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Effect of the Fraction and Size of Polar Groups on the Formation of Compact Conformations of a Polymer Chain with Variable Stiffness in Low-Polar Media

Yu. D. Gordievskaya^{a,b} and E. Yu. Kramarenko^{a,b,*}

^a Faculty of Physics, Moscow State University, Moscow, 119991 Russia

^b A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia

*e-mail: kram@polly.phys.msu.ru

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Abstract—The conformational behavior of a single semiflexible polymer chain with a variable fraction of polar groups (dipoles) is studied by the molecular dynamics method. Dipoles of the chain are simulated as two oppositely charged beads, one of which belongs to the backbone and another bead is a side group. The charged bead of the side group may freely rotate around the backbone, and the size of the side bead and the distance between oppositely charged groups (dipole length) are varied. The main attention is focused on studying the effect of backbone stiffness and an interplay of excluded volume and electrostatic interactions on the conformational behavior of a chain and the structure of multiplets formed due to a strong electrostatic attraction in low-polar media.

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INTRODUCTION

Interest in the study of ion-containing polymers over decades is associated with their important role in the processes of functioning of living organisms as well as their wide use in advanced technologies. Examples are both numerous biopolymers (DNA, proteins, chitosan, gelatin), their modifications, and synthetic polymers (poly(methacrylic acid), sodium polyacrylate, polyethyleneimine).

The unique properties of ion-containing polymer systems and their diverse behavior compared with nonionic systems are determined by the presence of long-range electrostatic interactions. Therefore, ion-containing polymers possess high sensitivity to a change in a number of additional external factors affecting the relative contribution of electrostatics, for example, medium acidity and solvent ionic strength and polarity. Solutions and melts of polyelectrolyte chains [1, 2], grafted polymer layers [3, 4], interpolyelectrolyte complexes [5–7], micellar aggregates [8, 9], macro- and microgels [10–14], and polyionic liquids [15–17]—this is not the complete list of ion-containing systems which have found application in many fields: medicine, cosmetology, building, agricultural sector, food and oil and gas industries, and water treatment. A special place in this series is occupied by pharmaceuticals, because water-soluble biocompatible polymers may serve as drug delivery containers, sensors, and materials for matrices and coatings [4, 18, 19].

A separate class of ion-containing polymer systems is formed by the so-called dielectric polymers, whose units are strongly polarized and, hence, possess a high dipole moment. Among them are ionomers [20, 21], zwitter-ionic polymers [22–24], and dielectric elastomers [25–27]. The most known and used polyzwitterions are betaines (polycarboxybetaine, polysulfobetaine, and polyphosphobetaine). They are applied as fungicides, fire-resistant polymers, lube oil additives, emulsifiers, and wetting agents, and in the treatment industry [28]; they are intensively studied for creation of coatings that prevent fouling by hydrophobic compounds [29]. In addition, polymers whose structural components have dipole moments are electroactive, because application of an external electric field provokes the orientation of their dipole moments which causes a change in the conformation of chains, their reorganization and, as a consequence, a change in the dimensions of the whole sample. Electromechanical transducers based on dielectric polymers are used in automation and robotization, in prosthetics and for creation of artificial organs [30, 31].

Despite the practical importance of dielectric polymers, attention to the theoretical study of their behavior has been given only recently. In contrast to polyampholytes, for which charges of opposite signs are involved in the composition of the backbone, such macromolecules usually contain oppositely charged groups within one monomer unit, forming a permanent dipole on a chain. At the same time, particular

attention is focused on analysis of the effect of dipole–dipole interactions [32, 33]. The presence of polar groups in a chain is mostly described by specifying dipole moments to monomer units. If dipole–dipole interactions are taken into account in terms of these models along with conformational entropy and volume interactions, an increase in dipole moments always invokes decrease in the chain size and, in some cases, its collapse due to the effective worsening of solvent quality for chain units (renormalization of pair interactions). It should be emphasized that this conclusion is based on an approximation taking into consideration the contribution of electrostatic interactions within the framework of dipole approximation, which cannot be justified in the globular state of the chain, when the concentration of charges may be high and the contributions of multiparticle interactions and excluded volume of charged units of polar groups may be significant.

Actually, recent studies [34] taking into account the structure of polar groups directly, namely, as two oppositely charged beads, one of which is the backbone unit and the other is the side group, made it possible to reveal effect of the competition of electrostatic and excluded volume interactions of charged units on the conformational behavior of chains. Specifically, it was shown [34] that, in contrast to the main conclusion of theoretical calculations neglecting the structure of dipoles [32, 33, 35–37], a rise in the dipole moment owing to an increase in the size of the side group entails unfolding of a chain, all units of which are dipoles, because of the dominant contribution of excluded volume interactions.

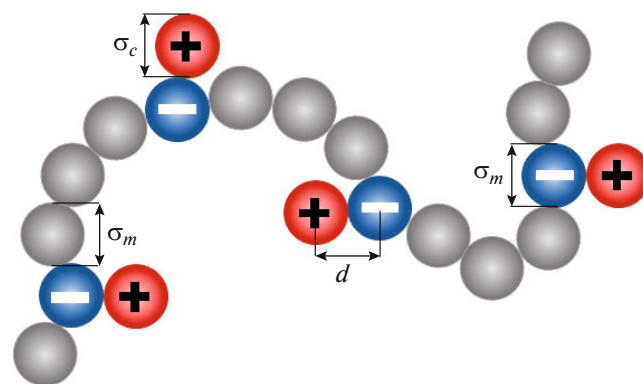
This work is a continuation of our research into the conformational behavior of a single polymer chain, in which a part of the units are polar groups (permanent dipoles), by the molecular dynamics method. This study provides a summary of the limiting case of a 100% dipole chain [34]; the main attention is given to gaining insight into effect of the fraction of polar groups on collapse of the chain and structure of ionic aggregates formed in low-polar media owing to electrostatic interactions. One of the basic issues that needs to be solved is whether the conclusion formulated in [34] for a chain consisting solely of dipoles is valid in the case of a chain containing, along with dipoles, nonpolar segments, for which a solvent is good. It should be expected that, with a decrease in the fraction of dipoles in the chain and, hence, in the contribution of electrostatic attraction, the globular state of the chain should become disadvantageous at a certain critical fraction of dipoles, which should depend on the polar group size and medium polarity. Moreover, computer simulation makes it possible to study in detail the morphology of ionic associates at the microscopic level, in particular, to analyze the presence of orientational correlations of dipoles in these associates

as a function of the size of dipoles, their fraction in the composition of the chain, and solvent polarity. Such an analysis is important for further development of theoretical models describing the behavior of a wide range of polymers carrying groups with a large dipole moment.

In addition, this paper addresses the influence of stiffness of the backbone on the formation of collapsed conformations of the dipole chain with enhancement of electrostatic attraction between polar groups. It is known that the presence of bending stiffness strongly affects the morphology of the globular state of the chain. For both neutral and charged stiff-chain macromolecules, toroidal globules were observed experimentally [38–40] and studied theoretically [41–43] and using computer simulation methods [44–46]. The case where the driving force of chain collapse was short-range interactions of chains in a poor solvent was investigated for the most part. In this study it is assumed that the solvent is good for the chain and collapsed conformations are formed via the electrostatic attraction of charged units in the composition of polar groups.

SIMULATION MODEL AND METHOD

We investigate the conformational behavior of dipolar polymer chain within the framework of the coarse-grained approach using molecular dynamics simulations. The chain is composed of 256 units, among which there are polar groups (dipoles). The fraction of regularly distributed polar groups of the polymer f is varied from 1 to 1/16. Each polar group is a pair of the backbone unit carrying charge $-qe$ and the side group with charge qe . Side groups may freely rotate around corresponding charged units of the chain. The remaining backbone units have no charges, and the system is electroneutral. The model of the polymer chain with polar groups is schematically shown below.



Blue and red beads designate negatively charged backbone units and positively charged side groups, respectively; they form the polar group with dipole

moment length d ; gray beads designate uncharged backbone units (color figures are available in the electronic version).

Computer simulations of the polymer chain with polar groups are based on the bead-spring model [47]. The potential energy of the system includes excluded

volume interactions between all species and electrostatic interactions between charged groups. It also takes into account chain stiffness and connectivity of units along the chain and in the composition of polar groups.

Excluded volume interactions are set using the Lennard-Jones potential (12–6):

$$U_{\text{LJ}} = \begin{cases} 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 - \left(\frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}^c} \right)^{12} + \left(\frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}^c} \right)^6 \right]; & r < R_{\alpha\beta}^c \\ 0; & r \geq R_{\alpha\beta}^c \end{cases}$$

Here r is a distance between centers of two particles of types α and β , and $R_{\alpha\beta}^c$ is the cutoff radius. The parameter of the Lennard-Jones potential is $\epsilon_{\text{LJ}} = 1.0$ in $k_{\text{B}}T$ units, where k_{B} is the Boltzmann constant, T is the absolute temperature, and $R_{\alpha\beta}^c = 2^{1/6}\sigma_{\alpha\beta}$ is taken for the simulation of good solvent conditions for the polymer chain. Parameter $\sigma_{\alpha\beta}$ of the Lennard-Jones potential is defined as a half-sum of sizes of interacting particles $\sigma_{\alpha\beta} = (\sigma_{\alpha} + \sigma_{\beta})/2$, where indices α and β denote either the side group or the backbone unit. One of the tasks of this study is to investigate effect of the size and length of dipole moment of polar groups on the conformational behavior of the chain and multiplets being formed in the system. With this aim in mind, the size of the backbone unit σ_m is set constant and it acts as a length unit and the size of the side group σ_c is varied. The dipole moment length is determined as $|\mathbf{d}| = (\sigma_m + \sigma_c)/2$, and it changes in the range of 0.75–1.50.

The relationship between monomer units along the chain is given by the FENE (Finite Extensible Nonlinear Elastic) potential:

$$U_{\text{FENE}} = -\frac{1}{2}k_0R_0^2 \ln \left(1 - \frac{r^2}{R_0^2} \right),$$

where k_0 is the stiffness of a spring and R_0 is its maximum extension of the bond. In our computer simulation, the values of potential parameters are fixed: $k_0 = 20$ and $R_0 = 2.0$. This choice specifies the equilibrium bond length equal to 1.0, and length fluctuations do not exceed 10%.

The average length of the dipole moment is determined by the combination of FENE and Lennard-Jones potentials between oppositely charged units of the polar group:

$$U_{\text{bond}} = -\frac{1}{2}k_dR_d^2 \ln \left(1 - \frac{r^2}{R_d^2} \right) + 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon_{\text{LJ}},$$

where stiffness is $k_d = 100.0$ and parameters σ and R_d are varied depending on the simulated length of the dipole moment.

Chain stiffness is set by the following condition on the potential energy of bending deformation:

$$U_{\text{bend}}(\theta) = k(1 - \cos \theta)$$

(θ is the angle between directions of two neighboring units of the backbone). In the case of fully extended conformation (rod), all angles θ are zero; this state is characterized by the lowest potential energy of bending deformation. Parameter k is the characteristic of stiffness; in our computer experiments, its value is varied from 0 to 15 in $k_{\text{B}}T$ units; accordingly, we consider chains from flexible to stiff with the persistence length $\tilde{l} \sim k$ for $k \gg 1$.

Electrostatic interactions between charged species in the composition of polar groups of the chain in a medium with dielectric constant ϵ are taken into account using the Coulomb potential

$$U_{\text{Coul}} = \frac{Z_{ij}q^2e^2}{\epsilon r},$$

where $Z_{ij} = 1$ and $Z_{ij} = -1$ for like-charged and oppositely charged species i and j .

The strength of electrostatic interactions is characterized by the dimensionless parameter λ ,

$$\lambda = \frac{q^2l_{\text{B}}}{\sigma_m}$$

where l_{B} is the Bjerrum length, that is, the distance at which the electrostatic energy of two species carrying single charges is comparable with the thermal energy,

$l_{\text{B}} = \frac{e^2}{\epsilon k_{\text{B}}T}$. Parameter λ varies in the range from 1 to 16; we examine the cases where both weak and strong Coulomb forces are present in the system.

A chain is placed in a cubic simulation box with periodic boundary conditions with volume 300^3 . The box size is larger than the polymer contour length, so that excluded volume interactions of the chain with its image are excluded, which corresponds to the simula-

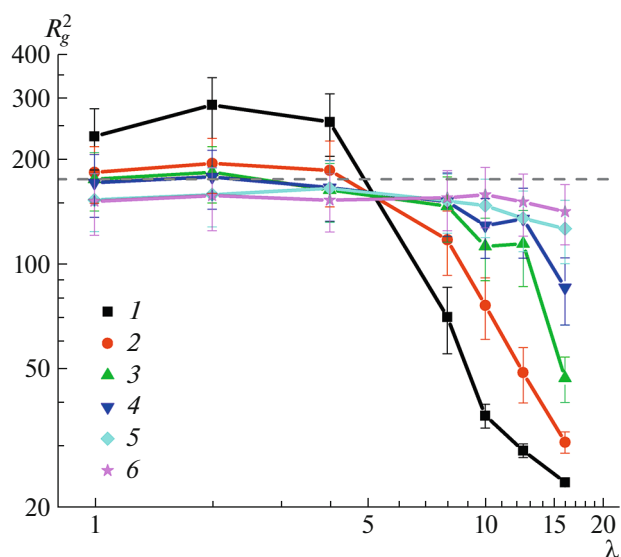


Fig. 1. (Color online) Mean-square radius of gyration R_g^2 of the flexible ($k = 0$) chain with different fraction of polar groups f as a function of parameter of electrostatic interactions λ . $f = (1)$ 1, (2) 1/2, (3) 1/3, (4) 1/4, (5) 1/8, and (6) 1/16. The dashed horizontal line indicates the value of $R_g^2 = 175$ for the neutral polymer chain without polar groups.

tion of a dilute polymer solution. The solvent is set implicitly, indicating the dielectric constant of the medium.

Computer simulation is carried out using the LAMMPS software package. A Langevin thermostat is used to maintain constant temperature ($k_B T = 1.0$) of the system; the friction coefficient is the same for all particles $\xi = \tau^{-1}$, where $\tau = \sqrt{m\sigma_m^2/\epsilon_{LJ}}$ is the unit time in computer simulation; and all particles have the same dimensionless mass $m = 1.0$. Coulomb interactions were calculated by the PPPM (particle-particle/particle-mesh) method with an accuracy of 10^{-4} . The integration step was chosen to be 0.005. All values are given in dimensionless units. The system reached equilibrium in the course of $(5-10) \times 10^6$ steps depending on the fraction of charged units in the chain and the value of parameter λ . The data presented below were derived by averaging over independent realizations obtained for the pre-equilibrated system over 20×10^6 steps.

RESULTS AND DISCUSSION

Size and Peculiarities of the Structure of a Flexible Chain with Different Fraction of Polar Groups

It is well known that the degree of charging of both polyelectrolyte and polyampholyte chains strongly influences the character of phenomena associated with their conformational behavior and the structure of ionic aggregates in the case of a small fraction of

charged units [48, 49]. The polymer chain, which contains dipoles, despite similarity to the above-described systems, has its own features of the conformational behavior. Specifically, as opposed to polyelectrolytes, in which mobile counterions are present, in a dipole chain, all charges are immobilized on the chain. Difference in the behavior of the dipole chain and statistical polyampholytes consists in fixation of the distance between oppositely charged groups in the composition of the dipole and a change in the character of correlation effects. The structural peculiarity of the dipole composed of a charged backbone unit and an oppositely charged side group is responsible for a considerable difference in the behavior of the simulated chain from the behavior of polyampholytes, whose charges alternate along chain. This difference should be especially evident during the formation of ionic associates in low-polarity media in the case of a small fraction of charged groups in the chain.

The dependence of mean-square radius of gyration R_g^2 of a flexible ($k_B = 0$) chain with different fraction f of polar groups on the parameter of electrostatic interactions λ is shown in Fig. 1. In the case of weak Coulomb forces ($\lambda < 5$), the size of the chain slightly increases with the fraction of polar groups, which is associated with a rise in the contribution of excluded volume due to an increase in the amount of side groups. If the parameter of electrostatic interactions is high ($\lambda > 5$), the role of effective attraction grows owing to the presence of oppositely charged species: the higher the value of λ and the fraction of polar groups, the more compact the chain conformation is realized. Formation of the globular state with enhancement of electrostatic interactions is typical of both polyelectrolyte chains [50, 51] and polyampholytes [52]. The driving force of chain collapse is the electrostatic attraction of the correlation origin. At a small fraction of dipoles ($f = 1/8$ and $1/16$), attraction is too small in order to overcome repulsion due to volume interactions of units and the chain remains in the swollen state in the studied range of λ .

The excluded volume and dipole moment of side groups also affect the size of the polymer chain (Fig. 2). If Coulomb forces are weak ($\lambda = 1$), then the chain extends because of steric reasons at a considerable fraction of side groups: the larger the side group, the more pronounced the chain swelling with increasing f (Fig. 2a). It is interesting to consider the case $\lambda = 10$, where the chain conformation is controlled by the competition of repulsion between units due to the presence of excluded volume of side groups, which tends to grow with increasing d , and attraction due to electrostatic interactions, which also depends on the value of the dipole moment d . As f grows, the first factor dominates at $d > 1.25$ and the size of the chain increases, while the second factor prevails at $d \leq 1.0$, which provokes collapse of the chain (Fig. 2b). It should be emphasized that destabilization of the glob-

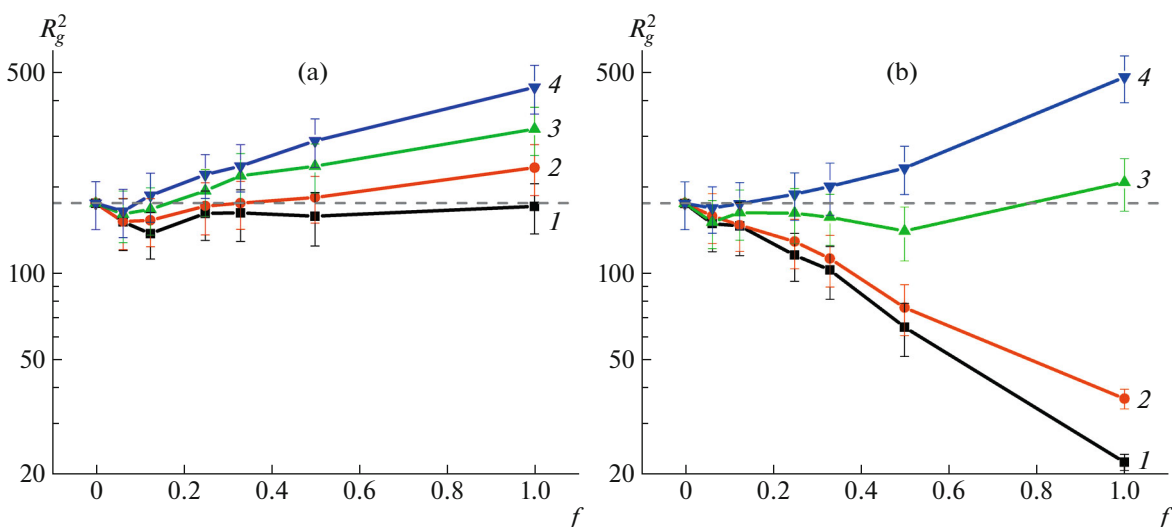


Fig. 2. (Color online) Dependence of mean-square radius of gyration R_g^2 of flexible ($k = 0$) chain on the fraction f of polar groups at dipole moment size $d = (1)$ 0.75, (2) 1.0, (3) 1.25, and (4) 1.50. $\lambda = (a)$ 1 and (b) 10. The dashed horizontal line indicates the value of $R_g^2 = 175$ for the neutral polymer chain without polar groups.

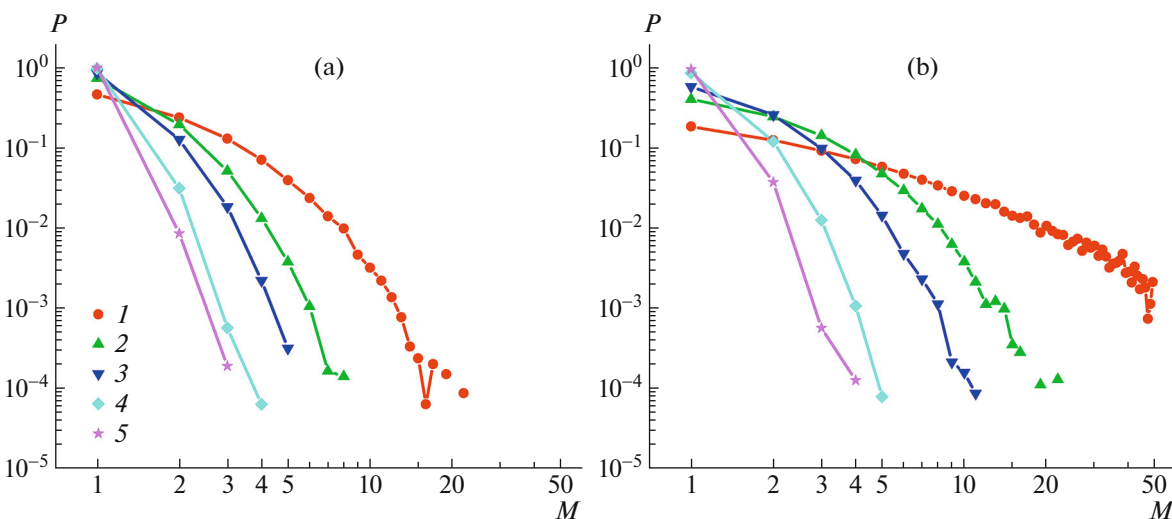


Fig. 3. (Color online) Probability P to find the polar group in the cluster of M polar groups at electrostatic interaction parameter $\lambda = (a)$ 10 and (b) 16 for flexible ($k = 0$) chain with the fraction of polar groups $f = (1)$ 1/2, (2) 1/3, (3) 1/4, (4) 1/8, and (5) 1/16.

ular state of the dipole chain in the case of bulky side groups is similar to the absence of the collapse of polyelectrolytes (single chains and gels) with bulky counterions [13, 48, 53, 54].

As was noted above, the collapse of the chain with polar groups occurs due to electrostatic attraction between charged backbone units and oppositely charged side groups. At small f values, polar groups are united into ionic clusters. Figure 3 shows the probability P to find the polar group in the cluster composed of M polar groups at parameters of electrostatic interac-

tions $\lambda = 10$ and 16 for a flexible chain with different fractions of polar groups f . For the single polar group (dipole), the aggregation number is $M = 1$; for the aggregate of two dipoles, $M = 2$; etc. With increase both in the fraction of polar groups f and in the value of λ , the maximum aggregation number grows. Note that, in the case of $f = 1/2$, the studied chain contains 64 polar groups, and at $\lambda = 16$, formation of a cluster composed of 40 or more polar groups is possible. High values of the aggregation number are also observed for chains with the fractions of polar groups $f = 1/3$ and

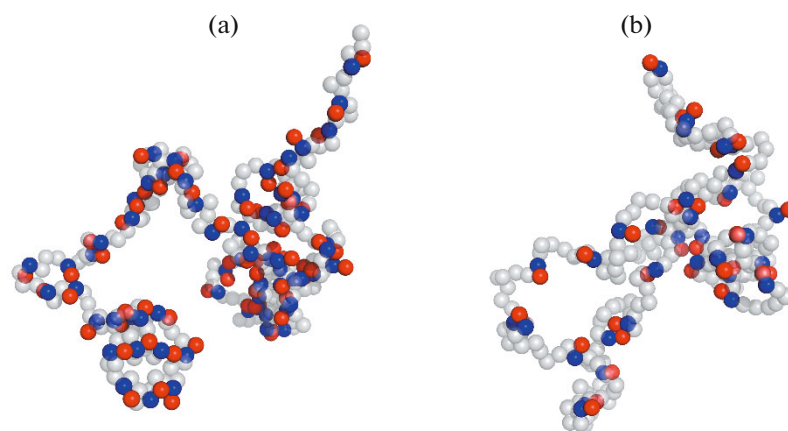


Fig. 4. (Color online) Snapshots of conformation of the chain with the fraction of polar groups $f =$ (a) $1/4$ and (b) $1/8$ at $\lambda = 16$. Gray beads are neutral units, blue beads are charged backbone units, and red beads are oppositely charged side units (color figures are available in the electronic version).

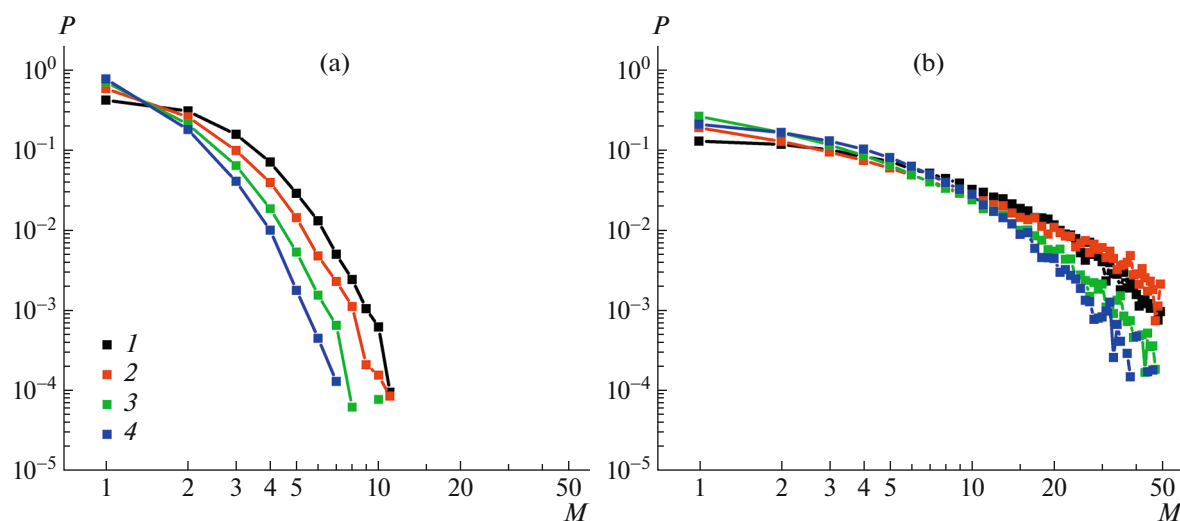


Fig. 5. (Color online) Probability P to find the polar group in the cluster composed of M polar groups at $\lambda = 16$ for the flexible ($k = 0$) chain with the fraction of polar groups $f =$ (a) $1/4$ and (b) $1/2$ at $d =$ (1) 0.75 , (2) 1.0 , (3) 1.25 , and (4) 1.50 .

$1/4$. This is due to the fact that, at high f values, instantaneous chains consisting of alternating charged backbone units and side groups dominate (Fig. 4a)—dipoles tend to align one behind the other into a chain. Similar chain aggregates were observed in polyelectrolyte chains at high values of λ , but only with counterions, whose diameter was much smaller than the size of the monomer unit [48].

At a small amount of polar groups, aggregates composed of two to six polar groups are formed; in Fig. 4b, several quadrupoles are clearly seen.

The probability P to find the polar group in the cluster decreases with the aggregation number M (Fig. 3). However, in low-polar media, distributions are fairly wide, especially in the case of not overly

small f values, so that, for example, for $f = 1/2$, the total amount of aggregates is higher than the amount of single dipoles both at $\lambda = 16$ and 10 .

The formation of clusters composed of polar groups also depends on their sizes. As is clear from Fig. 5, with increasing dipole size, the probability to find it in the single state grows and, accordingly, the probability of cluster formation decreases, which at first glance seems to be counterintuitive. In fact, an increase in the dipole moment should enhance electrostatic interactions facilitating aggregation. However, let us recall that the dipole size increases owing to an increase in the size of the side group, which appears to be very substantial. Taking into account the excluded volume of the side unit in the composition of the dipole makes it possible to reveal regime in which

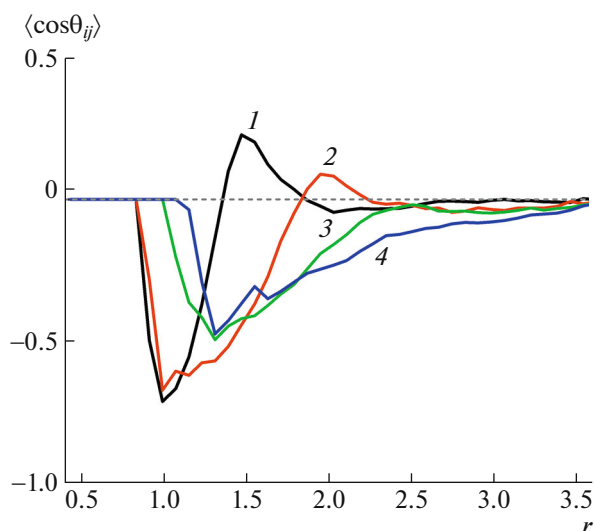


Fig. 6. (Color online) Distribution of mean cosine $\langle \cos \theta_{ij} \rangle$ of angle between dipoles of polar groups as a function of the distance between monomer units of corresponding polar groups. $k = 0$; $\lambda = 16$; $f = 1/4$; $d = (1) 0.75$, (2) 1.0, (3) 1.25, and (4) 1.50.

the excluded volume of side groups preventing the approach of units to each other plays the decisive role.

An analysis of orientational correlations of dipoles of a chain in the space shows that at distances on the order of monomer unit size, dipoles largely orient in an antiparallel manner relative to each other (Fig. 6); this orientation is typical for ionic aggregates composed of two polar groups. For a chain with large side groups, orientational correlations decay to zero at dis-

tances exceeding the size of the polar group. However, at a small size of the side unit ($d = 0.75$ and 1.0), there is the maximum cosine of the angle between the directions of dipoles corresponding to predominantly similarly directed dipoles in aggregates reflecting the formation of dipole chains.

Effect of Stiffness of a Chain with Different Fraction of Polar Groups on Its Conformational Behavior

An increase in the stiffness of the polymer chain, which is described by parameter k in our model, considerably influences the conformational behavior of the polymer chain. In the case of weak electrostatic interactions ($\lambda < 5$), just the value of the parameter k defines the magnitude of the radius of gyration of the polymer chain, which at $k \gg 1$ ceases to depend on the fraction of polar groups. When Coulomb forces dominate in the system ($\lambda > 5$), the stiff chain with $k = 5$ and 10 collapses to a globule in a manner similar to that of a flexible chain (Fig. 7). With increasing k the coil-to-globule transition shifts to higher values of λ , which is associated with competition between a gain in electrostatic interactions and a loss in the potential energy of bending deformation of the chain (Fig. 7b).

A qualitatively different compact structure—torus—is realized at chain stiffness $k = 15$. In [55], formation of the toroidal globule due to electrostatic attraction was observed for the rigid-chain polymer containing 100% polar groups. In this study, it is shown that the torus also exists in the case of reduction in the fraction of polar groups, namely, at $f = 1/2$. Formation of the toroidal globule is well seen on the density distribution of units of the backbone relative to its center of mass (Fig. 8). At $k < 13$, the density is uni-

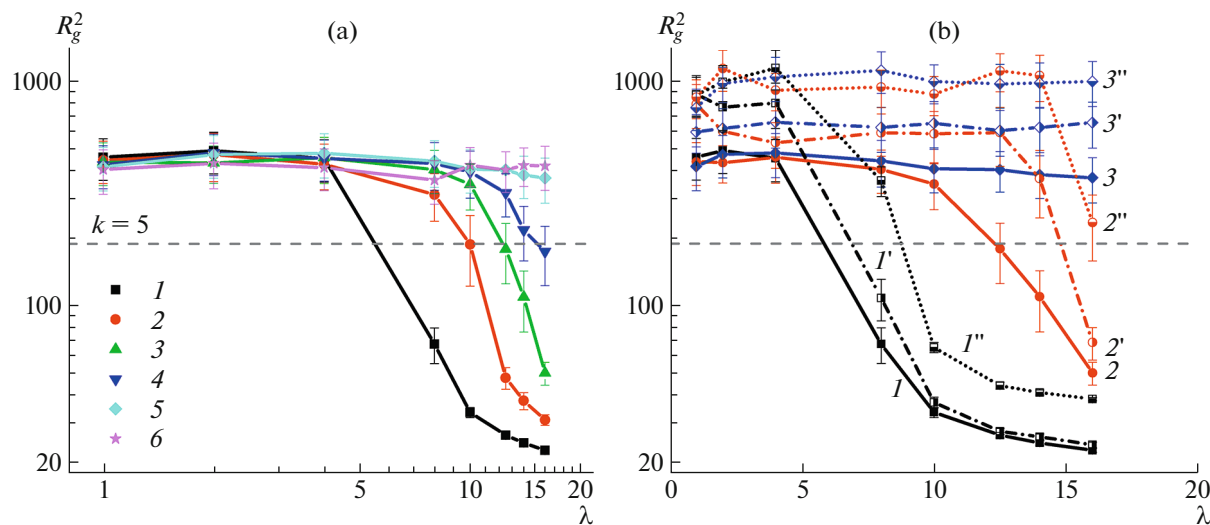


Fig. 7. (Color online) Mean-square radius of gyration R_g^2 of the stiff chain at (a) $k = 5$ and (b) $k = 5, 10$, and 15 with different fraction of polar groups f as a function of electrostatic interaction parameter λ . (a): $f = (1) 1$, (2) 1/2, (3) 1/3, (4) 1/4, (5) 1/8, and (6) 1/16; (b): $k = (I-3) 5$, $(I'-3) 10$, and $(I''-3) 15$; $f = (1, I, I'') 1$, $(2, 2', 2'') 1/3$, and $(3, 3', 3'') 1/8$.

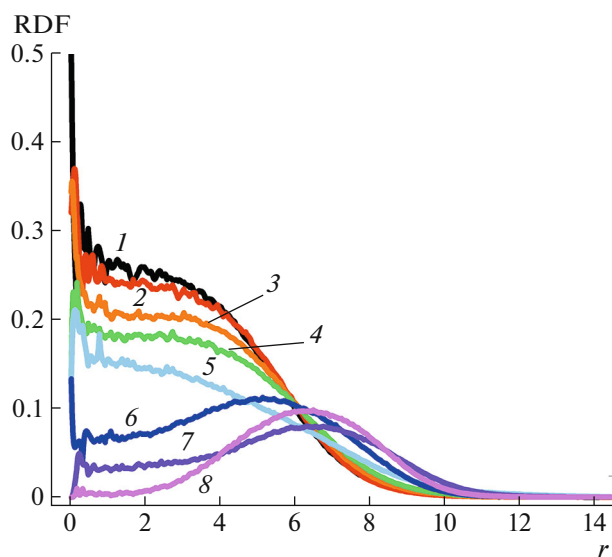


Fig. 8. (Color online) Radial distribution function (RDF) of chain units of different stiffness k with fraction of polar groups $f = 1/2$ at $\lambda = 16$. $k = (1)$ 0, (2) 5, (3) 10, (4) 11, (5) 12, (6) 13, (7) 14, and (8) 15.

form in the center of the compact structure and then decays with increasing distance from the center. This behavior corresponds to the conventional spherical globule. Graphs obtained for stiffer chains with $k \geq 13$ qualitatively differ from the analogous graphs for flexible chains: chain units are arranged in a layer at a certain distance from the center of mass of the structure and in the center their density decays almost to zero; the given distribution corresponds to the torus conformation (Fig. 9a). Note that, because polar groups are regularly distributed along chain, the torus is represented by several chain turns connected by “links”—clusters of polar groups. This is especially evident on snapshots of metastable conformations, toroidal and cylindrical structures, in the case of $f = 1/3$ (Fig. 9b).

The presence of several metastable states of the dipole chain with the fraction of polar groups $f = 1/3$ is well seen on the histogram of distribution of its gyration radius at $\lambda = 16$ and $k = 15$ (Fig. 10b), which in contrast to the case of $f = 1/2$ (Fig. 10a) shows several peaks. In the range of small R_g values, a peak corresponds to the torus, medium values correspond to the cylindrical structure, and high values correspond to the extended conformation. As was shown in [55], the stiff chain composed of 256 units, each of which is a dipole, forms a stable toroidal conformation in the case of considerable electrostatic interactions. However, the presence of several metastable states is characteristic of shorter chains ($N = 128, 64,$ and 32) with the 100% content of polar groups. Thus, reduction in the fraction of dipoles in the composition of the rigid-chain polymer in much the same way as decrease in chain length leads to destabilization of the toroidal globule and causes appearance of metastable states. It should be mentioned that the coexistence of several metastable states was previously observed for short stiff neutral chains under poor solvent conditions [46], block copolymers with alternating flexible and stiff blocks [56], and polyelectrolyte chains with multivalent ions [57]. In the latter case, the driving force of chain collapse was electrostatic interactions likewise in the case considered in this study. Despite a certain identity in the behavior of rigid-chain uncharged polymers, polyelectrolytes, and dipolar macromolecules in low-polar media, the detailed structure of the globular conformations being formed is determined by both the structural features of chains and the origin of intramolecular interactions [41–46, 55, 57].

CONCLUSIONS

The conformational behavior of a single semiflexible polymer chain with a variable fraction of polar groups (dipoles) was studied by molecular dynamics simulation. The dipoles were simulated directly as two oppositely charged beads, one of which belonged to the backbone and the other was the side group. The

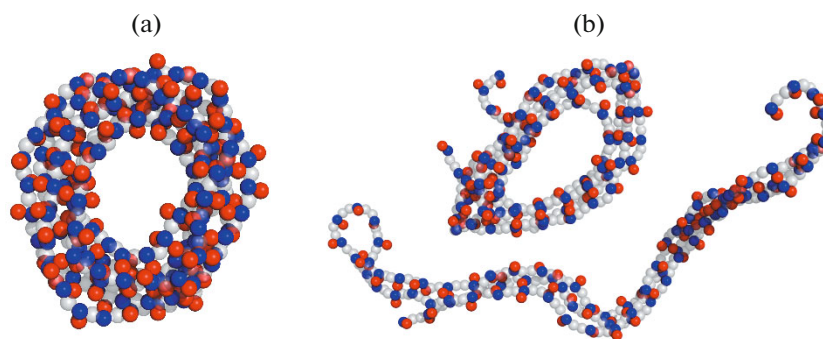


Fig. 9. (Color online) Snapshots of chain conformations with the fraction of polar groups $f = (a)$ 1/2 and (b) 1/3 at $\lambda = 16$ and $k = 15$. Gray beads are neutral units, blue beads are charged backbone units, and red beads are oppositely charged side groups. Color figures are available in the electronic version.

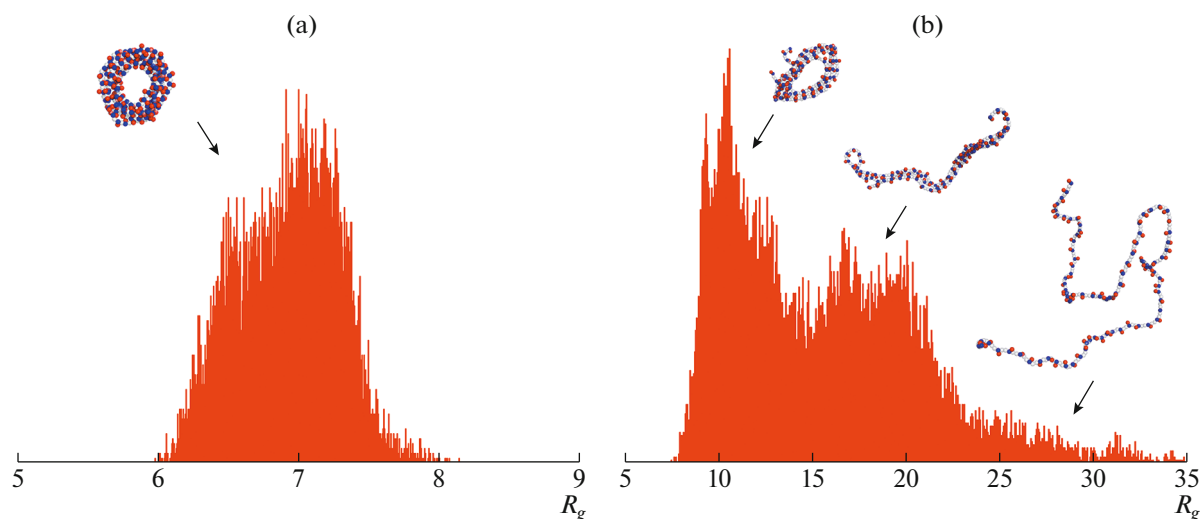


Fig. 10. (Color online) Histograms of distribution of root-mean-square radius of gyration of chain R_g with the fraction of polar groups $f =$ (a) $1/2$ and (b) $1/3$ at $\lambda = 16$ and $k = 15$. Chain conformation snapshots are shown in accordance with the observed peaks.

advanced model of the dipole chain may be used to describe real systems, such as polyelectrolytes in low-polar solvents, macromolecules with zwitter-ionic groups, and dielectric elastomers.

The main direction of the study concerns analysis of the effect of stiffness of the backbone and an interplay of excluded volume and electrostatic interactions on the conformational behavior of the chain and the structure of ionic aggregates formed due to strong electrostatic attraction of charges in low-polar media.

The persistence length \tilde{l} of the backbone was defined by the stiffness parameter k of bending deformation potential, $\tilde{l} \sim k$ at $k \gg 1$ and chains from flexible ($k = 0$) to stiff ($k = 15$) were simulated. The fraction of regularly distributed polar groups of the polymer f was varied from 1 to $1/16$, and the length of their dipole moment $|\mathbf{d}|$ was varied in the range from 0.75 to 1.50. Cases of both weak ($\lambda = 1$) and strong ($\lambda = 16$) electrostatic interactions in the system were considered.

In polar media, a flexible polymer chain swells with increasing fraction of polar groups due to the excluded volume of side groups. In a low-polar solvent at $\lambda \gg 1$, the conformational behavior of the dipole chain considerably depends on the size of polar groups. If the size of the side group is on the order of or smaller than the size of the backbone monomer unit, an increase in the fraction of polar groups leads to the collapse of the chain due to electrostatic interactions of charged units. If side groups are sufficiently large, then the contribution of their excluded volume prevails over electrostatic attraction and the chain remains swollen even at $\lambda \gg 1$.

Collapse of the chain is accompanied by the formation of ionic aggregates. It was shown that the highest possible aggregation number at the fixed value of parameter λ diminishes with decreasing fraction of polar groups. The characteristic morphology of ionic aggregates at $f = 1/2$ is instantaneous dipole chains including almost all polar groups of the chain, while for chains with a low fraction of dipoles $f = 1/16$ aggregates containing two polar groups united into a quadrupole dominate.

As the stiffness of the chain increases, the region of the coil-to-globule transition shifts to higher values of electrostatic interaction parameter, which is associated with the enhanced competition between the gain in electrostatic interactions and the loss in the potential energy of bending deformation. In the case of stiff chains ($k = 15$) and a significant fraction of polar groups ($f = 1/2-1/3$), the compact conformation of the torus is realized instead of the spherical globule. It is demonstrated that, at the fixed value of $\lambda \gg 1$, reduction in the fraction of dipoles in the chain entails destabilization of the toroidal globule. Specifically, if at $\lambda = 16$ stiff chains consisting of 256 backbone units with the fractions of dipoles $f = 1$ and $f = 1/2$ form stable tori, then for chains with the fraction of polar groups $f = 1/3$ there is the coexistence of several metastable states: torus, cylindrical globule, and extended conformation. As the fraction of polar groups decreases further ($f \leq 1/4$), the chain does not collapse at all.

Our study of the conformational behavior of a single polymer chain with variable stiffness and different fraction and size of polar groups in low-polar media lays the basis for deeper understanding of the micro-

scopic picture of ionic aggregates formed by dielectric polymers containing groups with the permanent dipole moment.

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