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Microphase separation in topologically constrained ring copolymers

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This paper presents results of the Monte Carlo simulation of dense melts of symmetric diblock copolymer rings using the cooperative motion algorithm. Due to topological constraints, i.e., the entire absence of entanglements prevents the self-avoiding ring melts from adopting Gaussian statistics, and the scaling exponent ν is found to be $\nu=0.45\pm0.01$, where the radius of gyration R_g scales with chain length N as $R_g \sim N^{\nu}$. The loss of entropy due to the missing chain ends of the rings reduces the microphase separation transition temperature in block copolymer rings with respect to dense melts of linear diblock copolymers by almost 40%. This compares surprisingly well to random phase approximation calculations. With decreasing temperature the copolymer rings strongly stretch in the direction of the axis connecting the two centers of mass of the block. The symmetric diblock copolymer rings undergo a microphase separation transition into a lamellar structure with a wavelength smaller than that for linear diblock copolymers by a factor 0.51–0.55.

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Topological problems are of significant importance in many fields of physics [1,2]. Many different applications are the result of special topological properties of field theories. Polymer scientists are in an extraordinary position since polymer molecules of special topology can be produced [3].

Polymer rings are a basic example for such topologically constrained systems. Even without any selective A-B interaction among the monomers rings are expected to show a behavior from linear chains. The rings considered in this paper are not entangled with each other, nor are they self-knotted. These topological constraints prevent the rings from adopting Gaussian statistics. Several disputed scaling arguments are discussed in the literature [4,5]. A correct theoretical description of cyclic diblock copolymers with partially incompatible blocks has, however, not yet been given. The random phase approximation (RPA) deals with the copolymer rings as providing ideal Gaussian behavior [6,7]. Obviously this assumption is rather crude. Moreover the loss of entropy due to the connection of the chain ends of the rings may reduce the microphase separation transition temperature with respect to the corresponding dense melts of similar linear diblock copolymers. With decreasing temperature the copolymer rings change their conformation. The symmetric diblock copolymer rings undergo a microphase separation transition into a lamellar structure.

The cooperative motion algorithm (CMA) allows to simulate dense polymer melts on a lattice [8–10]. To our knowledge the CMA is the only lattice algorithm for the simulation of dense, incompressible, and monodisperse polymeric systems in contrast to the bond breaking algorithm [11]. In the CMA every lattice site is occupied by one and only one monomer. Real polymer systems are compressible and so in a more realistic simulation vacancies have to be introduced. The reason for using the CMA in this study is twofold. First the usual formulation of the RPA is given in terms of the incompressible limit (which can be relaxed simply [12]), and second the algorithm is more effective the fewer vacancies are present. Indeed in a previous publication [13] we have shown that the introduction of vacancies in this algorithm is possible. In that work the phase behavior of linear diblock copolymers has been studied where amongst other variables the vacancy concentration has been varied systematically. We succeeded in presenting all results in scaled form, i.e., with master curves, where the vacancy concentration is scaled out. In the case of diblock copolymer rings two chains of either monomer type A or type B are connected at both ends to form the cyclic copolymer with length $N=N_A+N_B$. Additionally the rings are assumed to be nonconcatenated and non-self-entangled.

The volume fractions of the two species A and B are ϕ_A and ϕ_B. As noted earlier the lattice in the CMA is occupied entirely by monomers of the two species, leading automatically to the incompressibility constraint $\phi_A+\phi_B=1$. The two types of monomers are partially compatible and interaction parameters ϵ_{ij} are introduced, i.e., $\epsilon_{AA}=\epsilon_{BB}=0$ and $\epsilon_{AB}=1$. In usual Monte Carlo algorithms new polymer configurations are generated by jumps of monomers onto free sites in the lattice. In dense incompressible systems new chain configurations can be generated by successive cooperative rearrangements of monomers along a closed random path. Technical details of the CMA are summarized in a previous paper [10] and not reconsidered in this study.

The following results are obtained by simulations on a fcc lattice, where the bonds have the length $a=\sqrt{2}$. The possible bond angles are $\alpha=60°, 90°, 120°$, and $180°$ with degeneracy $d_\alpha=4, 2, 4$, and 1. Each of the monomers has $q=12$ nearest neighbors in the simulation. We used

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lattices of sizes $L^3=20^3$ and 24^3 containing 4000 or 6912 monomers, and used ring sizes from $N=16$, 20, 24, 48. These may appear very small, and for a previous study on athermal ring melts a much wider range was used [14]. The aim of this paper is to take into account thermal interactions and concentrate on their effects. Since we already have the correct scaling for the rings of the sizes used in the present study as given by Pakula and Geyler [14] in the athermal limit, small rings are used to decrease the equilibration time. To reduce boundary effects, the usual periodic boundary conditions have been employed. The simulations were performed on DEC stations 5000/120, 5000/125, and 5000/200.

The most effective way of generating an initial configuration for the cyclic polymers in the CMA is to fill the lattice with rings in a totally ordered state, such that no entanglements appear from the beginning. This procedure assures that neither knots nor entanglements of chains occur at any time later in the simulation.

In the athermal melt no AB interactions between the monomers are relevant apart from the overall excluded volume interaction, i.e., $\epsilon=0$ or $k_BT/\epsilon\to\infty$. Depending on the temperature a system with $N=20$, for example, needs a thermalization time of approximately 4.75×10^5 MCS/ring. We sample for a span of around 5.75×10^6 MCS/ring every 1000 MCS/ring, to avoid close correlations between the configurations. Diblock copolymer rings in the athermal limit behave as excluded volume rings in melts. Thus the first step in analysis is to observe the configurations in dense polymer ring melts and to compare the results to melts of linear polymers. It is well known that in dense melts of linear chains the excluded volume interaction is screened and the radius of gyration R_g scales with chain length N as $R_g\sim N^\nu$ with $\nu=0.5$, which is a well-known result [8,10,13,15,16]. Polymer rings may behave differently. In addition to the excluded volume interaction the constraint of nonconcatenation exists. These effects have been estimated using different (scaling) arguments. Khokhlov and Nechaev [4] postulate an exponent $\nu=\frac{1}{3}$, whereas Cates and Deutsch [5] expect $\nu=\frac{2}{5}$ in three dimensions. Pakula and Geyler [9] simulated using the CMA dense melts of polymer rings. For rings of sizes from $N=16$ to 512 they observed ν to be $\nu=0.45$ [8,9]. Although the ring size in the present work is of much narrower range we confirm these results, i.e., $\nu=0.45\pm0.01$ is found. This is slightly higher than the crude estimate of Cates and Deutsch, but obviously smaller than the Gaussian exponent 0.5. Recently we performed a path-integral analysis of the nonconcatenating ring melt where we found an exponent $\nu=0.42$ [17].

The main purpose of this paper is the simulation of the phase behavior of diblock copolymer rings. Therefore only rather *small* rings can be used with a reasonable simulation time. To test the results for cyclic polymers we compare these with those obtained for linear polymers of the same range of chain length. For linear chains we obtain $\nu=0.52$, i.e., the excluded volume interaction is screened. The exponent $\nu=0.45\pm0.01$ for the rings shows that indeed the topological constraints prevent the cyclic polymers from adopting Gaussian melt statistics. Problems could be expected in such cases when the usual formulation of the RPA is used, since it treats the excluded volume interaction as a small perturbation. The RPA takes only certain diagrams into account and a change in the exponent of the correlation length is not obtained. Such more sophisticated details will be presented in an analytical study separately [17].

Despite these principal difficulties Marko [6] and Benmouna, Borsali, and Benoit [7] investigated diblock copolymer rings using the RPA neglecting all topological constraints, which can be described mathematically by Gaussian integrals [18]. Rings described by excluded volume interactions only can be called *topological phantom rings* [17]. The condition for the microphase separation transition (MST) can be expressed as $(\chi_FN)_c=C$, where the constant C is given by the architecture of the copolymer. The random phase approximation for linear diblock copolymers yields $C=10.495$ [19]. For T-shaped diblock copolymers Olvera de la Cruz and Sanchez found C to be equal to 13.5 [20]. References [6,7] suggest that cyclic diblock phantom rings exhibit a similar condition for the microsphase separation transition as linear copolymers. Marko calculated the constant for cyclic copolymers as $C=17.8$ [6], and Benmouna, Borsali, and Benoit as $C\approx18$ [7]. Similar to this it would be mentioned that linear multiblock structures with more than one junction point between the blocks should also show a higher constant C than linear diblock copolymers [21].

Symmetric diblock copolymer rings are expected to undergo a phase transition into a lamellar structure, similar to linear or T-shaped diblock copolymers. Monte Carlo simulations of linear (see, for example, [10,13]) and T-shaped diblock copolymers [22] have shown the appearance of the periodic stucture. It is interesting to compare their transition temperatures to those of linear diblock copolymers and diblock rings. Due to their architecture rings have less conformational entropy than linear diblock copolymers and the energy entropy balance should be different for cyclic diblocks. Intuitively it is clear that the phase transition will occur at lower temperatures for cyclic diblock systems. These intuitive guesses can be observed by the simulations (Fig. 1). An efficient way to determine the critical temperature of the MST is analysis of the specific heat. The computation of the specific heat is commonly performed via the fluctuation-dissipation theorem $C_V=(1/k_BT^2)(\langle E^2\rangle-\langle E\rangle^2)$ from the energy of the entire system E. At the critical temperature the specific heat exhibits a pronounced peak. We find that the critical temperatures for cyclic diblock copolymers are much lower than those of linear diblock chains of the same length. We calculate the ratio of the critical temperatures $T_{\text{linear}}/T_{\text{cyclic}}=1.61$ (1.88) for the smaller (largest) simulated polymers. The interaction parameter χ_F is usually assumed to be inversely proportional to temperature T by $\chi_F=\epsilon(q-2)/k_BT$. ϵ is the monomer interaction parameter and q the coordination number of the lattice. Taking into account this correspondence, this ratio corresponds surprisingly well to the predictions for *topological phantom rings* $(\chi_FN)_c^{\text{Marko}}/(\chi_FN)_c^{\text{Leibler}}\approx1.7$ obtained from Marko [6] using the random phase approximation. This result is very surprising. It will be reported in a subsequent publication how this coincidence appears

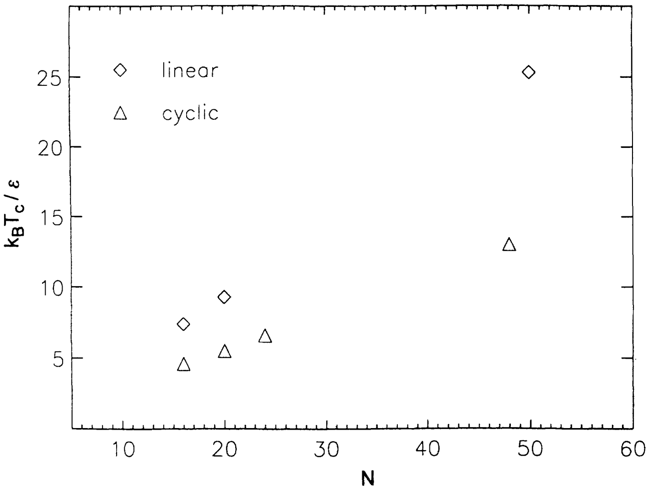

FIG. 1. Comparison of the critical temperatures of simulated linear and cyclic diblock copolymers. The critical temperature k_BT_ϵ/ϵ of diblock copolymer rings is approximately 40% lower than for linear copolymers of the same length.

from analytical calculations [17]. An intuitive way to understand this is that the topology does not matter very much on the length scales of the microphase separation, which takes place at a certain wave vector. Despite this fair agreement we would like to comment on the absolute values of critical temperatures of both simulated linear and cyclic diblock copolymers. They are smaller by a factor of almost 2 than the theoretical predictions of Leibler and Marko.

Below the critical temperature k_BT_c/ϵ the microphase separation transition of the symmetric diblock copolymer rings into a lamellar structure occurs. The wavelength λ of this lamellar structure is proportional to the radius of gyration of the polymer. The radii of gyration, respectively, the wavelengths of the periodic structure, of the diblock copolymer rings are smaller by a factor $R_g^{\text{cyclic}}/R_g^{\text{linear}}=0.51-0.55$ than the radii of linear diblock copolymers of the same chain lengths. This can be interpreted as phases formed by linear chains that have to fold once within the phases. The length scales of the phases formed by diblock rings are therefore half of those of linear diblock copolymers (Fig. 2).

Simulations of linear diblock copolymer systems have shown [10,13,23] that the chains stretch by 10–15% with decreasing temperature. The reason for this stretching effect is the strong effective repulsive interaction between A and B monomers in the melt. As an aside we remind the reader of the calculation of the effective monomer potentials between the different monomers in the interacting melt [13]. From those potentials the configurations of single chains in melts can be determined. With decreasing temperature or increasing values of χ_FN, the potentials become very large at the critical point for a fixed wave vector k^*, which reflects the wavelength of the ordered structure. Such effective interactions can be calculated for diblock rings also. The two blocks of the rings have even fewer possibilities to separate from each other compared to linear diblock

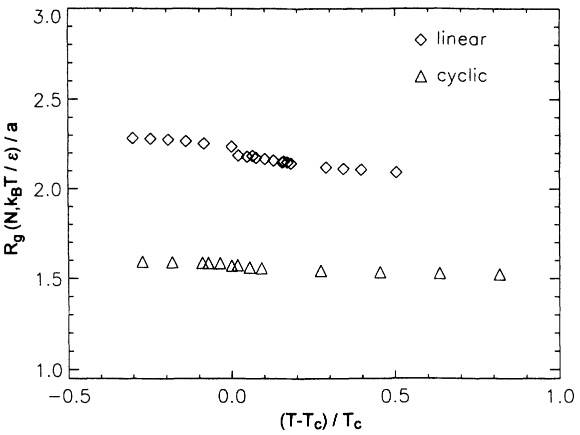

FIG. 2. Comparison of the radii of gyration of linear and cyclic diblock copolymers of length $N=20$. The radii of the copolymer rings are smaller than the radii of the linear copolymers by a factor of 0.51.

copolymers, and it is necessary to investigate the ring conformation. Three quantities are relevant: the distance between the centers of mass of the two blocks R_{AB},

$$R_{AB}=\sqrt{\langle(\mathbf{R}^A_{\text{c.m.}}-\mathbf{R}^B_{\text{c.m.}})^2\rangle}\ , \tag{1}$$

the radius of gyration of the blocks R_g^α,

$$R_g^\alpha=\left[\frac{1}{nN/2}\sum_{i=1}^{n}\sum_{j=1}^{N/2}(\mathbf{r}_j^i-\mathbf{R}^{\alpha i}_{\text{c.m.}})^2\right]^{1/2} \tag{2}$$

($\alpha=A,B$), and the end-to-end distance of the blocks $R_{\text{end}}^{\text{block}}$,

$$R_{\text{end}}^{\text{block}}=\left[\frac{1}{n}\sum_{i=1}^{n}(\mathbf{r}^i_{N/2}-\mathbf{r}^i_1)^2\right]^{1/2} . \tag{3}$$

With decreasing temperature we observe a strong increase by 20–25% of the radius between the two centers of mass of the two blocks (Fig. 3). The length of the vector R_{AB} increases continuously while lowering the tem-

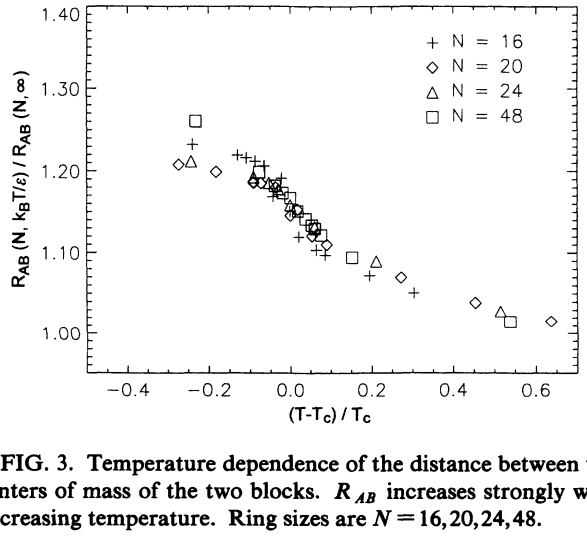

FIG. 3. Temperature dependence of the distance between the centers of mass of the two blocks. R_{AB} increases strongly with decreasing temperature. Ring sizes are $N=16,20,24,48$.

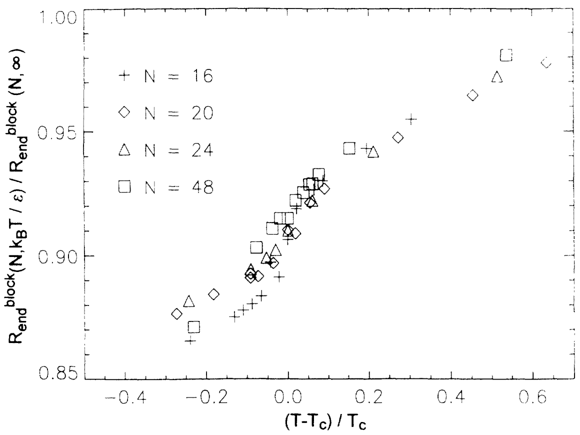

FIG. 4. Temperature dependence of the end-to-end vector of the single blocks. $R_{\mathrm{end}}^{\mathrm{block}}$ shrinks continuously with decreasing temperature. Ring sizes are $N = 16,20,24,48$.

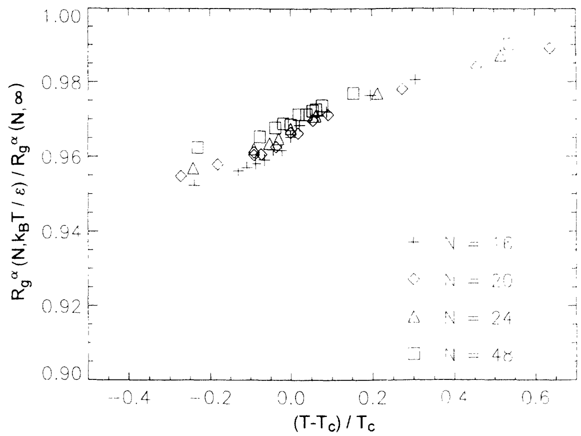

FIG. 5. Temperature dependence of the radius of gyration of the single blocks. $R_g^\alpha(\alpha = A,B)$ shrinks continuously with decreasing temperature. Ring sizes are $N = 16,20,24,48$.

perature. The effect is more pronounced than for linear diblock copolymers (15% [13]). For linear diblock copolymers it has been shown [13] that the increase of R_{AB} underlines the axial character of Gaussian chains and the chains stretch, i.e., the chains do not swell isotropically.

In rings similar results can be expected. To see this, consider the long mean axis $\mathbf{R}_{AB}$. The end-to-end vector of the blocks serves as such a second independent axis. Figure 4 shows a strong reduction of the end-to-end vector of the blocks $F_{\mathrm{block}}^{\mathrm{end}}$ by almost 15%. Together with the increase of R_{AB} this gives rise to the assertion that the ring copolymers stretch during the cooling process. This stretching effect is remarkable, as the two ends of the two blocks are linked together. At temperatures k_BT/ϵ below the microphase separation transition temperature k_BT_c/ϵ the blocks are shaped like two hairpins.

The radius of gyration of the individual blocks shrinks for cyclic diblock copolymers (Fig. 5). Linear diblock copolymers only show a very small shrinking effect. The shrinking effect can be understood in terms of effective *AA* or *BB* interaction which changes sign and becomes attractive. Such effects are well known in the macro phase separations of polymer blends [24,12,25], i.e, the polymers shrink in the pure domains, which consist either of species *A* or *B*. In copolymer systems the spatial extension of the phases is smaller than in binary mixtures. This phenomenon happens also at finite length scales, i.e., at scales proportional to the inverse of the critical wave vector. Therefore the "screening effect," i.e., the attractive potential between monomers of the same species, is reduced. The overall stretching effect for copolymers is a special copolymer effect and is due to the connectivity of the two blocks.

The diblock copolymer rings change their sizes with decreasing temperature. Linear diblock copolymers behave in a similar manner. Mean-field descriptions as given by Leibler [19] for linear diblock copolymers and by Marko [6] for cyclic copolymers cannot explain this variation of the polymer size with temperature. A self-consistent treatment using the effective potentials between two monomers in the dense melt [13] solves this problem [26].

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