Claredon Press: Oxford, 1990.
- ¹⁵⁸ N.Yu. Starovoitova, A.V. Berezkin, Yu. A. Kriksin, O.V. Gallyamova, P.G. Khalatur, A.R. Khokhlov, “Modeling of radical copolymerization near a selectively adsorbing surface: Design of gradient copolymers with long-range correlations// Macromolecules, in press

-
- ¹⁵⁹ Peng, C.-K.; Buldyrev, S.V.; Havlin, S.; Simons, M.; Stanley, H.E.; Goldberger, A.L. *Phys. Rev. E* 1994, 49, 1685; Hu, K.; Ivanov, P.Ch.; Chen, Z.; Carpana, P.; Stanley, H.E. // *Phys. Rev. E* -2001. -V.64. -P.011114.
- ¹⁶⁰ Dokholyan, N.V.; Buldyrev, S.V.; Havlin, S.; Stanley, H.E. // *Phys. Rev. Lett.* -1997. -V.79. -P.5182.
- ¹⁶¹ Fay, R.; Jerome, R.; Tessie, Ph. J. // *Polym. Sci. Polym. Phys. Ed.* -1982. -V.20. -P.2209.
- ¹⁶² Hashimoto, T.; Tsukahara, Y.; Tachi, K.; Kawai, H. // *Macromolecules* -1982. -V.16. -P.648.
- ¹⁶³ Davis, K.A.; Matyjaszewski, K. *Statistical, Gradient, Block and Graft Copolymers by Controlled/Living Radical Polymerizations*, Springer: Berlin and New-York, 2002.
- ¹⁶⁴ Alberts, B. et al., *Molecular Biology of the Cell*, 4 ed. (Garland Publ., New York, 2002).
- ¹⁶⁵ Bustamante, C.; Keller, D.; Oster // *G. Acc. Chem. Res.* -2001. -V.34. -P.412-420.
- ¹⁶⁶ Keller, D.; Bustamante, C. // *Biophys. Journal.* -2000. -V.78. -P.541-556.
- ¹⁶⁷ Vilfan, A.; Frey, E.; Schwabl, F. // *Eur. Phys. J. B* -1998. -V.3. -P.535-546.
- ¹⁶⁸ Prost, J.; Chauwin, J.-F.; Peliti, L.; Ajdari, A. // *Phys. Rev. Lett.* -1994. -V.72. -P.2652-2655.
- ¹⁶⁹ Feller, W. *An Introduction to Probability Theory and its Applications*, 3 ed.; John Wiley & Sons: New York, 1970.
- ¹⁷⁰ H.C. Andersen // *J. Comput. Phys.* -1983. -V.52. -P.24.
- ¹⁷¹ L. Wesson and D. Eisenberg // *Prot. Sci.* -1992. -V.1. -P.227.