(2) Randall, J. C. *Polymer Sequence Determination*; Academic: New York, 1977.
(3) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules 8*, 687–689.
(4) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267–270.
(5) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270–275.
(6) Suter, U. W.; Neuenschwander, P. *Macromolecules* **1981**, *14*, 528–532.
(7) Cheng, H. N.; Lee, G. H. *Polym. Bull. (Berlin)* **1985**, *13*, 549–556.
(8) Xu, Z.; Mays, J.; Chen, X.; Hadjichristidis, N.; Schilling, F. C.; Bair, H. E.; Pearson, D. S.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2560–2566.
(9) Cheng, H. N.; Lee, G. H. Paper presented at the 12th FACSS Meeting, Philadelphia, PA, Oct 1985.

Dynamic Monte Carlo Study of the Conformational Properties of Long Flexible Polymers

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In this paper we present results of Monte Carlo (MC) studies of long-chain polymers confined to a diamond lattice in which both repulsive and attractive interactions have been included. The hard-core repulsive part of the segment–segment interaction is modeled by the exclusion of multiple occupancy of lattice sites. Attractive interactions, ϵ_a, are associated with every pair of nonbonded nearest-neighbor segments. No preference for any of the three possible (one trans, t, and two gauche, g) rotational states of every internal bond is assumed. Thus the chain stiffness results only from lattice restrictions. The polymer occupies n lattice vertices, connected by $n - 1$ bonds; $n - 3$ conformational states define the chain conformation.

A dynamic sampling method has been used, incorporating reptation type and 3-bond kink motions of the chain backbone, together with 2-bond random flips of the chain ends. The details of the sampling procedure are similar to those in ref 1. We performed simulations on chains of length $n = 100, 200, 400,$ and 800. The reduced temperature $T^* = k_B T / \epsilon_a$ was varied from infinity [the case of an athermal self-avoiding walk (SAW)] to unity, which is well below both the Θ-point and the collapse transition. At a given T^*, $(2–6) \times 10^6$ [$(1.5–4.5) \times 10^7$] iterations (one attempt at a reptation step plus several attempts at kink flips) have been performed for chains of $n = 100$ [800]. Depending on n, the conformation of the polymer has been analyzed every 100–1000 cycles of the MC algorithm. Hence from 2×10^4 to 6×10^4 relatively independent "measurements" contributed to the ensemble averages, which were calculated as the appropriately weighted arithmetic mean of the quantity of interest. For some sets of the model parameters (n, T^*), the standard deviations from the mean have been evaluated on the basis of runs obtained with different streams of pseudo random numbers.

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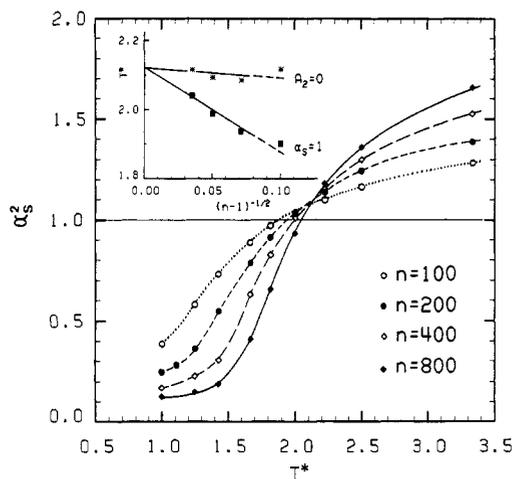
Figure 1. Plot of the expansion factor α_s^2 vs. reduced temperature T^* for various chain lengths. The inset shows the extrapolation to infinite chain length of the temperature at which the second virial coefficient $A_2 = 0$ and the temperature where $\alpha_s^2 = 1$.

The results are presented in Table I, where the mean-square end-to-end distance (radius of gyration) $\langle R^2 \rangle$, ($\langle S^2 \rangle$), the average number of polymer nearest-neighbor pairs per bead (no contacts down the backbone are considered) $\langle \nu \rangle$, and the average fraction of gauche states per degree of rotational freedom $\langle f_g \rangle$ have been listed vs. T^{*-1}. The second column of Table I contains the number of iterations in the MC process.

The dimensions of the athermal SAW's are fit very well by the relation $\langle R^2 \rangle \sim \langle S^2 \rangle \sim (n - 1)^{1.186 \pm 0.004}$, in good agreement with previous work.[2,3] As the temperature decreases, the chain dimensions decrease and the number of nearest neighbors increases. The fraction of gauche states also increases slightly, approaching in the high-density state values somewhat greater than the ideal chain $\langle f_g \rangle$ of $2/3$. One should note that even the local properties, i.e., $\langle f_g \rangle$ and $\langle \nu \rangle$, are chain-length dependent over the range of n under consideration. While $\langle f_g \rangle$ is weakly n dependent over the entire range of temperature, $\langle \nu \rangle$ depends much more strongly on chain length especially in the low-temperature region (globular state), probably reflecting surface effects.

The expansion factor $\alpha_s^2 = \langle S^2 \rangle / \langle S^2_0 \rangle$ vs. T^* is presented in Figure 1 for various chain lengths. $\langle S^2_0 \rangle$ has been calculated for a finite length n by employing the RIS model with discrete independent rotational states[4] (a nonreversing random walk on a diamond lattice). As seen in Figure 1, the Θ-temperature Θ_S, defined as that when $\alpha_s^2 = 1$, varies with chain length. Applying Sanchez's mean field theory (eq 52a of ref 5) to the MC data, we found that it fits our data very well in the vicinity of the Θ-point ($\pm \Delta \epsilon_a / k_B T \simeq 0.1$) when the chain length is rescaled by the persistence length (which is about 3.2 bond lengths). A slightly better fit in the vicinity of the Θ-point was found by using the renormalization group approach of Duplantier, Jannink, and des Cloizeaux (DJC),[6] giving some evidence for a tricritical state of polymers near the Θ-state. However the value of y (the three-body term) (see eq 3 of ref 6) is found to be 0.066, an order of magnitude larger than was reported in ref 6. Both approaches also enabled us to obtain Θ_A, the temperature where the second virial coefficient vanishes. For finite chains, Θ_S and Θ_A are different, with Θ_A far less dependent on molecular weight. The dimensions of the finite length coil at Θ_A are noticeably greater than those for an ideal chain, i.e., $\alpha_s^2 > 1$. As shown in the inset of Figure 1, both estimates of the Θ-temperature coincide in the limit that $n = \infty$, consistent

Table I
Statistics of Flexible Chains[a]

T^{*-1}	iter $\times 10^6$	$\langle R^2 \rangle$	$\langle S^2 \rangle$	$\langle \nu \rangle$	$\langle f_s \rangle$
			$n = 100$		
0.0	6	941.8	148.5 ·	0.0576	0.6297
0.2	2	831.0	133.1	0.0788	0.6417
0.3	2	777.8	125.4	0.0922	0.6468
0.4	2	697.1	113.9	0.1104	0.6540
0.45	4	646.5 (0.6)	107.5 (0.1)	0.1218 (1)	0.6570 (5)
0.5	6	602.0 (2.6)	101.3 (0.1)	0.1346 (2)	0.6602 (3)
0.55	4	559.3 (6.1)	95.0 (0.8)	0.1484 (11)	0.6641 (3)
0.6	2	499.8	86.8	0.1659	0.6678
0.7	2	388.2	71.4	0.2066	0.6750
0.8	2	289.9	56.6	0.2549	0.6842
1.0	2	157.0	37.7	0.3503	0.6943
			$n = 200$		
0.0	10	2148.0 (11.0)	344.1 (3.9)	0.0595 (7)	0.6290 (8)
0.2	5	1903.5	304.2	0.0818	0.6410
0.3	5	1693.3	274.4	0.0994	0.6460
0.4	5	1497.7	246.1	0.1201	0.6523
0.45	5	1361.9	224.8	0.1336	0.6564
0.5	5	1215.0	203.9	0.1520	0.6600
0.55	5	1053.2	180.8	0.1724	0.6633
0.6	5	882.6	155.6	0.1988	0.6679
0.7	5	558.5	108.2	0.2663	0.6744
0.8	5	313.9	71.8	0.3436	0.6798
0.9	5	210.4	55.5	0.4091	0.6843
1.0	5	167.1	48.7	0.4544	0.6895
			$n = 400$		
0.0	30	4882.1 (31.2)	777.8 (2.4)	0.0609 (2)	0.6285 (3)
0.2	10	4205.4	673.3	0.0848	0.6387
0.3	10	3765.1	607.4	0.1020	0.6448
0.4	10	3133.5	516.3	0.1273	0.6520
0.45	10	2754.2	458.4	0.1438	0.6562
0.5	10	2403.0	401.5	0.1660	0.6596
0.55	10	1867.9	328.5	0.1935	0.6625
0.6	10	1370.2	250.6	0.2340	0.6661
0.7	10	546.1	121.5	0.3456	0.6731
0.8	10	326.3	90.2	0.4241	0.6753
1.0	10	208.4	66.9	0.5422	0.6838
			$n = 800$		
0.0	30	11223.0 (52.0)	1757.0 (7.0)	0.0675 (23)	0.6279 (4)
0.2	15	9481.0	1484.0	0.0911	0.6391
0.3	30	8418.0 (2.0)	1322.0 (2.0)	0.1083 (20)	0.6450 (1)
0.4	30	6686.0 (55.0)	1086.0 (6.0)	0.1331 (13)	0.6516 (2)
0.45	45	5789.0 (56.0)	941.0 (15.0)	0.1490 (17)	0.6554 (2)
0.5	30	4517.0 (118.0)	745.0 (19.0)	0.1783 (16)	0.6590 (6)
0.55	15	2990.0	524.0	0.2183	0.6628
0.6	30	1731.0 (95.0)	327.6 (17.1)	0.2773 (79)	0.6673 (14)
0.7	15	570.7	150.8	0.4121	0.6704
0.8	30	379.5 (9.0)	118.8 (3.1)	0.5025 (42)	0.6745 (1)
1.0	15	284.2	99.8	0.6126	0.6857

[a] The numbers in parentheses indicate the standard deviation of the mean.

with the existence of a Θ-point.[5-8] The width of the Θ-region diminishes as $(n - 1)^{-1/2}$, in agreement with theory.[6,9] Sanchez and DJC theory give $k_B\Theta/\epsilon_a = 2.12 \pm 0.02$ and 2.14, respectively, in the limit that $n \to \infty$, slightly lower than the value 2.25 ± 0.05 given by Kremer et al.[10] on the basis of careful extrapolation of the MC data for shorter chains ($n \leq 120$). (Analysis of $\langle R^2 \rangle$ gives a similar result.) We tend to ascribe the difference in Θ to a finite chain length effect. To check our estimation of the Θ-point an additional series of simulations has been performed at $k_B\Theta/\epsilon_a = 2.12$. We find $\langle S^2 \rangle \sim (n - 1)^{0.995}$ and $\langle R^2 \rangle \sim (n - 1)^{1.022}$, in good agreement with the expected dependence of $\langle R^2 \rangle \sim \langle S^2 \rangle \sim (n - 1)$. Finally, we note that collapse to the dense globular state of flexible polymers is continuous. The width of the crossover region decreases with increasing chain length, as predicted by recent theories.[5-7,11] However, even the relatively long polymers studied here are too short to display the theoretically predicted de-

pendence $\langle R^2 \rangle \sim (n - 1)^{2/3}$ in the globular state.[7,11]

References and Notes

(1) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *85*, 3585.
(2) Rapaport, D. C. *J. Phys. A.: Math. Gen.* **1985**, *18*, 113.
(3) McCrackin, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973**, *6*, 859.
(4) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York: 1969.
(5) Sanchez, I. C. *Macromoleucles* **1979**, *12*, 980.
(6) Duplantier, B.; Jannink, G.; des Cloizeaux, J. *Phys. Rev. Lett.* **1986**, *56*, 2080.
(7) Moore, M. A. *J. Phys. A.: Math. Gen.* **1977**, *10*, 305.
(8) Bruns, W. *Macromolecules* **1984**, *17*, 2826.
(9) de Gennes, P.-G. *J. Phys. Lett.* **1978**, *39*, 299.

(10) Kremer, K.; Baumgärtner, A.; Binder, K. *J. Phys. A.; Math. Gen.* 1981, 15, 2879.

(11) de Gennes, P.-G. *Scaling Concepts in Polymer* Physics; Cornell University: Ithaca, NY, 1979.

Microphase Separation in Block Copolymer/Homopolymer Blends

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Phase separation in a blend of long polymers is properly described by mean field theory.[1] The phase diagram may be obtained from a lattice model free energy of mixing (Flory–Huggins free energy)

$$f[\phi(\mathbf{r})] = \frac{\phi(\mathbf{r})}{N_A} \ln \phi(\mathbf{r}) + \frac{(1 - \phi(\mathbf{r}))}{N_B} \ln (1 - \phi(\mathbf{r})) + \chi\phi(\mathbf{r})(1 - \phi(\mathbf{r})) \quad (1)$$

where ϕ is the concentration of component A, N_A and N_B are the number of monomers in the A and B chains, respectively, and χ is the usual interaction parameter.

The mixture is homogeneous at high temperatures where the entropic term dominates the free energy. The blend phase separates into two systems, one richer in component A and the other richer in component B when the temperature is lowered below $\chi_t(\phi)$. For a blend with $N_A = N_B$ the critical value at which immiscibility first occurs is $\chi_c = 2/N$ and $\phi_c = 1/2$. The system with original concentration ϕ_0 is metastable for $\chi > \chi_t(\phi_0)$. The limit of metastability for a given ϕ_0 is at the spinodal point $\chi_s(\phi_0)$; below $\chi_s(\phi_0)$ the system is unstable. The spinodal point is an inflexion point in the free energy

$$\left.\frac{\partial^2 f}{\partial \phi^2}\right|_{\phi=\phi_0} = S^{-1}(\mathbf{q}=0) = 0 \quad (2)$$

$S(\mathbf{q})$ is the Fourier transform of the density–density correlation function and can be obtained directly from scattering experiments

$$S(\mathbf{r} - \mathbf{r}') = \langle \Delta\phi(\mathbf{r})\Delta\phi(\mathbf{r}') \rangle$$

$$S(\mathbf{q}) = \int \exp(i\mathbf{q}\cdot\mathbf{r})S(\mathbf{r}) \, d\mathbf{r}$$

with $\Delta\phi(\mathbf{r}) = \phi_0 - \phi(\mathbf{r})$.

The scattering function for this blend is[2]

$$S^{-1}(\mathbf{q}) = \frac{1}{\phi_0 D(x_A)N_A} + \frac{1}{(1 - \phi_0)D(x_B)N_B} - 2\chi \quad (3)$$

where $x_i = q^2R_i^2$ with $R_i^2 = (l^2/6)N_i$ (i = A, B) the radius of gyration, and $D(\mu)$ is the Debye function defined as

$$D(\mu) = (2/\mu^2)[\mu + e^{-\mu} - 1] \quad (4)$$

In the limit $x_i = q^2R_i^2 \ll 1$ (i = A, B) the scattering function takes on the Ornstein–Zernike form

$$S^{-1}(\mathbf{q}) \propto (\xi^{-2} + q^2) \quad (5)$$

where the correlation length ξ measures the intensity of

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the light scattered at $\mathbf{q} = 0$. The correlation length diverges at the spinodal point $\chi_s(\phi_0)$ as

$$\xi^{-2} = 2[\chi_s(\phi_0) - \chi]\frac{18}{l^2}\phi_0(1 - \phi_0) \quad (6)$$

where

$$\chi_s(\phi_0) = \frac{1}{2N_A\phi_0} + \frac{1}{2N_B(1 - \phi_0)} \quad (7)$$

In the case where the A and B chains are chemically linked at the end points, the phase separation occurs on length scales of the order of the radius of gyration of the block copolymer, $R^2 = l^2N/6$ with $N = N_A + N_B$. Let f be the fraction of A monomers along the block copolymer. If the melt is quenched below $\chi_t(f)$, the block copolymer microphase separates into an ordered structure.[3] Leibler found that for $f \neq 0.5$ a body-centered cubic microphase structure is formed at $\chi = \chi_t(f)$, for deeper quenches a hexagonal cylinder, and for quenches $\chi \geq \chi_s(f)$ the microphase separation proceeds by spinodal decomposition and forms a one-dimensional lamellar structure. He found that the critical point is at $\chi_c = 10.5/N$ and $f_c = 0.5$; at this point the phase separation proceeds by spinodal decomposition to a lamellar structure. The spinodal point for microphase separation $\chi_s(f)$ is determined by the condition

$$S^{-1}(\mathbf{q})|_{\mathbf{q}=\mathbf{q}^*} = 0 \quad (8)$$

where $\mathbf{q}^*$ determines the wave vector at which the concentration fluctuations are maximum. The scattering function for a block copolymer is[3]

$$S(x) = \frac{N}{\dfrac{D_1}{D_fD_{1-f} - \Delta D^2} - 2\chi N} \quad (9a)$$

where

$$D_\alpha = \alpha^2 D(\alpha x) \quad (9b)$$

$$\alpha = f, (1 - f), \text{ or } 1 \qquad x = q^2R^2$$

with $D(\mu)$ given by eq 4 and

$$\Delta D = \Delta D(x, f) = \frac{1}{2}[D_1 - (D_f + D_{1-f})] \quad (10)$$

When homopolymer is added to a block copolymer, the phase diagram is very rich and complicated. For example, when the concentration of homopolymer is low, there can be transitions to different ordered morphologies, and as the homopolymer concentration increases, transitions to micellar structures are possible. Let ϕ be the concentration of homopolymer made of N_C monomers of type C and $(1 - \phi)$ the concentration of block copolymer with degree of polymerization N and with the fraction of A monomers along the chain given by f. An inspection of the lattice model free energy for such systems[4]

$$f[\phi(\mathbf{r})] = \frac{\phi(\mathbf{r})}{N_C} \ln \phi(\mathbf{r}) + \frac{(1 - \phi(\mathbf{r}))}{N} \ln (1 - \phi(\mathbf{r})) + [\chi_{AC}f + \chi_{BC}(1 - f) - \chi_{AB}f(1 - f)]\phi(\mathbf{r})(1 - \phi(\mathbf{r})) \quad (11)$$

where χ_{ij} is the usual net interaction between ij monomers, reveals an immiscibility curve or liquid–liquid phase transition.

From eq 11 the spinodal temperature of a system with mean concentration $\phi_0 = \phi$ can be calculated by using eq 2. The spinodal temperature is given by the familiar expression

$$2\chi_s(f,\phi) = \frac{1}{N_C\phi} + \frac{1}{N(1 - \phi)} \quad (12)$$