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Concentration Dependence of Ring Polymer Conformations from Monte Carlo Simulations

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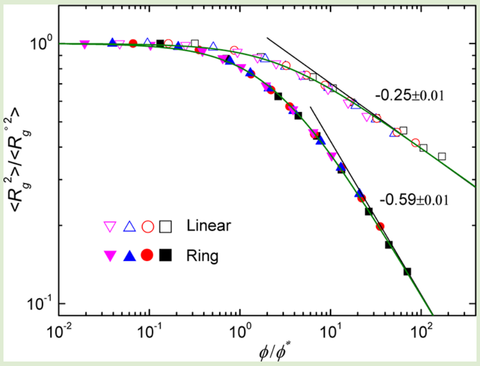
ABSTRACT: The concentration dependence of the conformations of ring polymers is investigated by lattice Monte Carlo simulations and compared with that of linear polymers. The relative radii of gyration of linear polymers follow a universal master curve as a function of the scaled concentration for various chain lengths, with a scaling relationship $\langle R_g^2 \rangle \sim \phi^{-0.25}$, which is consistent with scaling theory and neutron scattering experiments. Ring polymers of different lengths also follow a universal behavior with a broad crossover to a scaling behavior $\langle R_g^2 \rangle \sim \phi^{-0.59}$ for long chains. The scaling relationship between the concentration dependence and the chain-length dependence of the radius of gyration implies $\langle R_g^2 \rangle \sim N^{0.72}$, indicating highly collapsed conformations for long-chain ring polymers in the melt.



DNA is often found in the form of a ring in nature; plasmids in bacteria, mitochondrial DNA in eukaryotic cells, and DNA in λ phages have a circular form, for example.[1] The existence of long DNA of a meter size in a micrometer-size cell nucleus raises an intriguing question on how they are packed and sustained in a collapsed state.[2] In higher eukaryotic cells such as mammalian cells, chromosomes are highly compressed in the cell nucleus, not mixed together, and occupy a spatially limited region.[3] Recently, the visual conformation of chromosome territories was proposed to be analogous to that of ring polymers in melts.[4] In this regard, it is now well demonstrated that unknotted and nonconcatenated pure ring polymers in concentrated solutions or melts show markedly different conformations and dynamics as compared with linear polymers due to strong topological constraints.[5−12] However, the detailed understanding of both conformations and dynamics of ring polymers in concentrated solutions or melts are still lacking. Moreover, further studies of ring polymers are needed to provide a detailed understanding of more complicated systems such as knotted or concatenated ring polymers[13−16] and blends of linear and ring polymers,[17,18] which show significantly different physical properties from pure linear or ring polymer systems.

It is well known that linear polymers in concentrated solutions or melts approach an ideal Gaussian coil due to the balance of inter- and intramolecular excluded-volume interactions.[19−21] In dilute solutions of good solvents, the dominant contribution of the volume repulsion induces a swelling of polymers. For linear polymers, the transition from a swollen to an unperturbed Gaussian coil above the overlap concentration was shown by scaling theory, computer simulations, and neutron scattering experiments to follow a scaling behavior of the mean-square radius of gyration $\langle R_g^2 \rangle \sim \phi^{-0.25}$ as a function of polymer concentration ϕ.[21−24]

On the other hand, ring polymers exhibit collapsed conformations quite different from an unperturbed Gaussian coil in concentrated solutions or melts, while it is a swollen coil in dilute solutions of good solvents just like linear polymers.[25,26] The precise nature of collapsed conformations of rings in melts is still debated,[9,27−35] because the preparation of unknotted and nonconcatenated pure ring polymers of high molecular weights is a very challenging experimental task[6−10] and a huge computational time is required to fully simulate long-chain ring polymers.[32,36−38]

In this letter, the conformational changes of ring polymers with the concentration are studied and compared with the results for linear chains. The computational necessity to simulate the long chains within the reasonable simulation-time window is met by using an efficient lattice-based Monte Carlo (MC) simulation method.[30,36,37]

In this coarse-grained polymer model, repeating chemical units are replaced by a bead occupying a single site on a three-dimensional cubic lattice. Two nearest-neighbor beads are linked to form a bond, and a polymer chain consists of N beads, which correspond to the chain length. The system is filled with N_{ch} chains, in the periodic boundary conditions, which gives the density $\phi = N \cdot N_{ch}/V$, where $V = L^3$ and L is the length of the cubic simulation box. The movement of ring polymers consists

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of three kinds of motion comprised of the wedge-flip motion, the kink-rotation motion, and the kink-diffusion motion. The movement of linear polymers is the same as for the rings except that the end-bond motion replaces the wedge-flip motion at the chain ends. The kink-diffusion motion as a nonlocal movement has the advantage to speed up the relaxation time of polymers and reduce the computational time.[30,36,37] The excluded-volume effect, which is the condition that two distinct beads are forbidden to occupy the same lattice site, is imposed to ensure the topological constraints, not allowing the bond crossings between the chain segments and retaining the unknotted and nonconcatenated conformations as constructed from the initial configurations. The simulation time is given in units of attempted Monte Carlo steps (MCS) per bead in the simulation; that is, $N_{ch} \times N$ of the attempted moves constitute one MCS and the lattice spacing is unity. The wedge-flip, the kink-rotation, and the kink-diffusion motions are performed with the probability 1/4, 1/4, and 1/2, respectively. The systems are fully equilibrated by executing more than $\tau \sim O(10^8)$ MCS, including the kink-diffusion motion. During that time, the center of mass of polymer chains moves the distance of approximately four times of R_g even for the longest chain with $N = 5000$. The simulation box size L is approximately three times that of R_g to avoid the periodic boundary artifacts. The entanglement length of the simulated linear chain is approximately $N_e \approx 132$ at the density $\phi = 0.8$.[30]

The size of linear and ring polymers is characterized by the mean-square radius of gyration, $\langle R_g^2 \rangle$, as a function of the chain length N. Figure 1 shows the results for the highest concentrations (or melts) with $\phi = 0.8$. The data are obtained by time- and ensemble-averaging over N_{ch} chains after the system is equilibrated by calculating at every 10^5 MCS until reaching 10^8 MCS. The mean-square radius of gyration for linear polymers scales as $\langle R_g^2 \rangle \sim N^{1.03\pm0.02}$ for $N \geq 700$ and that of ring polymers shows $\langle R_g^2 \rangle \sim N^{0.72\pm0.04}$ for $N \geq 1000$. The recent simulation using the same MC method in the concentration $\phi = 0.5$ shows $\langle R_g^2 \rangle \sim N^{0.75\pm0.02}$ for rings in the long-chain regime,[30] when replotted and critically analyzed. (Since the value of ν continues to decrease with the concentration for ring polymers, it is difficult to see how a collapsed globular state with $2\nu = 2/3$ can be observed for $\phi = 0.5$, as claimed in previous publications.[30−33]) The scaling behavior $\langle R_g^2 \rangle \sim N^{2\nu}$ of ring polymers exhibits highly collapsed conformations with $2\nu = 0.72$, which is smaller than a Gaussian chain ($2\nu = 1.0$)[19−21] or a partially collapsed conformation ($2\nu = 0.8$) previously reported,[27−29] but larger than a crumpled globule structure ($2\nu = 2/3$)[30−33] or a lattice animal with screened excluded-volume interactions ($2\nu = 1/2$).[9,19,34,35] Interestingly, the observed value $2\nu = 0.72$ is close to $2\nu = 0.75$ predicted in a certain range of chain lengths for ring polymers,[16] but the predicted transition to $2\nu = 8/9$ at larger chain lengths is not indicated by our results in Figure 1. Also, although the topological constraints are quite different, branched sponge polymers with screened excluded-volume interactions are predicted to exhibit $2\nu = 11/15$;[39] this may imply that complex topological effects in general tend to significantly shrink the spatial conformations in polymer melts.

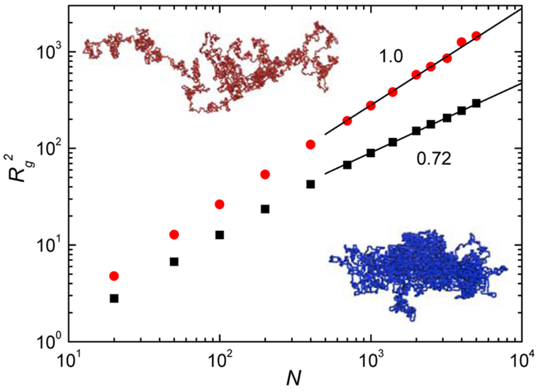

Figure 1. The mean-square radius of gyration $\langle R_g^2 \rangle$ for linear (red) and ring (black) polymers as a function of the chain length N in melts with $\phi = 0.8$. The linear chain results are fitted by an ideal Gaussian model. Sample snapshots of linear and ring polymers with $N = 5000$, viewed along a short principle axis, are shown in the upper left (red) and the lower right (blue) corner, respectively.

In Figure 2a the concentration dependence of the scaling exponents ν of the relationship $\langle R_g^2 \rangle \sim N^{2\nu}$ are shown as a function of the polymer concentration ϕ for linear and ring polymers (for $N \geq 1000$). The concentrations are changed from a very dilute solution $\phi = 0.0015$ to a highly concentrated solution (melt) $\phi = 0.8$. For $\phi = 0.0015$, the exponents for the linear and the ring polymer are given by $\nu = 0.587 \pm 0.004$ and 0.587 ± 0.001, respectively. The exponent for the linear chains is consistent with the value, $\nu = 0.588 \pm 0.001$ obtained from the renormalization group theory,[20] and the exponent for the ring polymers is also consistent with previous theories and simulations.[25,26,36,40] The swollen coil conformations of linear and ring polymers begin to change when the concentration exceeds the overlap concentration ϕ^*. As the concentration increases, the value of ν for linear polymers reaches a plateau of $\nu = 0.5$ expected for an ideal Gaussian coil, whereas the ν values for ring polymers continue to decrease with the concentration to yield a value $\nu = 0.36 \pm 0.02$ for $\phi = 0.8$.

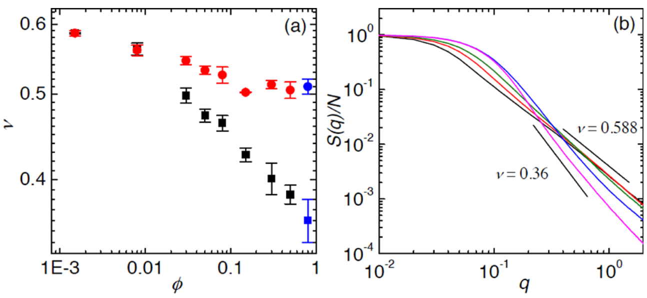

Figure 2. (a) Variation of the exponent ν versus the concentration ϕ as determined from the fit $\langle R_g^2 \rangle \sim N^{2\nu}$. The red circles and the black squares correspond to the linear and the ring polymers obtained in the long-chain regime with $1000 \leq N \leq 5000$. The two blue points for $\phi = 0.8$ correspond to the scaling exponents for the long-chain regime obtained from the results in Figure 1. (b) Static structure factors $S(q)$ of ring polymers with $N = 5000$ are shown for various concentrations: ϕ = 0.0015 (black), 0.03 (red), 0.08 (green), 0.3 (blue), 0.8 (magenta). Two straight lines correspond to the case of $\nu = 0.588$ and 0.36, respectively.

The static structure factors of ring polymers with $N = 5000$ for various concentrations are shown in Figure 2b. The static structure factor[19−21] is given by

$$S(q) = \frac{1}{N}\langle |\sum_{i=1}^{N} \exp(i\mathbf{q}\cdot\mathbf{r_i})|^2 \rangle \tag{1}$$

where $\mathbf{q}$ is the scattering vector and $\mathbf{r}_i$ is the position vector of the monomers. In the small q regime, the increase in $S(q)$ with the concentration is consistent with the overall compact conformation of rings and the development of local loop structures in high concentrations.[10,11,32] In the intermediate q regime, the self-similar structures are exhibited by displaying $S(q) \sim q^{-1/\nu}$ scaling behavior.[21−23] The variations of observed $S(q)$ for $N = 5000$ with the concentration, as expressed by ν from $S(q) \sim q^{-1/\nu}$, show a good agreement with the scaling exponent ν directly calculated from $\langle R_g^2\rangle \sim N^{2\nu}$ at each concentration.

The relative mean-square radii of gyration $\langle R_g^2\rangle/\langle R_g^{\circ 2}\rangle$ are shown in Figure 3 as a function of the scaled concentration ϕ/ϕ^* for various chain lengths. The R_g° is the radius of gyration in the dilute solutions and ϕ^* is the overlap concentration, which is expected to be comparable with the local concentration inside a single coil, expressed by $\phi^* = 3N/(4\pi\langle R_g^{\circ 2}\rangle^{3/2})$. The first notable aspect is that all the data points for linear and ring polymers are superimposed on respective master curves, represented by $\langle R_g^2\rangle/\langle R_g^{\circ 2}\rangle = (1 + \alpha\cdot\phi/\phi^*)^\beta$ with specific parameters α and β. The linear polymers exhibit the expected universal scaling behavior $\langle R_g^2\rangle/\langle R_g^{\circ 2}\rangle \sim (\phi/\phi^*)^{-0.25}$ above 10 times the overlap concentration. This result is in good agreement with the previous neutron scattering experiment by Daoud et al.,[24] who reported the concentration-scaling exponent for linear polystyrene chains to be −0.25 ± 0.02, and also with recent computer simulations.[23] Interestingly and remarkably, all the data points of ring polymers with different chain lengths are also nicely superimposed on a master curve with the scaling value $\beta = -0.59 \pm 0.01$, which is quite different from the previously reported results for which $\beta \geq -0.5$ (−0.5,[12] −0.34,[15] and −0.42,[16] respectively). This difference is most likely due to the narrower range of chain lengths and concentrations in previous studies, as shown by the dashed line fitted by using fixed $\beta = -0.5$. Although this fit may seem reasonable for $\phi/\phi^* < 10$, its shortcomings are clearly seen for $\phi/\phi^* > 10$ corresponding to the high chain lengths and concentrations that are not included in previous studies.

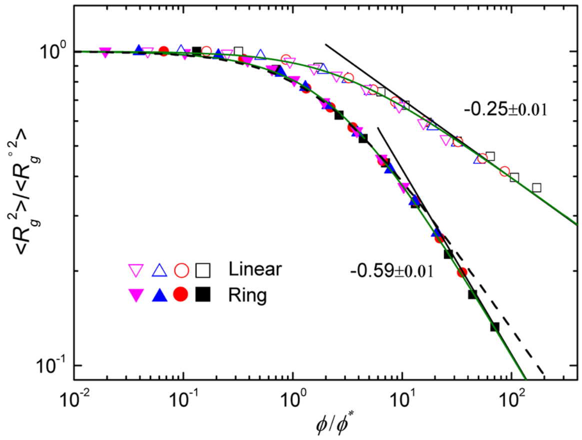

Figure 3. Relative mean-square radii of gyration $\langle R_g^2\rangle/\langle R_g^{\circ 2}\rangle$ vs the scaled concentration ϕ/ϕ^* for the various chain length N = 400 (magenta), 1000 (blue), 2000 (red), and 5000 (black). The open and closed symbols correspond to the linear and ring polymers, respectively. All the data points of the linear and ring polymer are superimposed on respective master curves, which are shown by green lines. The scaling behaviors of the long chains are shown with black straight lines with scaling values. The master curves for linear and ring polymers are given by $\langle R_g^2\rangle/\langle R_g^{\circ 2}\rangle = (1 + \alpha\cdot\phi/\phi^*)^\beta$, with $\alpha = 0.4$ and $\beta = -0.25$ for linear chains and $\alpha = 0.43$ and $\beta = -0.59$ for ring polymers, respectively. The dashed line is fitted by using fixed $\beta = -0.5$ (with $\alpha = 0.57$) to emphasize the importance of including the results for the high chain lengths and concentrations.

From this concentration scaling exponent, one can estimate the scaling behavior of chain-length dependence of radius of gyration in concentrated solutions. In concentrated solutions, the radius of gyration scales as $R_g \sim R_g^\circ(\phi/\phi^*)^m$ as a function of the concentration ϕ/ϕ^*.[19−21] The radius of gyration in dilute solutions scales as $R_g^\circ \sim N^{\nu_0}$ and the overlap concentration as $\phi^* \sim N/(R_g^\circ)^3 \sim N^{1-3\nu_0}$, where ν_0 is the scaling exponent in dilute solutions. By considering the relation, $R_g \sim R_g^\circ(\phi/\phi^*)^m \sim N^\nu$ in highly concentrated solutions or melts, where ν is the scaling exponent, the relation between ν and m is given by

$$\nu = \nu_0 - (1 - 3\nu_0)m \tag{2}$$

Hence, the chain-length exponent ν can be estimated from the observed concentration exponent of m. By taking $\nu_0 = 0.588$ and $m = \beta/2$, we get $\nu \approx 0.36$, which is in good agreement with the exponent $2\nu = 0.72$ obtained from the data of Figure 1.

As shown in Figure 3, the ring polymer shows a more pronounced conformational change with the concentration, as compared with the linear chains. This conformation change is also reflected in the overall shape of polymers. The shape characteristics of linear and ring polymers as a function of the concentration for $N = 5000$ is shown in Figure 4. The shape of polymer may be characterized by the eigenvalues of the radius of gyration tensor $\mathbf{T}$,[36,41−48] which is defined by

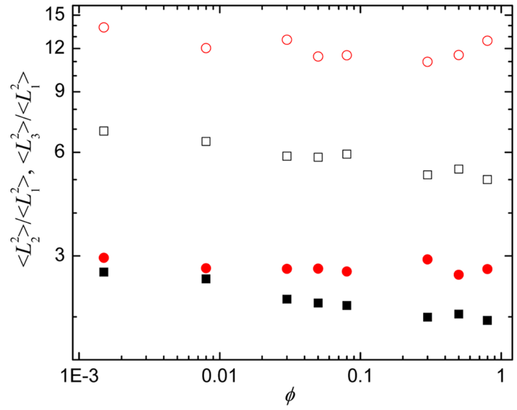

Figure 4. Eigenvalue ratios $\langle L_2^2\rangle/\langle L_1^2\rangle$ and $\langle L_3^2\rangle/\langle L_1^2\rangle$ of the radius of gyration tensor $\boldsymbol{T}$ as a function of the concentration ϕ for $N = 5000$. The red circles and the black squares correspond to the linear and the ring polymers. The closed and the open symbols stand for $\langle L_2^2\rangle/\langle L_1^2\rangle$ and $\langle L_3^2\rangle/\langle L_1^2\rangle$, respectively.

$$\mathbf{T}_{ij} = \frac{1}{N}\sum_{l=1}^{N}(x_{il} - \langle x_i\rangle)\left(x_{jl} - \left\langle x_j\right\rangle\right) \tag{3}$$

where x_{il} is the ith component of the lth bead position vector and $\langle x_i\rangle$ is the ith component of the polymer center-of-mass position vector. The eigenvalues of $\mathbf{T}$ are the squares of the principal radii, L_i^2 for $1 \leq i \leq 3$ ($L_1^2 \leq L_2^2 \leq L_3^2$). In the dilute solution with $\phi = 0.0015$, the ratio of $\langle L_1^2\rangle$:$\langle L_2^2\rangle$:$\langle L_3^2\rangle$ for the linear polymer gives 1:3.0:13.8, which represents a prolate conformation, as expected.[48] In highly concentrated solutions or melts of $\phi = 0.8$, the prolate shape of linear polymers is less extended with the ratio $\langle L_1^2\rangle$:$\langle L_2^2\rangle$:$\langle L_3^2\rangle$ = 1:2.9:11.2.[30,32,43,48]

On the other hand, the ring polymer shows $\langle L_1^2 \rangle$:$\langle L_2^2 \rangle$:$\langle L_3^2 \rangle$ = 1:2.7:6.9 for $\phi = 0.0015$, which is a less extended prolate than that of a linear polymer, as expected.[48] As the concentration increases, the anisotropy of the ring-polymer shape decreases overall, and in the melt ($\phi = 0.8$), the ring polymer is strongly collapsed, but the shape still remains prolate with $\langle L_1^2 \rangle$:$\langle L_2^2 \rangle$:$\langle L_3^2 \rangle$ = 1:2.0:5.2.[30,32,43,48]

In this study, the conformational properties of ring polymers as a function of the concentration have been investigated by using the MC simulation method. The linear chains show a transition behavior from a swollen coil to an ideal Gaussian coil with increasing concentration. All the data points of relative radii of gyration with different chain lengths in terms of scaled concentrations are nicely superimposed on a master curve, which gives the experimentally observed scaling behavior, $\langle R_g^2 \rangle \sim \phi^{-0.25}$. In comparison, ring polymers also show a swollen coil conformation in dilute solutions, just like linear polymers, but they assume a highly collapsed non-Gaussian conformation at highly concentrated solutions or melts. Remarkably, all the data points of relative radii of gyration, plotted as a function of scaled concentrations, are also nicely superimposed on a master curve with the scaling behavior $\langle R_g^2 \rangle \sim \phi^{-0.59}$. By adopting this scaling behavior with the concentration for long chains, we obtain the scaling relation $\langle R_g^2 \rangle \sim N^{0.72}$, which is consistent with the scaling behavior obtained directly from the chain length dependence in melts. We would like to point out that this relationship between the exponents of the concentration and of the chain length dependence suggests an experimentally feasible way to investigate the conformational properties of ring polymers. That is, the study of the polymer conformations as a function of the concentration will provide the dependence of their conformations on the chain length. Although the ring polymer is strongly collapsed in melts, the instantaneous shape still remains quite anisotropic with $\langle L_1^2 \rangle$:$\langle L_2^2 \rangle$:$\langle L_3^2 \rangle$ = 1:2.0:5.2, which is expected to be important in understanding the chain dynamics of entangled melts.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Berg, J. M.; Tymoczko, J. L.; Stryer, L. *Biochemistry*, 5th ed.; W. H. Freeman and Company: New York, 2002.
(2) Grosberg, A. Y. *Polym. Sci., Ser. C* **2012**, *54*, 963.
(3) Meaburn, K. J.; Misteli, T. *Nature* **2007**, *445*, 379.
(4) Vettorel, T.; Grosberg, A. Y.; Kremer, K. *Phys. Today.* **2009**, *62*, 72.
(5) Robertson, R. M.; Smith, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 4824.
(6) Roovers, J. *Macromolecules* **1985**, *18*, 1359.
(7) Mckenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 498.
(8) Kawaguchi, D.; Masuoka, K.; Takano, A.; Tanaka, K.; Nagamura, T.; Torikai, N.; Dalgliesh, R. M.; Langridge, S.; Matsushita, Y. *Macromolecules* **2006**, *39*, 5180.
(9) Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. *Nat. Mater.* **2008**, *7*, 997.
(10) Brás, A. R.; Pasquino, R.; Koukoulas, T.; Tsolou, G.; Holderer, O.; Radulescu, A.; Allgaier, J.; Mavrantzas, V. G.; Pyckhout-Hintzen, W.; Wischnewski, A.; Vlassopoulos, D.; Richter, D. *Soft Matter* **2011**, *7*, 11169.
(11) Hur, K.; Winkler, R. G.; Yoon, D. Y. *Macromoleclues* **2006**, *39*, 3975.
(12) Iyer, B. V. S.; Shanghag, S.; Juvekar, V. A.; Lele, A. K. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 2370.
(13) Sogo, J. M.; Stasiak, A.; Martínez-Robles, M. L.; Krimer, D. B.; Hernández, P.; Schvartzman, J. B. *J. Mol. Biol.* **1999**, *286*, 637.
(14) Grosberg, A. Y. *Phys. Rev. Lett.* **2000**, *85*, 3858.
(15) Rosa, A.; Orlandini, E.; Tubiana, L.; Micheletti, C. *Macromolecules* **2011**, *44*, 8668.
(16) Lang, M.; Fischer, J.; Sommer, J.-U. *Macromolecules* **2012**, *45*, 7642.
(17) Halverson, J. D.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. *Phys. Rev. Lett..* **2012**, *108*, 038301.
(18) Iyer, B. V. S.; Lele, A. K.; Shanbhag, S. *Macromolecules* **2007**, *40*, 5995.
(19) Grosberg, A. Y.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; American Institute of Physics: New York, 1994.
(20) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(21) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(22) Paul, W.; Binder, K.; Heermann, D. W.; Kremer, K. *J. Phys. II (Paris)* **1991**, *1*, 37.
(23) Huang, C.-C.; Winkler, R. G.; Sutmann, G.; Gompper, G. *Macromolecules* **2010**, *43*, 10107.
(24) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(25) des Cloizeaux, J. *J. Phys. Lett.* **1981**, *42*, L433.
(26) Baumgärtner, A. *J. Chem. Phys.* **1982**, *76*, 4275.
(27) Cates, M. E.; Deutsch, J. M. *J. Phys. (Paris)* **1986**, *47*, 2121.
(28) Brown, S.; Szamel, G. *J. Chem. Phys.* **1998**, *109*, 6184.
(29) (a) Müller, M.; Wittmer, J. P.; Cates, M. E. *Phys. Rev. E* **1996**, *53*, 5063. (b) Müller, M.; Wittmer, J. P.; Cates, M. E. *Phys. Rev. E* **2000**, *61*, 4078.
(30) Vettorel, T.; Grosberg, A. Y.; Kremer, K. *Phys. Biol.* **2009**, *6*, 025013.
(31) Suzuki, J.; Takano, A.; Deguchi, T.; Matsushita, Y. *J. Chem. Phys.* **2009**, *131*, 144902.
(32) Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. *J. Chem. Phys.* **2011**, *134*, 204904.
(33) (a) Sakaue, T. *Phys. Rev. Lett.* **2011**, *106*, 167802. (b) Sakaue, T. *Phys. Rev. E* **2012**, *85*, 021806.
(34) Obukhov, S. P.; Rubinstein, M.; Duke, T. *Phys. Rev. Lett.* **1994**, *73*, 1263.
(35) Khokhlov, A. R.; Nechaev, S. K. *Phys. Lett.* **1985**, *112A*, 156.
(36) Jagodzinski, O.; Eisenriegler, E.; Kremer, K. *J. Phys. I (France)* **1992**, *2*, 2243.
(37) Vettorel, T.; Reigh, S. Y.; Yoon, D. Y.; Kremer, K. *Macromol. Rapid Commun.* **2009**, *30*, 345.
(38) Hur, K.; Jeong, C.; Winkler, R. G.; Lacevic, N.; Gee, R. H.; Yoon, D. Y. *Macromolecules* **2011**, *44*, 2311.
(39) Douglas, J. F. *Phys. Rev. E* **1996**, *54*, 2677.
(40) des Cloizeaux, J.; Mehta, M. L. *J. Phys. (Paris)* **1979**, *40*, 665.
(41) Kuhn, W. *Kolloid Z.* **1934**, *68*, 2.
(42) Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756.
(43) (a) Šolc, K. *J. Chem. Phys.* **1971**, *55*, 335. (b) Šolc, K. *Macromolecules* **1973**, *6*, 378.
(44) Fuereder, I.; Zifferer, G. *J. Chem. Phys.* **2011**, *135*, 184906.

(45) Aronovitz, J. A.; Nelson, D. R. *J. Phys. (Paris)* **1986**, *47*, 1445.
(46) Diehl, H. W.; Eisenriegler, E. *J. Phys. A: Math. Gen.* **1989**, *22*, L87.
(47) Rudnick, J.; Gaspari, G. *Science* **1987**, *237*, 384.
(48) Bishop, M.; Michels, J. P. J. *J. Chem. Phys.* **1985**, *82*, 1059.