

# Simulation of Gradient Copolymers Synthesis via Conformation-Dependent Graft Copolymerization near a Uniform Adsorbing Surface

Anatoly V. Berezkin,<sup>\*,†,‡</sup> Pavel G. Khalatur,<sup>‡,§</sup> and Alexei R. Khokhlov<sup>‡,§,||</sup>

Department of Physical Chemistry, Tver State University, Tver 170002, Russian Federation, Institute of Organoelement Compounds, Moscow 119991, Russian Federation, Department of Polymer Science, University of Ulm, Ulm D-89069, Germany, and Physics Department, Moscow State University, Moscow 119899, Russian Federation

Received February 6, 2006; Revised Manuscript Received September 14, 2006

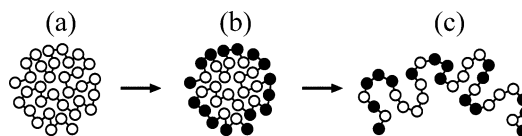
**ABSTRACT:** A statistical model is developed for radical graft copolymerization in a solution of monomers A and B in the vicinity of a surface selectively adsorbing the monomers of type A and corresponding copolymer sections. The influence of the monomer concentrations and the short-range monomer A–surface attraction on the copolymer sequence is investigated. It is shown that under certain conditions, the adsorption copolymerization can yield gradient copolymers. We find three copolymerization regimes corresponding to different values of dimensionless adsorption energy  $u$ . When the growing macroradical is weakly or nonadsorbed,  $u < u_c$  ( $u_c$  is the critical adsorption energy), the statistical properties of graft copolymers approach asymptotically, in the long-chain limit, to those of a random copolymer. If  $u \geq u_c$ , the statistics of designed and random copolymers is very different. In the vicinity of  $u_c$ , the adsorption copolymerization leads to copolymers with the largest compositional nonuniformity and well-pronounced gradient that extends along the entire chain. In the strong adsorption regime,  $u \gg u_c$ , the statistical properties of the graft copolymers do not depend on  $u$  and are determined mainly by the concentration of the monomer A in the adsorption layer.

## Introduction

Gradient copolymers (GCs), characterized by local composition monotonically varying along the chain, have attracted growing attention over recent years. The range of possible applications of these copolymers is quite wide.<sup>1–5</sup> In the solutions or melts they can form diverse structures, such as lamellar mesophases, hexagonally packed cylinders, spheres arranged in body-centered cubic lattice, bicontinuous double-gyroid structures, etc.<sup>1,2</sup> GCs can be used as surfactants, and particularly, as compatibilizers in polymer blends.<sup>4</sup> Grafting of these copolymers yields surfaces which can change the structure and properties, depending on external conditions.<sup>5</sup>

GCs are usually obtained via “living” polymerization.<sup>6–11</sup> The gradient arises here due to the continuous variation of the monomer ratio during synthesis. However, this technique allows producing sequences with a relatively simple statistics only. Conformation-dependent sequence design (CDSD)<sup>12,13</sup> is an alternative approach to the synthesis of copolymers with nontrivial statistics, including GCs. The essence of this approach is in polymer-analogous transformation or copolymerization in such reaction system, where the sequence of monomer units formed during synthesis and the equilibrium conformation of the reacting macromolecule are interdependent. This interdependence results from the self-organization of monomers and copolymer macromolecules in the reaction system.

The synthesis of copolymers reported in refs 14–16 is a typical example of polymer-analogous CDSD. The conditions in the reaction system compel an initially homopolymeric chain



**Figure 1.** Conformation-dependent sequence design via polymer-analogous chemical reaction: (a) the template globular conformation of the homopolymer chain; (b) the chemical modification; (c) the resulting sequence. Modified monomer units are shown in black.

to take the desired template conformation, e.g., a globular one as shown in Figure 1. One part of the monomer units is screened from the solution in this conformation, while the other part is accessible for chemical modification. This modification generates copolymers with the so-called Lévy-flight-type long-range correlations in the sequences.<sup>17,18</sup> The nontrivial statistical properties of these copolymers cause their unusual conformational behavior. In polar solvents these copolymers can form, similarly to globular proteins, stable globules with a hydrophobic core and a polar envelope.

Copolymerization is another possible way of conformation-dependent design. The main condition for its successful realization is self-organization of monomers and growing macroradicals during synthesis. In the initial moment of the process this self-organization consists of inhomogeneous distribution of differing comonomers over the reaction system. Interfaces, supramolecular aggregates of monomers with additional inert compounds, nanoparticles, and macroradicals themselves capable of selectively adsorbing one of the comonomers can be used to ensure these concentration inhomogeneities.

The scale of the concentration inhomogeneities, which arise in the reaction system, should be comparable with the size of macromolecule. Then, the macroradical with units inheriting their properties from the monomers would be embedded in the concentration fields of monomers. Thus, the equilibrium mac-

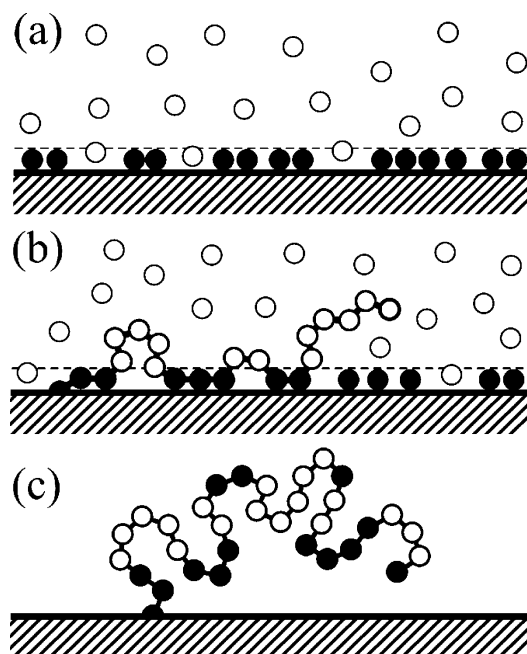
\* To whom correspondence should be addressed at the Institute of Organoelement Compounds. E-mail: berezkin.anatoly@rambler.ru.

<sup>†</sup> Department of Physical Chemistry, Tver State University.

<sup>‡</sup> Institute of Organoelement Compounds.

<sup>§</sup> Department of Polymer Science, University of Ulm.

<sup>||</sup> Physics Department, Moscow State University.



**Figure 2.** Graft adsorption copolymerization near the surface that selectively adsorbs one of the comonomers: (a) the reaction system before the polymerization; (b) the chain propagation; (c) the resulting sequence.

roradical conformation becomes interconnected with its primary sequence, and the existing sequence of units determines the order of their further addition via local monomer concentrations near the active center.

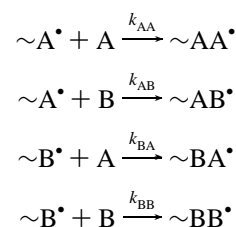
Certainly, the conformation-dependent copolymerization is most effective when the chain propagation is slower than the diffusion of monomers and the formation of the equilibrium macroradical conformation.

The first experimental synthesis of amphiphilic polymers via conformation-dependent copolymerization of polar and hydrophobic monomers in a polar solvent was reported in refs 19–22. It was shown theoretically<sup>23–26</sup> that this process can yield GCs. Block length distribution for these copolymers is not exponential, as for random copolymers, but obeys a power law. Statistical peculiarities of these copolymers ensure their unusual protein-like conformational behavior.

Another polymerization process that also realizes the CDS principles is graft copolymerization of two types of monomers (A and B) in a solution near a uniform impenetrable surface, when the latter selectively adsorbs monomers and monomer units of type A (Figure 2). It was shown recently<sup>27–29</sup> using Monte Carlo simulations and the bond-fluctuation model that this process also yields GCs. Block length distribution for A monomer units in generated sequences is exponential, but the distribution of B blocks obeys a power law. An analytical theory of adsorption copolymerization was proposed in refs 29 and 30, for the case, when units of type A cannot desorb. A theory of a similar process was developed in ref 31. However, these papers deal with copolymerization in the strong adsorption regime only, and the influence of the adsorption energy on the copolymer statistics was not discussed there. The present article is aimed at a more detailed theoretical investigation of the role of adsorption interactions during graft conformation-dependent copolymerization. The case of single-layer adsorption of one of the comonomers is considered.

**Model and Simulation Technique.** In this study, we use the following statistical model of radical copolymerization. The propagation of the grafted chain is considered as a sequential

addition of monomer units of the type A or B to the free active end of macroradical. There are four possible ways in which monomer can be added:



where  $k_{XY}$  are reaction rate constants of the interaction between active center X and monomer Y. Relations between these constants are usually expressed through the reactivity ratios  $r_A = k_{AA}/k_{AB}$ , and  $r_B = k_{BB}/k_{BA}$ .

The type of unit, that is added in each chain propagation act, is determined using a random number generator with the condition  $p_{AA} + p_{AB} = 1$ , and  $p_{BA} + p_{BB} = 1$  imposed on the probabilities  $p_{XY}$  of monomer Y addition to the active center X. The above-mentioned probabilities can be expressed via average monomer concentrations ( $\bar{c}_A$  and  $\bar{c}_B$ ) near the active center:

$$p_{AA} = \frac{r_A \bar{c}_A}{r_A \bar{c}_A + \bar{c}_B}, \quad p_{AB} = 1 - p_{AA}, \quad p_{BB} = \frac{r_B \bar{c}_B}{\bar{c}_A + r_B \bar{c}_B}, \quad p_{BA} = 1 - p_{BB} \quad (1)$$

For simplicity, it is assumed that the rate of propagation does not depend on the chemical structure of the active center ( $r_A = r_B = 1$ ), so the “ideal” copolymerization is considered, when the probabilities of monomers A and B addition are

$$p_A = \frac{\bar{c}_A}{\bar{c}_A + \bar{c}_B}, \quad p_B = \frac{\bar{c}_B}{\bar{c}_A + \bar{c}_B} \quad (2)$$

The average concentrations depend on local monomer concentrations in the solution and near the surface. We assume that the concentration of monomer A in the adsorption layer exceeds that in the solution bulk by a factor  $q$ , while the concentration of the nonadsorbable monomer B is everywhere the same. Then, the dimensionless local concentrations can be conveniently normalized by the monomer B concentration:

$$c_A^S = q c_A^0, \quad c_B^0 = c_B^S = 1, \quad q = \exp[-\epsilon/k_B T] \equiv \exp[u] \quad (3)$$

Here  $c_A^0$  and  $c_A^S$  are the dimensionless concentrations of monomers A in the bulk and in the adsorption layer, respectively,  $c_B^0$  and  $c_B^S$  are the dimensionless concentrations of the monomers B,  $\epsilon$  is the energy of a single adsorption contact,  $k_B$  is the Boltzmann constant,  $T$  is temperature, and  $u$  denotes the dimensionless energy of adsorption contact ( $u = -\epsilon/k_B T$ ).

The average concentrations are connected with local concentrations via the probability  $f_S$  of finding the active center near the surface:

$$\bar{c}_A = f_S c_A^S + (1 - f_S) c_A^0, \quad \bar{c}_B = 1 \quad (4)$$

Usually, chain propagation is a kinetically controlled process. Therefore, the macroradical changes its conformation many times between the propagation acts, and the probability  $f_S$  should be averaged over the macroradical conformations for a current chain length  $n$ . This averaging is a significant theoretical

problem. However, exact calculation of the statistical weight of each macroradical conformation is possible if the macroradical is considered as an ideal (Gaussian) chain on a cubic lattice. The computational procedure is realized as follows.

The first monomer unit of the grafted chain is placed at the origin. The surface coincides with the  $XOY$  plane; the  $z$  axis is normal to the surface and directed to the bulk of the solution. If the distance between the  $n$ th monomer unit and the surface  $z_n = 0$ , then the unit contacts with the surface, and if this unit belongs to the A type, then it is adsorbed.

Let us introduce a variable  $\alpha_n(\mathbf{r})$  that is defined as follows:  $\alpha_n(\mathbf{r}) = 1$  if the  $n$ th unit located at the point  $\mathbf{r} = \{x, y, z\}$  is adsorbed, and  $\alpha_n(\mathbf{r}) = 0$  if the unit is not adsorbed. If the macroradical of length  $n$  has in some conformation  $k$  adsorption contacts with the surface, and its active center is located at the point  $\mathbf{r}$ , the possible number of such conformations is denoted as  $\beta_n(k, \mathbf{r})$ . The following recurrence equation determines the value of  $\beta_n(k, \mathbf{r})$

$$\beta_n(k, \mathbf{r}) = \sum_{\mathbf{r}'(\mathbf{r})} \beta_{n-1}(k - \alpha_n(\mathbf{r}), \mathbf{r}') \quad (5)$$

Here,  $\mathbf{R}'(\mathbf{r})$  is the set of all possible locations of the monomer unit ( $n-1$ ) if the  $n$ th unit is located at  $\mathbf{r}$ ;  $\mathbf{r}'$  is the point belonging to the set  $\mathbf{R}'(\mathbf{r})$ . For a simple cubic lattice,  $\mathbf{R}'(\mathbf{r})$  includes 6 points when  $\mathbf{r} = \{x, y, z > 0\}$ , and 5 points if  $\mathbf{r} = \{x, y, 0\}$ . For the first monomer unit, one has

$$\left. \begin{aligned} \beta_1(0, \mathbf{r}) &= 0 \\ \beta_1(1, \mathbf{r} = \{0, 0, 0\}) &= 1, \quad \beta_1(1, \mathbf{r} \neq \{0, 0, 0\}) = 0 \\ \beta_1(k > 1, \mathbf{r}) &= 0 \end{aligned} \right\} \quad (6)$$

If the sequence of monomer units in the macroradical is known, then the number of conformations  $\beta_N(k, \mathbf{r})$  for the chain of arbitrary total length  $N$  can be found by sequential calculation of  $\beta_n(k, \mathbf{r})$  values in all lattice points  $\mathbf{V}$  at  $n = 2, 3, \dots, N$ . Then, the thermodynamic functions can be found from the following equations:

$$Z = \sum_{\mathbf{V}} \sum_{k=0}^{n_A} \beta_N(k, \mathbf{r}) q^k, \quad U = Z^{-1} \sum_{\mathbf{V}} \sum_{k=0}^{n_A} k \epsilon \beta_N(k, \mathbf{r}) q^k, \\ F = -k_B T \ln Z, \quad TS = U - F \quad (7)$$

$$c_V = \frac{\partial U}{\partial T} = Z^{-1} \sum_{\mathbf{V}} \sum_{k=0}^{n_A} (k \epsilon)^2 \beta_N(k, \mathbf{r}) q^k - \\ [Z^{-1} \sum_{\mathbf{V}} \sum_{k=0}^{n_A} k \epsilon \beta_N(k, \mathbf{r}) q^k]^2, \quad A = U / (\epsilon n_A) \quad (8)$$

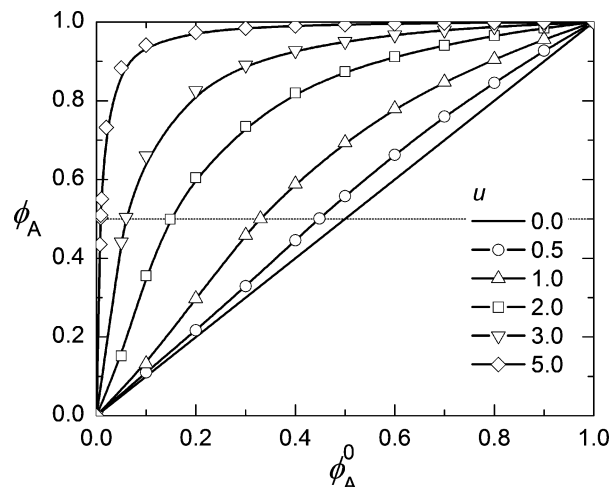
Here  $n_A$  is the number of A monomer units in sequence,  $Z$  is the partition function,  $U$  is the potential energy,  $A$  is the adsorption degree of A monomer units,  $F$  is the free energy,  $S$  is the entropy, and  $c_V$  is the heat capacity. Finally, the probability to find the active center in an arbitrary lattice point  $\mathbf{r}$  is

$$v(\mathbf{r}) = Z^{-1} \sum_{k=0}^{n_A} \beta_N(k, \mathbf{r}) q^k \quad (9)$$

and the probability of its location near the surface is

$$f_S(N) = \sum_{\mathbf{V}_{XOY}} v(\mathbf{r}) = Z^{-1} \sum_{\mathbf{V}_{XOY}} \sum_{k=0}^{n_A} \beta_N(k, \mathbf{r}) q^k \quad (10)$$

Here  $\mathbf{V}_{XOY}$  is a set of points with  $z = 0$ .



**Figure 3.** Fraction of A monomer units in the 500-unit copolymers vs the monomer A fraction in the bulk  $\phi_A^0 = c_A^0 / (c_A^0 + 1)$ . The adsorption energies,  $u$ , are shown in the legend.

In our study, chain propagation is modeled as follows. Before the addition of the next monomer to the sequence of current length  $n$ , the  $\beta_n(k, \mathbf{r})$  values are calculated for all  $\mathbf{r}$ , where  $\beta_n(k, \mathbf{r}) \neq 0$ . Then the probability to meet the active center in the adsorption layer  $f_S$  is estimated from eq 10. Equation 3 determines the average concentration of monomer A near the active center, and the corresponding probability  $p_A$  is found from eq 2. If a random number uniformly distributed between 0 and 1 is less than this probability, then the monomer unit of type A is added, otherwise the monomer unit of type B is added. After that this cycle is repeated for the longer sequence of length  $n + 1$ . Chain propagation proceeds until the necessary chain length  $N$  is reached. A large number of sequences are generated for the investigation of their statistical properties.

## Results and Discussion

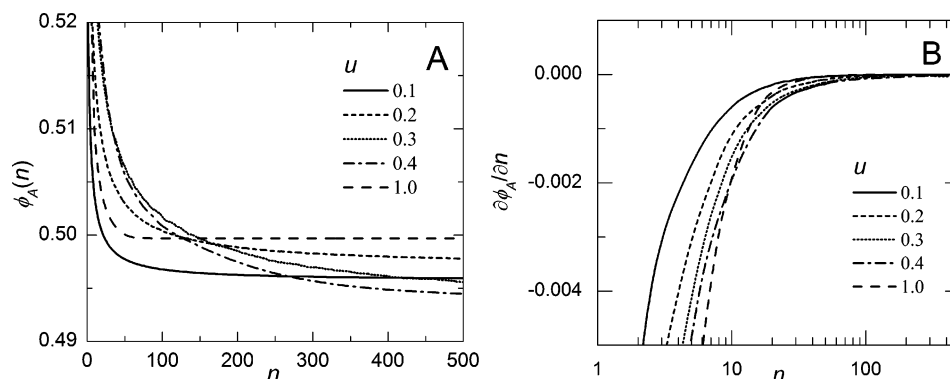
In the simulation,  $10^4$  independent sequences of length  $N = 500$  were generated for each combination of the monomer concentrations and the adsorption energy. The dimensionless energy of the adsorption monomer(A)-surface contact,  $u$ , was varied over the range from 0 to 10.

In the case of adsorption copolymerization, there are only two independent parameters, which determine the copolymer composition and statistics: adsorption energy and monomer ratio in solution (the concentration  $c_A^S$  is connected with  $c_A^0$  via eq 3). The copolymer composition curves (see Figure 3) were obtained by variation of these parameters.

Figure 3 shows that in the case of a fixed solution composition, the adsorption leads to an increase in the fraction of adsorbing monomer (A) units in the copolymer, as expected. This is explained by the growth of monomer A concentration in the adsorption layer.

For the sake of simplicity, the discussion presented in this paper will mainly be focused on the systems where the chemical AB composition of resulting copolymers is equimolar,  $\phi_A = \phi_B = 0.5$ . As a matter of fact, the equimolar composition is of special interest. To generate such copolymers, we changed the bulk concentration  $c_A^0$  simultaneously with  $u$ . Concentrations  $c_A^0$ , which are necessary for the synthesis of equimolar copolymers at a given  $u$ , were found from Figure 3 using the expression  $c_A^0 = \phi_A^0 / (1 - \phi_A^0)$ .

To analyze the local compositional inhomogeneity of synthesized copolymers, we calculated the probabilities to find a monomer unit of type A at the  $n$ th position from the beginning



**Figure 4.** (A) Local copolymer composition (averaged over  $10^4$  independent sequences) and (B) its derivative as functions of monomer number in the chain for a few values of  $u$ , at  $\phi_A = 0.5$  and  $N = 500$ .

of a growing macromolecule,  $\phi_A(n)$ , which characterizes intramolecular chemical inhomogeneity along the chain. For an ideal random copolymer in which chemically different segments follow each other in statistically random fashion, the  $\phi_A(n)$  function should coincide with the average fraction of A segments for any  $n$ . For a random-block copolymer, the fraction of one component averaged over many sequences should also be uniform along the chain.

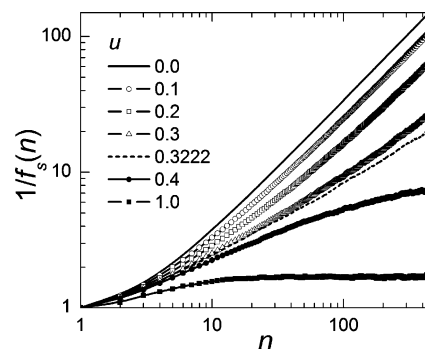
Figure 4a presents the local copolymer composition  $\phi_A(n)$ . It is seen that when  $u > 0$ , the polymerization process simulated in this study yields copolymers with a well-defined gradient structure. For such copolymers, the  $\phi_A(n)$  function smoothly decreases with  $n$ . It should be stressed that we define the gradient in strictly mathematical sense, as a drift of the average instantaneous composition along the chain. In other words, we say that a copolymer is a gradient one if the derivative of this local composition  $\partial\phi_A/\partial n \neq 0$  for any finite  $n$  value. As seen from Figure 4b, this is indeed the case for all the values of  $u$  and the chain length under consideration.

Also, it should be kept in mind that speaking about gradient copolymers, we have to consider their ensemble generated by the same synthetic process, not a single chain which can, in principle, have an arbitrary statistics. Note that in the range  $u = 0.3$ – $0.4$ , the composition gradient is most pronounced for the model studied here. As will be shown below, this adsorption energy corresponds to the critical adsorption energy.

To understand how adsorption energy influences the gradient structure, it is necessary to bear in mind that the local copolymer composition is determined by the solution monomer concentrations, which are constant during synthesis, and also by the probability of active center being located near the surface  $f_s$ . The origin of the gradient is the dependence of the probability  $f_s(n)$  on the current macroradical length  $n$ . This dependence can be easily found for a nonadsorbable Gaussian chain on a simple cubic lattice.

In the  $u \rightarrow 0$  limit, the value  $f_s^{\epsilon=0}(n)$  for a given  $n$  is defined by the ratio of two values. The numerator of this ratio is the number of conformations of a nonadsorbable chain consisting of  $n$  units, when both chain ends are placed on the surface (the distance between the ends is arbitrary). The denominator of the ratio is the number of conformations of the same chain in the case when only one chain end is grafted while the other is free. Let us assume that among  $n - 1$  bonds of this chain, only  $k$  bonds are perpendicular to the surface. According to ref 32, the number of possible combinations of  $k$  bonds, which produce chains with  $z_1 = 0, z_2 \geq 0, z_3 \geq 0, \dots, z_n \geq 0$  is described by binomial coefficient

$$\eta = \binom{k}{k/2} \quad (12)$$



**Figure 5.** Average value of the inverse probability  $1/f_s(n)$  as a function of the macroradical length  $n$  for different adsorption energies, at  $\phi_A = 0.5$  and  $N = 500$ . The curve corresponding to the critical adsorption energy,  $u_c = 0.322$ , is shown with dotted line.

Among these, there are  $\eta_s$  combinations such that the last unit lies at the surface ( $z_n = 0$ ):

$$\eta_s = \frac{1}{k+1} \binom{k}{k/2} \quad (13)$$

Since among  $n - 1$  bonds there are on the average  $k = (n - 1)/m$  bonds perpendicular to the surface, where  $m$  is the space dimensionality ( $m = 3$ ), finally we have

$$f_s^{\epsilon=0}(n) = \frac{\eta_s}{\eta} = \frac{1}{k+1} = \frac{1}{(n-1)/m+1} \quad (14)$$

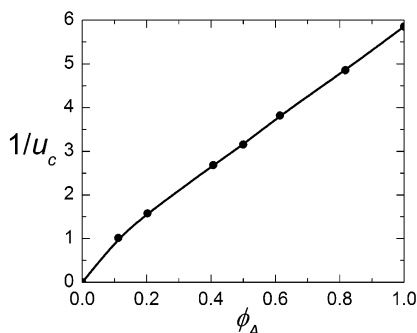
The last equation agrees well with our numerical calculations already at small values of  $n$ . Thus, in the  $u \rightarrow 0$  limit, the scaling dependence  $f_s(n) \sim n^{-1}$  is expected. Figure 5 shows that for the model studied in this paper, this scaling behavior is observed at  $n \gtrsim 10^2$  and for nonzero adsorption energy, up to its critical value  $u_c$  at which the  $f_s(n)$  function deviates from a linear one and approaches to a constant level in the  $n \rightarrow \infty$  limit. Below, we will call the copolymerization regime when  $u < u_c$  the “non-adsorbing regime”. In this regime, the chain practically does not adsorb on the surface but stays near it only due to grafting of chain end. On the other hand, at  $u \gtrsim u_c$ , we observe a qualitatively different behavior and therefore we deal with an adsorbed copolymer. The critical energy  $u_c$  that can be estimated from the  $f_s(n)$  function is close to 0.322 for 1:1 copolymer composition. Practically the same value of  $u_c$  was found from the average fraction of adsorbed segments  $A(u)$  (not shown).

Thus, the condition

$$\lim_{n \rightarrow \infty} f_s(n)|_{u < u_c} = 0 \quad (15)$$

means that the active center “leaves” the adsorption layer, as





**Figure 6.** Value of  $u_c^{-1}$  as a function of the average copolymer composition  $\phi_A$  at  $N = 500$ .

the chain grows. Because of that the local copolymer composition and the statistical properties of the grafted copolymer should asymptotically correspond to those typical for an infinitely long random copolymer synthesized in solution under similar conditions. Note that the probability  $f_S(n)$  could be considered as a “memory function”, which shows that in the nonadsorbing regime the chain gradually “forgets” that it is grafted to the surface. However this is not the case for the chains of any finite length (due to its grafting) and in the vicinity of the critical adsorption energy  $u_c$ . Indeed, our calculations show that the memory of the surface does not decay even for 500-unit freely jointed chain in which one unit corresponds to a statistical segment. The memory becomes more pronounced when  $u$  is increased (see Figure 5). Certainly, at  $u < u_c$ , the magnitude of the composition gradient is very weak so that its experimental detection is not possible.

It is clear that the critical adsorption energy should strongly depend on the average copolymer composition  $\phi_A$ . In particular, we expect that  $u_c \rightarrow \infty$  when  $\phi_A \rightarrow 0$ . Figure 6 shows  $u_c$  as a function of  $\phi_A$ . We found that at  $\phi_A \gtrsim 0.2$ , the dependence of  $u_c^{-1}$  on  $\phi_A$  can be approximated by a linear function. This scaling agrees well with the results of Sumithra and Baumgaertner,<sup>33</sup> as well as with Gutman and Chakraborty<sup>34</sup> for entirely random copolymers. Because the critical values of adsorption energy of obtained GC and random copolymers of the same composition are very close, it is reasonable to expect the similar scaling behavior for these copolymers in the whole range of adsorption energies.

Let us now consider the polymerization process at  $u > u_c$ . According to well-known results of the work,<sup>33</sup> above the critical adsorption energy random copolymers of arbitrary composition follow the scaling relation

$$R_{\perp} \sim [f_A \exp(b_f - 1/u)]^{-v_1/(1-v_2)} \quad (16)$$

Here  $R_{\perp}$  is component of the chain gyration radius, which is perpendicular to the surface,  $v_1$  and  $v_2$  are correlation length exponent and crossover exponent respectively (for Gaussian chains  $v_1 = v_2 = 0.5$ ), and  $b_f$  is a constant (according with<sup>33</sup>  $b_f = 1.6$ ). Consequently, above the critical adsorption energy for long enough chains, the thickness of adsorption layer does not depend on the polymerization degree. And in the limit  $n \rightarrow \infty$  the average probability for active center to be located in the adsorption layer should have a constant nonzero value:

$$\lim_{n \rightarrow \infty} f_S(n)|_{u > u_c} = \text{const} > 0 \quad (17)$$

In other words, in this case the memory of the surface does not vanish even in the  $n \rightarrow \infty$  limit. This conclusion agrees well with our simulation shown in Figure 5 for  $u > u_c$ . As a

result, the statistical properties of grafted and random long-chain copolymers are different.

In this regime of copolymerization, the main reason for the gradient structure is just an “end effect”, which has two causes, of physical and statistical natures, respectively. The physical cause is an influence of grafting, which is significant, when adsorption of units A is relatively weak. To explain this effect, the adsorbed chain can be considered as an array of blobs, each of them attracted to the surface with an energy on the order of  $k_B T$ .<sup>35</sup> Due to grafting, the first blob distinguishes itself from others that have approximately the same structure. As a result, the probability  $f_S$  changes on the initial section of the sequences.

However, we would like to mention certain differences between an adsorbed copolymer chain with a fixed chemical composition and a growing macroradical. The last one is a “dynamic system”. Indeed, if the gradient copolymer is forming, it can be represented as an array of nonidentical blobs of increasing size and having different content of B monomer units. So, the influence of physical factors on the gradient can be reinforced by synergistic effect of adsorption polymerization. Similar behavior has been discussed in ref 29.

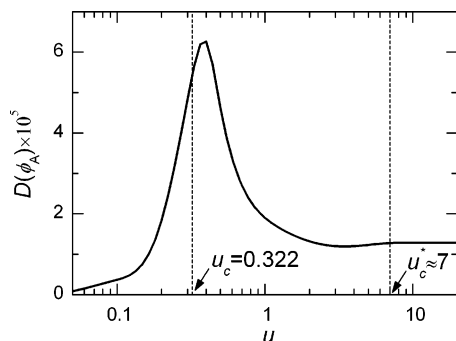
As the adsorption energy  $u$  grows, the physical effect of grafting attenuates, and characteristic size of the gradient region shorten (see Figure 5), because physisorbed monomer units become undistinguishable from the grafting point. Let us denote the minimal adsorption energy, when physical effect of grafting disappears, as some new critical adsorption energy  $u_c^*$  (absolute value of  $u_c^*$  is discussed later). At the adsorption energies higher than  $u_c^*$ , the desorption of A monomer units is small and can be neglected. We will call this a strong adsorption regime. In this regime, identical behavior of grafted and adsorbed monomer units leads to the fact that the statistical structure of the chain does not depend on its length. For this reason, each sequence that is formed here can be considered as a piece of some infinitely long nongradient sequence. The gradient, which has a statistical nature, arises because all finite-size sequences are “clipped out” from the infinite one in nonrandom way: these sequences always start with blocks of type A.

Even if the copolymer composition,  $\phi_A$ , tends to  $\phi_A = 0.5$ , the probability  $p_{AA} > p_{AB}$ , because adsorption copolymerization is a non-Markovian process. Therefore, if the chain begins from monomer unit of type A, this increases the probability that the following monomer unit also will have type A and so on. The size of such initial gradient section is determined by the transition probability  $p_{AA} = c_A^S / (c_A^S + r_A^{-1})$  (see eqs 1 and 4).

To discuss the influence of adsorption energy on the gradient in more specific way, let us to introduce a quantitative measure of the gradient as the dispersion of the preaveraged local copolymer composition:

$$D = N^{-1} \sum_{n=1}^N [f_A(n)]^2 - [N^{-1} \sum_{n=1}^N f_A(n)]^2 \quad (18)$$

The dispersion  $D$  is shown in Figure 7 as a function of  $u$ . It is seen that the dependence of  $D$  on the adsorption energy has a well-pronounced maximum. This effect has the following explanation. The dependence of  $f_S$  on  $n$  is not the only origin of the gradient; the difference between the monomer A concentration in the solution and near the surface also contributes to this effect. Figure 5 shows that the variation of  $f_S(n)$  is fastest in the absence of adsorption. Nevertheless, it is clear from the discussion presented above that no gradient copolymer can be synthesized at  $u = 0$ , because  $c_A^0 = c_A^S$ . As the adsorption intensity grows, the difference  $c_A^S - c_A^0$  increases



**Figure 7.** Value of gradient in composition vs the dimensionless adsorption energy ( $\phi_A = 0.5$ ,  $N = 500$ ).

in contrast to the difference  $f_S(1) - f_S(N)$ . Therefore, the magnitude of the gradient should have a maximum. As we can see from Figure 7, this is indeed the case. The most important fact is that the largest compositional nonuniformity is observed just for  $u \approx u_c$ . As the value of  $u$  is further increased, the compositional nonuniformity becomes weaker, and it reaches a plateau in the strong adsorption regime, for  $u \gg u_c$ .

It is instructive to compare the calculated values  $D$  with those for some model (gradient) copolymer, e.g., with linear variation of AB composition along the chain. The local chemical composition of such copolymer is a linear function of  $n$

$$\phi_A(n) = \frac{\Delta\phi}{N}n + \langle\phi_A\rangle - \frac{\Delta\phi}{2} \quad (19)$$

where  $\Delta\phi$  is the amplitude of the composition variation, and  $\langle\phi_A\rangle$  is an average copolymer composition.

For  $N$ -unit copolymer, the mean square value  $\langle\phi_A^2\rangle$  is given by

$$\langle\phi_A^2\rangle = N^{-1} \int_0^N [\phi_A(n)]^2 dn = \frac{(\Delta\phi)^2}{12} + \langle\phi_A\rangle^2 \quad (20)$$

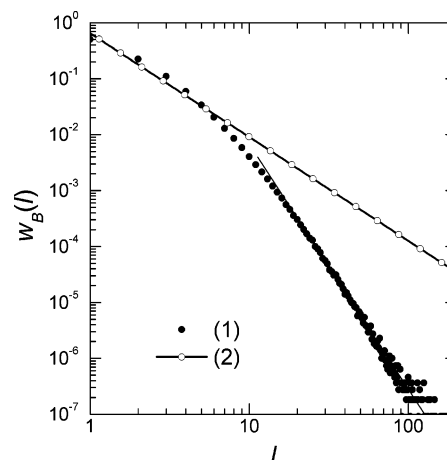
Hence, for  $D$ , we have the following simple expression

$$D = \langle\phi_A^2\rangle - \langle\phi_A\rangle^2 = (\Delta\phi)^2/12 \quad (21)$$

If we take the maximum value of  $\Delta\phi = 1$  (which can be realized experimentally, e.g., in “living” radical polymerization), we obtain  $D = 1/12$ . It is seen from Figure 7 that this composition dispersion is much larger as compared to that observed for our designed copolymers for any  $u$ . The point is that in our calculation, the propagation rate does not depend on the chemical structure of polymerizing monomers and active center. In principle, the composition dispersion and the magnitude of the gradient can be considerably increased when the preferable addition of one of the monomers is taken into account.

As mentioned above, when  $u > u_c$ , the compositional nonuniformity decays with increasing  $u$ . Moreover, the gradient becomes independent of  $u$  when the strong adsorption regime is attained. From Figure 7 we have found that the transition to this regime takes a place at critical adsorption energy  $u_c^* \approx 7$ . This critical value was found by comparative analysis of dependences  $D(u)$  for copolymers with different compositions. For some of them this crossover point is even more pronounced than in Figure 7.

As mentioned above, in the strong adsorption regime, at  $u > u_c^*$ , adsorption energy already does not influence the chain conformation. Because of that, the copolymers that have the same composition are characterized also by equal statistics and



**Figure 8.** Block length distribution functions for nonadsorbing blocks B ( $N = 500$ ,  $u = 10$ ,  $\phi_A = 0.5$ ): (1) calculations by our model; (2) results of the model.<sup>29</sup>

amplitude of gradient. As follows from eq 16, this regime is realized when

$$b_f \gg 1/u \quad \text{or} \quad u \gg 1/b_f = 0.625 \quad (22)$$

Equation 22 shows that the critical value  $u_c^*$ , as distinct from  $u_c$ , is a constant for a given system. It does not depend on copolymer composition and chain length.

Statistical properties of copolymers obtained during copolymerization in the strong adsorption regime have been discussed in refs 29 and 31. All theoretical models, including one developed in the present work, predict exponential distribution for blocks of the type A, because the probability of block A elongation is always constant and equal to the transition probability  $p_{AA}$ . However, there are differences for distribution of B blocks.

We have found that this distribution is described by a power law in the long chain limit

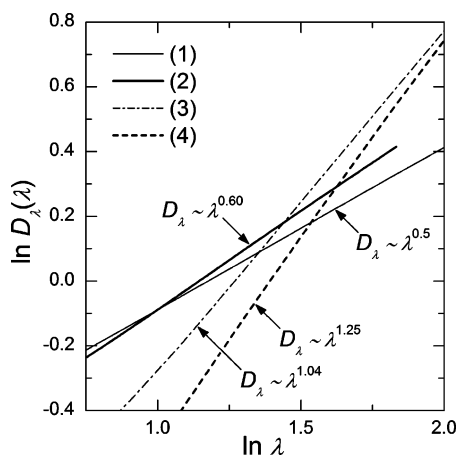
$$w_B(l) \sim l^{-\alpha} \quad (23)$$

The power exponent  $\alpha$  depends on the copolymer composition. As one can see from Figure 8,  $\alpha = -5.48$  for the copolymer composition  $\phi_A = 0.5$ .

The power law for  $w_B(l)$  was also found in ref 29. However the power exponent  $\alpha = 3/2$  is obtained there, and it was a constant for sequences of different composition. These differences arise because the model<sup>29</sup> considers each separate chain as “quenched”, i.e., the macroradical cannot change the conformation during polymerization. This is possible for rigid polymers or during polymerization in highly viscous systems, when reaction rate significantly exceeds chain relaxation rate. As a result, each block B in this model is a realization of one-dimensional random walk process.

Because of that, the gradients obtained in our model and in the theory<sup>29</sup> are also not the same. If we predict relatively fast attenuation of gradient in the strong adsorption regime, then for “quenched” macromolecules there are long-range compositional correlations extending along the entire chain for any  $N$ .<sup>29</sup> Therefore, these copolymers have more correlated structure than the chains which can change the conformation during synthesis.

An effective method for quantitative evaluation of these correlations is the so-called detrended fluctuation analysis developed by Stanley and co-workers.<sup>36–39</sup> In this approach, each AB copolymer sequence is transformed into a sequence



**Figure 9.** Dispersion of copolymer composition depending on size of segment for (1) random copolymers, (2) for copolymers obtained by adsorption copolymerization in the strong adsorption regime (at  $u = 10$ ), (3) for copolymers obtained by grafted synthesis of “quenched” molecules,<sup>29</sup> and (4) theoretical results of the work<sup>29</sup> for such “quenched” chains.

of symbols  $+1$  and  $-1$ . One can find an average dispersion of such discrete function on the section of length  $\lambda$ . For random copolymers dispersion  $D_\lambda$  is connected with the “window size”  $\lambda$  through a power law  $D_\lambda \sim \lambda^{1/2}$ . For correlated sequences nonpower dependence  $D_\lambda(\lambda)$  takes place, or the power exponent of such dependence exceeds  $1/2$ .

As seen from Figure 9, grafted copolymerization always yields sequences with power laws for  $D_\lambda(\lambda)$ . And the power exponents in all the cases (excepting random sequences obtained in absence of adsorption) exceed  $1/2$ . It means that there are long-range correlations in synthesized sequences, but there is not any characteristic scale length of these correlations; i.e., scale invariance of correlations takes place. Copolymers obtained during propagation of “quenched” macroradicals demonstrate more pronounced correlations (larger power exponents) than those generated in the present work for kinetically controlled copolymerization in the strong adsorption regime. This result agrees well with the conclusion about weaker gradient of sequences obtained in the latter case.

## Conclusion

We have proposed a statistical mechanical model of an irreversible graft copolymerization in the solution of two polymerizing monomers A and B for the case when the surface selectively adsorbs monomers and monomer units of type A. The growth of polymer chains during the addition copolymerization produced a monodisperse system. The influence of the solution monomer concentrations and the adsorption energy on the chemical composition and the statistical properties of the copolymer sequences was investigated. The focus was on the copolymers with equimolar AB composition.

We have found that, under certain preparation conditions, the adsorption copolymerization can yield quasirandom copolymers with the strong compositional nonuniformity and well-pronounced gradient sequences. To characterize the magnitude of the gradient, we have introduced a parameter  $D$  that describes the dispersion of the local copolymer composition  $\phi_A(n)$  along the chain. The dependence of  $D$  on the adsorption energy  $u$  for the copolymers with the same average composition has a maximum near the critical adsorption energy  $u_c$  of the macroradical. It means that in the vicinity of  $u_c$ , the gradient structure of the resulting copolymer sequences becomes most pronounced.

It was shown that there are three regimes of the adsorption

copolymerization which correspond to different adsorption energies. (i) In the nonadsorbing regime ( $u \ll u_c$ , where  $u_c \approx 0.322$  is the critical adsorption energy in the case of equimolar copolymer composition,  $\phi_A = \phi_B = 0.5$ ) the probability for the active center to be located near the surface behaves as  $f_s(n) \sim 1/n$ , where  $n$  is the macroradical length. Therefore, in this regime, the chain propagation leads to asymptotical convergence of the local copolymer composition to that of random copolymers synthesized in a solution under the same conditions. For finite values of  $n$ , a fast change in the local chemical composition is observed for initial sections of the growing macroradical. (ii) In the weak adsorption regime ( $u \gtrsim u_c$ ) the probability  $f_s$  is nonzero for any  $n$  and  $u$ . As a result, the local copolymer composition in the long-chain limit differs essentially from that of a random copolymer synthesized in the solution bulk. In the vicinity of  $u_c$ , the magnitudes of the compositional nonuniformity and gradient are maximal, and the gradient extends along the entire chain for any chain length. The value of  $u_c^{-1}$  was found to be a linear function of  $\phi_A$  at  $\phi_A \gtrsim 0.2$ . (iii) For the strong adsorption regime ( $u > u_c^*$ , where  $u_c^* \approx 7$ ), the copolymer statistics does not depend on  $u$  and is determined only by the solution monomer concentrations. Thus, the adsorption energy can help to ensure versatile and accurate control of the statistics of the resulting copolymers obtained via the conformation-dependent adsorption copolymerization.

One of the main limitations of our polymerization model is the fact that it does not include intrachain excluded volume effects and interchain interactions; therefore, self-intersections are possible in the model chain. The ideal (Gaussian) chain model discussed in this paper is the simplest one among those that can be used for studying conformation-dependent surface copolymerization. However, even for this minimal model, a meaningful formulation and an exact solution of the problem are possible. The excluded volume interaction consists of repulsion of monomer units at small distances and prevents them being localized simultaneously in the same spatial region. Taking into account the excluded volume exactly is a far more complex problem than that of the ideal chain; therefore complex models must be used for its solution (e.g., models developed on the basis of self-consistent field theory). However, certain general conclusions about the role of excluded volume effects can be drawn based on simple arguments. First of all, we note that the probability  $f_s$  defined by eq 10 already accounts for the excluded volume interaction between chain segments and surface. Introduction of additional interaction terms into the expression for the statistical weight  $q$  [see eq 3] describing the intrachain excluded volume interaction would not change the ratio defined by eq 9, but would decrease the number of chain conformation with  $z = 0$ . The same is true for a multiple chain system in the presence of interchain interactions between neighboring growing chains. As a result, the excluded volume interaction would make the probability  $f_s$  smaller and, respectively, the critical adsorption energy larger. Therefore, the minimal model we discussed here gives the lowest estimate of the transition between nonadsorbed, weakly adsorbed, and strongly adsorbed polymers. Nevertheless, we do not expect qualitative changes in general properties of the polymers generated via surface-induced conformation-dependent copolymerization. The same conclusion has been drawn in ref 29. Certainly, for a system consisting of densely grafted chains (as in a polymer brush), we expect qualitatively different behaviors.

**Acknowledgment.** The authors thank A. A. Lazutin for fruitful discussions. The financial support from SFB-569 (Project B13) “Smart Copolymers Near Surfaces”, and the Russian

Foundation for Basic Research (Projects 04-03-32185 and 05-03-32157) is highly appreciated. A.V.B. acknowledges the Deutscher Akademischer Austauschdienst (DAAD), German Science Foundation (DFG), and Russian Science Support Foundation for financial support.

## References and Notes

- (1) Aksimentiev, A.; Holyst, R. *J. Chem. Phys.* **1999**, *111*, 2329.
- (2) Lefebvre, M. D.; Cruz, M. O.; Shull, K. R. *Macromolecules* **2004**, *37*, 1118.
- (3) Pakula, T.; Matyjaszewski, K. *Macromol. Theory Simul.* **1996**, *5*, 987.
- (4) Shull, K. R. *Macromolecules* **2002**, *35*, 8631.
- (5) Pickett, G. T. *J. Chem. Phys.* **2003**, *118*, 3898.
- (6) Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.; Mayadunne, R.; Meijs, G.; Moad, C.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291.
- (7) Matyjaszewski, K.; Ziegler, M. J.; Arehart, S. V.; Gresza, D.; Pakula, T. *J. Phys. Org. Chem.* **2000**, *13*, 775.
- (8) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
- (9) Davis, K. A.; Matyjaszewski, K. *Statistical, Gradient, Block and Graft Copolymers by Controlled/Living Radical Polymerizations*, Springer: Berlin and New York, 2002.
- (10) Lutz, J.-F.; Pakula, T.; Matyjaszewski, K. *Advances in controlled/living radical polymerization*, American Chemical Society: Washington, DC, 2003.
- (11) Dettmer, C. M.; Gray, M. K.; Torkelson, J. M.; Nguyen, S. T. *Macromolecules* **2004**, *37*, 5504.
- (12) Khokhlov, A. R.; Khalatur, P. G. *Physica A* **1998**, *249*, 253.
- (13) Khokhlov, A. R.; Khalatur, P. G. *Phys. Rev. Lett.* **1999**, *82*, 3456.
- (14) Virtanen, J.; Baron, C.; Tenhu, H. *Macromolecules* **2000**, *33*, 336.
- (15) Virtanen, J.; Tenhu, H. *Macromolecules* **2000**, *33*, 5970.
- (16) Virtanen, J.; Lemmetyinen, H.; Tenhu, H. *Polymer* **2001**, *42*, 9487.
- (17) Govorun, E. N.; Ivanov, V. A.; Khokhlov, A. R.; Khalatur, P. G.; Borovinsky, A. L.; Grosberg, A. Y. *Phys. Rev. E* **2001**, *64*, 040903-4.
- (18) Kuchanov, S. I.; Khokhlov, A. R. *J. Chem. Phys.* **2003**, *118*, 4672.
- (19) Lozinskii, V. I.; Simenel, I. A.; Kurskaya, E. A.; Kulakova, V. K.; Grinberg, V. Y.; Dubovik, A. S.; Galaev, I. Y.; Mattiasson, B.; Khokhlov, A. R. *Dokl. Chem.* **2000**, *375*, 273.
- (20) Lozinsky, 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. Y.; Galaev, I. Y.; Mattiasson, B.; Khokhlov, A. R. *Macromolecules* **2003**, *36*, 7308.
- (21) Siu, M.-H.; Zhang, G.; Wu, C. *Macromolecules* **2002**, *35*, 2723.
- (22) Siu, M.-H.; He, C.; Wu, C. *Macromolecules* **2003**, *36*, 6588.
- (23) Berezkin, A. V.; Khalatur, P. G.; Khokhlov, A. R. *J. Chem. Phys.* **2003**, *118*, 8049.
- (24) Berezkin, A. V.; Khalatur, P. G.; Khokhlov, A. R.; Reineker, P. *New J. Phys.* **2004**, *6*, 44.
- (25) Khokhlov, A. R.; Berezkin, A. V.; Khalatur, P. G. *J. Polym. Sci.* **2004**, *42* (A), 5339.
- (26) Berezkin, A. V.; Khalatur, P. G.; Khokhlov, A. R. *Polym. Sci. (Russia)* **2005**, *47* (A), 66.
- (27) Starovoitova, N. Y.; Khalatur, P. G.; Khokhlov, A. R. *Dokl. Chem.* **2003**, *392*, 242.
- (28) Starovoitova, N. Y.; Khalatur, P. G.; Khokhlov, A. R. In *Forces, Growth and Form in Soft Condensed Matter: At the Interface between Physics and Biology*; Skjeltorp, A. T.; Belushkin, A. V., Eds.; NATO Science Series II: Mathematics, Physics and Chemistry; Kluwer: Dordrecht, The Netherlands, 2004; Vol. 160, 253 pp.
- (29) Starovoitova, N. Y.; Berezkin, A. V.; Kriksin, Y. A.; Gallyamova, O.; Khalatur, P. G.; Khokhlov, A. R. *Macromolecules* **2005**, *38*, 2419.
- (30) Kriksin, Y. A.; Khalatur, P. G.; Khokhlov, A. R. *J. Chem. Phys.* **2005**, *122*, 114703.
- (31) Kuchanov, S. I.; Khokhlov, A. R. *Macromolecules* **2005**, *38*, 2937.
- (32) Feller, W. *Introduction to probability theory and its applications*; John Wiley & Sons: New York, 1966.
- (33) Sumithra, K.; Baumgaertner, A. *J. Chem. Phys.* **1999**, *110*, 2727.
- (34) Gutman, L.; Chakraborty, A. K. *J. Chem. Phys.* **1995**, *103*, 10733.
- (35) De Gennes, P.-G. *Scaling concepts in polymer physics*; Cornell University Press: Ithaca, NY, 1979.
- (36) Peng, C.-K.; Buldyrev, S. V.; Goldberger, A. L.; Havlin, S.; Sciortino, F.; Simon, M.; Stanley, H. E. *Nature* (London) **1992**, *356*, 168.
- (37) Peng, C.-K.; Buldyrev, S. V.; Havlin, S.; Simons, M.; Stanley, H. E.; Goldberger, A. L. *Phys. Rev. E* **1994**, *49*, 1685.
- (38) Dokholyan, N. V.; Buldyrev, S. V.; Havlin, S.; Stanley, H. E. *Phys. Rev. Lett.* **1997**, *79*, 5182.
- (39) Hu, K.; Ivanov, P. C.; Chen, Z.; Carpana, P.; Stanley, H. E. *Phys. Rev. E* **2001**, *64*, 011114.

MA0602800