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Monte Carlo study of diblock copolymers in dilute solution

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Abstract. — We investigate the conformational changes of symmetric diblock copolymer molecules in dilute athermal solvent due to chemical mismatch between the two blocks using Monte Carlo simulations. Renormalization group calculations based on the two parameter model predict that the effects of chemical mismatch on the size of diblocks appear only as corrections to scaling and that the value of the exponent governing the correction to scaling for the mean squared end-to-end distance of the molecule is 0.225. However, our results show that for strongly incompatible monomers the value of this exponent is much larger. We also find that the chemical mismatch causes the diblock molecule to assume a dumbbell shaped conformation and that the shape changes induced by the chemical mismatch obey a novel scaling relation.

Most new polymeric materials as well as biological systems contain chemically inhomogeneous chains. Despite its importance, the effects of chemical inhomogeneities on the chain statistics have not been studied in sufficient detail. Even the simplest case of a dilute copolymer solution with non-selective good solvent, which has recently received lots of attention, is poorly understood.

Solutions of A-B copolymers are particularly interesting because they form aggregates rich in A or B monomers as the concentration of copolymer increases. The shape of the copolymer chain in solution is extremely important to understanding these phenomena.

Renormalization group calculations based on the two parameter model predict that in the limit of infinite molecular weight the effects of chemical mismatch between the two blocks in dilute solutions of diblock copolymers vanish [1-3]. Any effects due to chemical mismatch appear only as corrections to scaling. For example, the ratio of the mean square end-to-end distance of a diblock chain R_c^2 to that of a homopolymer chain R_0^2 is given by

$$\frac{R_c^2}{R_0^2} = 1 - \frac{a}{N\nu_s}, \quad (1)$$

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where N is the polymerization index of the chains, a is a constant that varies from system to system, and the exponent χ_s is a "universal", model independent quantity. The value of χ_s is predicted to be 0.225 ± 0.005 [4].

In this letter we study the effects of the chemical mismatch on the conformation of isolated symmetric diblock copolymer molecules in non-selective good solvent by Monte Carlo techniques. We compute the exponent χ_s . We also compute a correlation function that is a sensitive measure of the swelling of the chain at the interface between the A and B blocks. We find that the chemical mismatch effects the chain conformations causing them to assume a dumbbell shape, and we show that the conformation changes obey a novel scaling relation.

Our results have implications in the analysis of semidilute polymer solutions containing more than one monomer species. In semidilute polymer solutions containing strongly incompatible monomers, non-selective good solvent screens the interactions between unlike monomers. The osmotic pressure π of such solutions containing two unlike monomer species A and B scales as

$$\pi \sim \frac{1}{\xi^d} (1 + a \phi^{\chi_s/(\nu d - 1)}) \quad (2)$$

where $\xi \sim \phi^{-\nu/(\nu d - 1)}$ is the screening length of the excluded volume interactions, a is a constant proportional to the Flory interaction parameter between A and B monomers, ϕ is the total monomer concentration, d is the spatial dimension, and ν is the exponent that describes the scaling of the size of polymer chains ($R \sim N^\nu$). At low polymer concentrations such systems are in an isotropic state, but as the concentration (or N) increases, the chains begin to overlap and eventually the systems undergo a transition to a state in which the number of A-B contacts is reduced. In A-B homopolymer semidilute solutions the segregation is macroscopic, occurring at infinite wavelength. In diblock copolymer semidilute solutions the segregation occurs at length scales of the order of S , the radius of gyration of the chains, and the segregated domains form ordered periodic structures known as microphases. The concentration of solvent at the transition scales as [5]

$$\phi_t \sim N^{-\Delta} \quad (3)$$

where $\Delta = (\nu d - 1)/(1 + \chi_s)$.

In our Monte Carlo simulations we model a block copolymer molecule of polymerization index N with an $N - 1$ step self-avoiding walk (SAW) on a three dimensional simple cubic lattice. The vertices of the SAW are assumed to correspond to monomers. The chemical mismatch between the A and B blocks of the molecule is modeled by pairwise interactions between monomers occupying nearest neighbor sites of the lattice. Three different interaction strengths ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} can be defined depending on the type of the two nearest neighbor monomers (See Fig. 1). However, in this letter we consider only the nonselective, athermal solvent case $\epsilon_{AA} = \epsilon_{BB} = 0$.

We use the pivot algorithm [6] to generate new chain conformations and Metropolis sampling to obtain equilibrium properties. The chains start in a stretched conformation and then are equilibrated with 5×10^6 MC steps. (Each pivot is one Monte Carlo step.) The chain lengths in our simulations vary from 48 to 256. Our homopolymer ($\epsilon = 0$) simulations and our diblock simulations with chain lengths of 48 and 64 involve 5.0×10^7 MC steps. Our diblock simulations of longer chains involve 2.5×10^7 MC steps.

The quantities we calculate include the squared end-to-end distance of the chain R^2 , and the squared radius of gyration S^2 . Additionally, on some shorter runs we calculate the spherically integrated center monomer-monomer correlation function $G_c(r)$. In terms of continuous

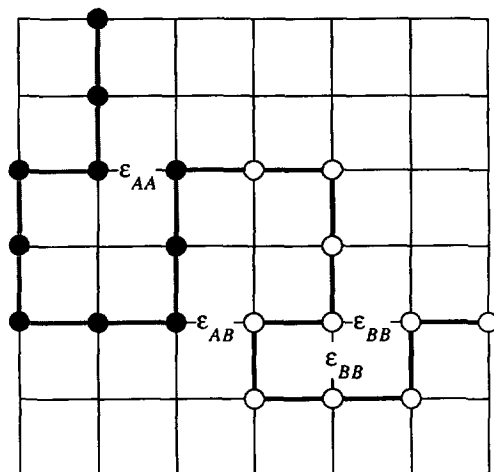


Fig.1. — A typical conformation of a symmetric diblock copolymer of length $N = 20$ on the lattice, drawn for simplicity in two dimensions, although our calculations are done in three dimensions. The two monomer species are distinguished by filled circles (\bullet) for A type and unfilled circles (\circ) for B type. The interaction energies between nearest neighbor monomer pairs ϵ_{AA} , ϵ_{BB} and ϵ_{AB} are shown explicitly.

variables $G_c(\tau)$ is defined as

$$G_c(\tau) = \int d\Omega \, r^2 \int_{N/2}^N dl \, \delta(\mathfrak{R}_l - \mathfrak{R}_{N/2} - \mathbf{r}) \quad (4)$$

where \mathfrak{R}_n is the position of the n th monomer of the chain. The function $G_c(\tau)$ is the average number of monomers per block at a distance τ from the center of the chain.

During a simulation, data for R^2 and S^2 are stored as time series. The means and the standard deviations of the time series are then calculated at the end of the simulation. However, in general, the time series data is correlated. Therefore, in order to get a proper standard deviation that can be used to determine errors the correlations must be accounted for, which can be done as follows [7]. The standard deviation σ_x of a given observable $\langle x \rangle$ calculated from n data points $\{x_i\}$ is

$$\sigma_x^2 = \frac{1}{n} \sum_{t=-(n-1)}^{n-1} \left(1 - \frac{|t|}{n}\right) C(t) \quad (5)$$

where $C(t)$ is the autocorrelation function

$$C(t) = \frac{1}{n - |t|} \sum_{i=1}^{n-|t|} (x_i - \langle x \rangle)(x_{i+|t|} - \langle x \rangle). \quad (6)$$

For large n , however, (5) becomes cumbersome to use. Instead, since $n \gg \tau$, the correlation time, we assume

$$\sigma_x^2 \approx \frac{1}{n} 2\tau C(0) \quad (7)$$

Table I. — *Simulation results for $\langle R^2 \rangle$. The uncertainty range corresponds to one standard deviation.*

N	$\epsilon_{AB} = 0.0$	$\epsilon_{AB} = 0.5$	$\epsilon_{AB} = 1.0$	$\epsilon_{AB} = 2.0$	$\epsilon_{AB} = 4.0$	$\epsilon_{AB} = 10.0$
48	107.789 ± 0.034	115.915 ± 0.037	118.912 ± 0.033	121.067 ± 0.036	121.928 ± 0.042	122.073 ± 0.038
64	153.030 ± 0.049	163.558 ± 0.053	167.255 ± 0.051	169.903 ± 0.057	170.874 ± 0.069	171.120 ± 0.066
96	249.346 ± 0.107	264.945 ± 0.148	269.936 ± 0.160	273.278 ± 0.162	274.627 ± 0.145	274.929 ± 0.131
128	352.112 ± 0.147	372.280 ± 0.208	378.795 ± 0.205	382.538 ± 0.182	384.294 ± 0.219	384.491 ± 0.181
160	460.135 ± 0.175	484.521 ± 0.274	491.520 ± 0.280	497.199 ± 0.245	498.360 ± 0.305	498.548 ± 0.280
192	571.928 ± 0.268	600.900 ± 0.373	608.706 ± 0.364	614.691 ± 0.341	616.770 ± 0.329	617.424 ± 0.352
256	805.404 ± 0.337	843.043 ± 0.517	853.821 ± 0.557	860.767 ± 0.502	862.534 ± 0.557	864.283 ± 0.516

and estimate τ by [8]

$$\tau = \frac{1}{2} \sum_{t=-M}^M C(t)/C(0) \quad (8)$$

where M is chosen such that $M \geq 10\tau(M)$.

To study the effects of the chemical mismatch between the two blocks on the chain statistics we simulate both homopolymers ($\epsilon_{AB} = 0$) and diblock molecules at various strengths of ϵ_{AB} . The diblock results are then contrasted with the homopolymer results to isolate the chemical mismatch effects.

Our simulation results for R^2 are summarized in table I. Using those results we calculate χ_s with a two parameter fit to equation (1). To do a proper fit it is necessary to know the error associated with the ratio of $\langle R_c^2 \rangle$ to $\langle R_0^2 \rangle$. Assuming that the results for R_c^2 and R_0^2 are normally distributed and sharply peaked, the distribution of results for the ratio can also be assumed to be normally distributed. The mean of the ratio's distribution is then simply the ratio of the means, and the standard deviation of the ratio's distribution σ_r is

$$\sigma_r = \frac{\langle R_c^2 \rangle}{\langle R_0^2 \rangle} \left[\left(\frac{\sigma_c}{\langle R_c^2 \rangle} \right)^2 + \left(\frac{\sigma_0}{\langle R_0^2 \rangle} \right)^2 \right]^{1/2} \quad (9)$$

where σ_c and σ_0 are the standard deviations corresponding to $\langle R_c^2 \rangle$ and $\langle R_0^2 \rangle$, respectively. Equation (9) can be derived using the method of steepest decent.

The curve fitting results for χ_s are plotted in figure 2. They show that χ_s is not constant, but instead varies with ϵ_{AB} . The deviation of χ_s with ϵ_{AB} is most likely due to further corrections to scaling from the finite molecular weight of the chains. As ϵ_{AB} is decreased those corrections vanish, and therefore the value that χ_s reaches asymptotically in the limit of vanishing ϵ_{AB} should be its universal value predicted by renormalization group calculations. Our results seem to be in agreement with those calculations in that limit. However, at large values of ϵ_{AB} the apparent value of χ_s is much larger than its universal value.

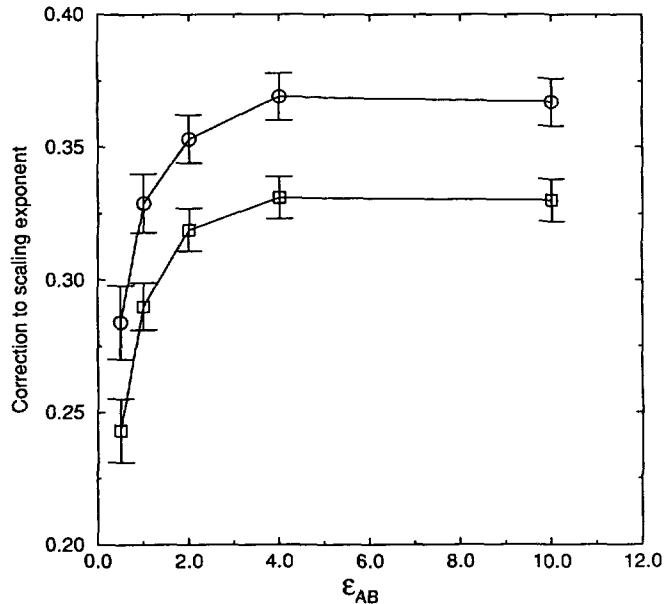


Fig.2. — Simulation results of the correction to scaling exponent for $\langle R^2 \rangle$ (○) and $\langle S^2 \rangle$ (□) as a function of chemical mismatch ϵ_{AB} . The error bars represent 95 % confidence limits.

This result affects the analysis of phase transformations in block copolymer non-selective semidilute solutions containing strongly incompatible monomers, and also in A-B homopolymer semidilute solutions containing strongly incompatible monomers. For such systems the scaling limit can correspond to extremely long chains. When finite length chains are used, since our results show that an apparent value of χ_s much larger than its universal value is measured, the apparent value of Δ , the exponent that describes the scaling of the concentration of solvent at the segregation transition in copolymer solutions, (see (3)) is smaller than its universal value. This may explain the results of some recent experiments. The universal value of Δ is predicted to be about 0.62, which is larger than the experimental values of 0.5 and 0.58 that have been measured for block copolymer solutions undergoing transition to periodic structures [9] and homopolymer mixtures undergoing liquid-liquid phase separation [10], respectively.

A similar analysis can be done on our data for S^2 , which is summarized in table II, to get a value of the exponent that describes the correction to scaling for the mean square radius of gyration. That is, the data for the radius of gyration of homopolymer chains S_0^2 and of diblock copolymer chains S_c^2 can be used in place of R_0^2 and R_c^2 for a two parameter fit of equation (1) to determine the equivalent to χ_s . Performing such an analysis, we find that the value of the exponent that describes the correction to scaling of the mean square radius of gyration of the chains is smaller than χ_s .

The fact that the correction to scaling exponents for R^2 and S^2 are different suggests that the chain stretching is *not* uniform along the length of the chain. These calculations, however, cannot determine the shape of the diblock molecules, which differ from the shape of homopolymer molecules because the two blocks repel each other.

To investigate the shape changes of diblock molecules due to the repulsion of the two blocks we choose to look at the $G_c(r)$, because this function is very sensitive to the mismatch of the

Table II. — Simulation results for $\langle S^2 \rangle$. The uncertainty range corresponds to one standard deviation.

N	$\epsilon_{AB} = 0.0$	$\epsilon_{AB} = 0.5$	$\epsilon_{AB} = 1.0$	$\epsilon_{AB} = 2.0$	$\epsilon_{AB} = 4.0$	$\epsilon_{AB} = 10.0$
48	17.0390 ± 0.0047	18.2655 ± 0.0050	18.7396 ± 0.0046	19.0898 ± 0.0056	19.2265 ± 0.0049	19.2495 ± 0.0054
64	24.1830 ± 0.0071	25.8058 ± 0.0074	26.4040 ± 0.0056	26.8373 ± 0.0079	26.9985 ± 0.0083	27.0409 ± 0.0076
96	39.4326 ± 0.0116	41.8930 ± 0.0225	42.7040 ± 0.0195	43.2762 ± 0.0210	43.4988 ± 0.0175	43.5456 ± 0.0184
128	55.7387 ± 0.0213	58.9402 ± 0.0284	59.9888 ± 0.0259	60.6654 ± 0.0228	60.9373 ± 0.0248	60.9890 ± 0.0247
160	72.8914 ± 0.0197	76.8062 ± 0.0316	77.9844 ± 0.0378	78.8518 ± 0.0377	79.1340 ± 0.0413	79.1342 ± 0.0428
192	90.6202 ± 0.0441	95.2870 ± 0.0443	96.6320 ± 0.0493	97.6148 ± 0.0430	97.9691 ± 0.0532	98.1148 ± 0.0660
256	127.795 ± 0.045	133.840 ± 0.069	135.606 ± 0.064	136.805 ± 0.071	137.183 ± 0.083	137.392 ± 0.086

two blocks. (The two point monomer-monomer correlation function is not as good because the correlations due to pairs of monomers that are of the same species are not directly affected by the mismatch of the two blocks. Those correlations, which contribute significantly to the two point correlation function, tend to wash out the mismatch effects which are most significant near the junction of the two blocks.)

For our lattice model, $G_c(r)$ is calculated as follows. During a simulation, we measure the mean center monomer-monomer correlation function

$$g_c(\mathbf{r}) = \left\langle \sum_{n=N/2}^N \delta_{\mathbf{r}_n - \mathbf{r}_{N/2}, \mathbf{r}} \right\rangle. \quad (10)$$

At the end of the simulation, we find the spherical average of this quantity $g_c(r)$ and then multiply the resulting function by $4\pi r^2$ to finally obtain $G_c(r)$. The above method of spherical integration produces smoother and, we believe, more accurate results than a straight forward spherical integration of $g_c(\mathbf{r})$.

The homopolymer spherically integrated center monomer-monomer correlation function $G_c^{(0)}(r)$ obeys the normalization condition

$$\int dr G_c^{(0)}(r) = N. \quad (11)$$

It is therefore plausible that the following scaling relation holds [11]

$$G_c^{(0)}(r) \sim \frac{N}{S} f(r/S). \quad (12)$$

Since the radius of gyration scales with N as $S \sim N^\nu$,

$$G_c^{(0)}(r) \sim N^{1-\nu} f(r/S) \quad (13)$$

or

$$f(r/S) \sim N^{\nu-1} G_c^{(0)}(r). \quad (14)$$

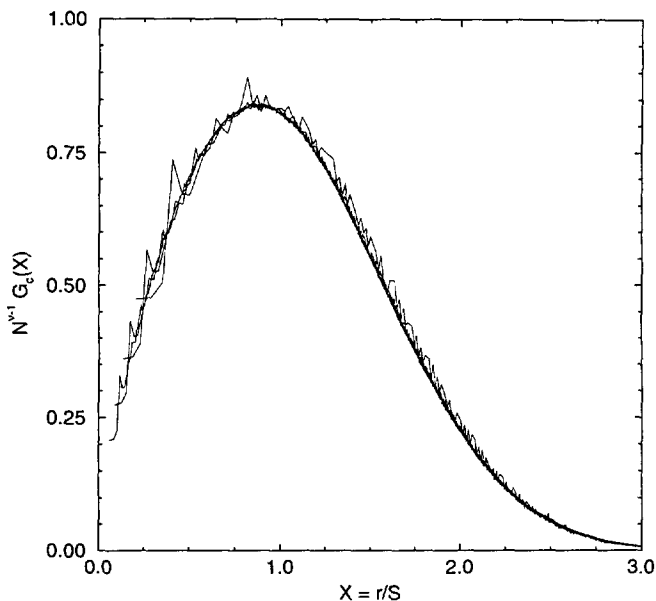


Fig.3. — Scaling plot for homopolymer spherically integrated center monomer-monomer correlation function $G_c(r)$. The results for chains of length $N = 64, 128, 256,$ and 512 are superimposed in the graph.

Figure 3 shows the scaling function $f(r/S)$.

To quantify the chemical mismatch effect we calculate the spherically integrated center monomer-monomer correlation function for diblock molecules $G_c^{(c)}(r)$ and compared the results to our results for the homopolymer $G_c^{(0)}(r)$ (see Fig. 4). In particular, we calculate the difference between $G_c^{(c)}(r)$ and $G_c^{(0)}(r)$, which we denote by $\Delta G_c(r)$. We find that $\Delta G_c(r)$ also obeys a scaling relation

$$\Delta G_c(r) \sim f_{\Delta}(r/S), \quad (15)$$

as shown in figure 5. This scaling relation can be understood as follows. Chemical mismatch effects occur only where A and B type monomers come in contact, which, when the blocks are strongly segregated, only occurs at the interface between the two blocks. Therefore, the chemical mismatch effects should be proportional to the number of A-B contacts, or the number monomers at the interface between the two blocks. The scaling function $f(r/S)$ for homopolymer chains is thus perturbed by the chemical mismatch effects between unlike monomers by an amount proportional to the number of monomers at the interface between the two blocks, and so, the scaling function for the change in $f(r/S)$ due to the chemical mismatch should scale as $f(r/S)$ times the number of monomers at the interface. Then, noting that the area (or volume) of the interface scales as S^2 , and that within the volume occupied by the polymer the density of monomers scales as N/S^3 . The number of monomers at the interface between the A and B blocks N_I scales as

$$\begin{aligned} N_I &\sim (\text{Interface Area}) \times (\text{Monomer Density}) \\ &\sim S^2 \times (N/S^3) \\ &\sim N/S \\ &\sim N^{1-\nu} \end{aligned} \quad (16)$$

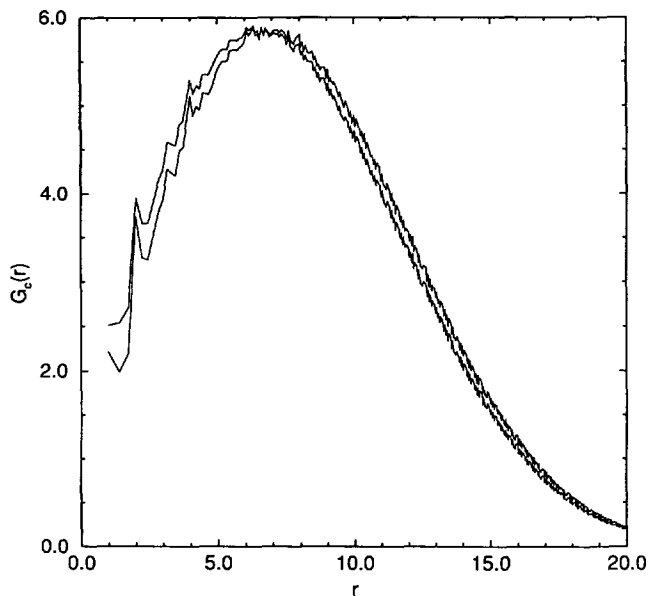


Fig.4. — Comparison of $G_c(r)$ for a homopolymer and a symmetric diblock copolymer of length $N = 128$. The curve corresponding to the diblock $G_c(r)$ is to the right of the curve corresponding to the homopolymer $G_c(r)$. The interaction energy between AB monomers in the diblock case is $\epsilon_{AB} = 1.0$. Most of the noise in the curves is due to lattice effects.

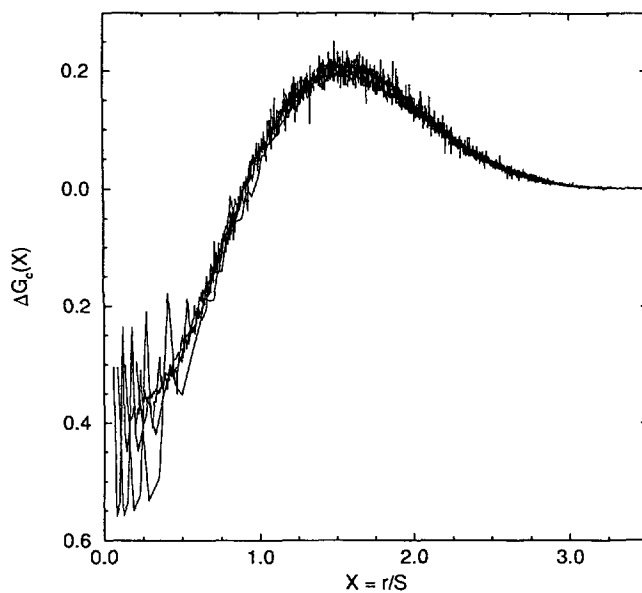


Fig.5. — Scaling plot for the difference between the homopolymer $G_c(r)$ and the diblock $G_c(r)$. The results for chains of length $N = 64, 128, 256,$ and 512 are superimposed in the graph. The interaction energy between AB monomers in the diblock molecules is $\epsilon_{AB} = 1.0$.

We have

$$\begin{aligned}
 \Delta G_c(r) &\equiv G_c^{(c)}(r) - G_c^{(0)}(r) \\
 &\sim N^{1-\nu} [f^{(c)}(r/S) - f^{(0)}(r/S)] \\
 &\sim N^{1-\nu} [N_1^{-1} f_\Delta(r/S)] \\
 &\sim f_\Delta(r/S).
 \end{aligned}
 \tag{17}$$

The form of the scaling function $f_\Delta(r/S)$, which is plotted in figure 5, shows that the conformations of isolated diblock chains do indeed have a dumbbell shape. An isolated homopolymer chain has an aspherical watermelon shaped configuration. However, in a diblock molecule the two blocks repel each other. $f_\Delta(r/S)$ shows that the repulsion of two blocks results in a depletion of monomers in a volume around the center of the chain of radius about $3S/2$. The excess monomers then bunch up at a distance about $2S$ from the center, thus giving the diblock molecule a dumbbell shape.

In conclusion, we have shown that chemical mismatch affects the the conformation of diblock copolymer chains and causes nonuniform stretching of the chains even in in nonselective good solvents. We also calculated the exponent χ_s which governs the corrections to scaling for copolymer solutions. We found that for systems with strongly incompatible monomers it is much larger than the value predicted by renormalization group calculations based on the two-parameter model. This result has important consequences to the analysis of phase transitions in semidilute copolymer solutions and may explain the discrepancies between some of the experiments that have been performed and renormalization group calculations. Our results are also expected to apply to other copolymer architectures, such as graphs and stars, as well as other copolymer compositions.

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