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Phase Transitions in Polymethylene Single Chains from Monte Carlo Simulated Annealing

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Folding of single isolated polymethylene chains was examined with Monte Carlo simulated annealing. All carbon and hydrogen atoms were considered explicitly by using van der Waals plus torsional potential functions. The calculations allowed continuous variation in each torsional degree of freedom. In addition, we examined the consequences of simplifying the calculations by restricting the carbons to be on a diamond lattice. Ensembles of conformations for larger chains ($C_N H_{2N+2}$, with $N = 16, 32, 64$) all show a transition from a random coil at high temperature to a globular form at low temperature. For longer chains ($N \geq 64$), this globularization transition is well described by the mean-field theory of Sanchez.

Introduction

The self-condensation transition behavior (collapse transition) of a chain molecule in dilute solution has been studied extensively by theory[1-3] and computer simulations.[4-7] Most studies have examined the asymptotic properties of very long chains ($N \to \infty$, where N is the number of segments), finding in this limit that the properties of the chain do not depend on the local stiffness of the chain. Recent Monte Carlo simulations by Kolinski et al.[6] show, however, that the transition behavior of the chain is highly dependent on the local stiffness of the chain as well as on the size of the chain. If the chain is too short or the temperature too low, the properties of the chain should become more dependent on the particular parameters of the chain. To examine the effect of the local properties of the chain on the transition behavior and structure, we used polymethylene as a specific model and carried out simulated annealing studies from 2100 to 100 K. We find a distinct globularization transition for larger chains ($N \geq 16$), which for $N \geq 32$ is well described by the one-parameter mean-field theory of Sanchez.[1]

Most previous simulations have used lattice models (simple cubic,[5] face-centered cubic,[5] diamond[6,7]), but in this study we allowed continuous variation in each torsional degree of freedom and calculated all nonbonding and torsional interactions. Comparisons with equivalent lattice calculations indicate systematic errors from use of such lattices.

Since solvent effects are not included, these simulations of isolated chains apply only to cases in which the solvent interactions are weak and the chain is immiscible.

Model and Sampling Procedure

We generated the polymethylene conformations using fixed bond distances and bond angles but allowing continuous variation of torsion angles. The potential function was chosen to reproduce the torsional potential function of *n*-butane (Abe et al.[8]) with $R_{C-C} = 1.53$ Å, $R_{C-H} = 1.10$ Å, $\theta_{C-C-C} = 112°$, $\theta_{H-C-C} = 109.5°$, and $\theta_{H-C-H} = 109.5°$. The total energy of the system is given by the sum of the torsional energy and nonbonding interactions:

$$E = \sum_{i=3}^{N-1} (V_0/2)(1 - \cos 3\phi_i) + \sum_{\text{allpair}} U_{ij} \qquad (1)$$

where $V_0 = 2.8$ kcal/mol and ϕ_i is the torsional angle of the *i*th bond. The van der Waals or nonbonded energy between atoms *i* and *j* is given by

$$U_{ij} = Be^{-CR_{ij}} - A/R_{ij}^6 \qquad (2)$$

where R_{ij} is the distance between atoms *i* and *j*. The sum is taken for all pairs of atoms except those involved directly in a bond stretching or bending interaction. van der Waals parameters are given in Table I.

TABLE I: **Nonbonding Energy Parameters**[a,b]

	A, Å⁶ kcal/mol	B, kcal/mol	C, Å⁻¹	ϵ_0, kcal/mol	R_0, Å	γ
H–H	45.2	9 950	4.54	0.072	2.6	11.8
H–C	127	86 100	4.57	0.083	3.1	14.3
C–C	363	908 600	4.59	0.106	3.6	16.5

[a] Reference 8. [b] ϵ_0 is the well depth, R_0 is the distance corresponding to the energy minimum, and γ is the normalized scale factor. The energy U is given by $U = Be^{-CR} - A/R^6 = [\epsilon_0/(\gamma - 6)][6e^{\gamma(1-\rho)} - \gamma\rho^{-6}]$, where $\rho = R/R_0$.

A simplification that reduces computer time is to precalculate all nonbonding energies as a function of R^2 with step size 0.005 Å². In the simulations, the value in the list corresponding to the nearest value of the desired R is used. This decreases the time by a factor of 3 but leads to the same energy within 0.1 kcal/mol when $R \geq 0.65R_0$. When $R \leq 0.65R_0$, each nonbonding potential energy is more then 10 kcal/mol, so that the error in this region should not have a large effect on the results.

Various methods have been suggested for trial movement in the Monte Carlo simulation of a polymer chain.[4] The reptation method[9] is used in this study because of its high efficiency and small calculational time. In this approach (see Figure 1), a terminal C–H bond to atom N is replaced with a new C–C bond to the $(N + 1)$ CH$_3$ group, while the first CH$_3$ group is contracted to an H (keeping a total of N carbons). When a C–C bond is replaced, the torsional angle (ϕ) of the new bond is chosen randomly. The trial movement is accepted with the probability

$$P_{\text{Tc}} = \min (1, e^{-\Delta E_{\text{Tc}}/k_B T}) \qquad (3)$$

where $\Delta E_{\text{Tc}} = E_{\text{T}} - E_{\text{c}}$, E_{T} is the energy of the trial conformation and E_{c} is the energy of the current conformation.

During the simulation, the following values are sampled and averaged at each temperature. Internal energy:

$$\langle E \rangle \qquad (4)$$

Specific heat:

$$\langle C \rangle = (\langle E^2 \rangle - \langle E \rangle^2)/k_B T^2 \qquad (5)$$

End-to-end length squared:

$$\langle R^2 \rangle = \langle (\vec{R}_1 - \vec{R}_N)^2 \rangle \qquad (6)$$

(1) Sanchez, I. C. *Macromolecules* **1979**, *12*, 980.
(2) Post, C. B.; Zimm, B. H. *Biopolymers* **1979**, *18*, 1487.
(3) Muthukumar, M. *J. Chem. Phys.* **1984**, *81*, 6272.
(4) Baumgärtner, A. In *Application of the Monte Carlo Method in Statistical Physics*; Binder, K., Ed.; Springer-Verlag: Berlin, 1984; pp 145–180.
(5) McCrackin, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973**, *6*, 859.
(6) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *85*, 3583.
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(8) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
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Radius of gyration:

$$\langle S^2 \rangle = (1/N^2) \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle (\vec{R}_i - \vec{R}_j)^2 \rangle =$$

$$(1/N) \sum_{i=1}^{N} \langle (\vec{R}_i - \vec{R}_{CM})^2 \rangle \quad (7)$$

where $\vec{R}_{CM}$ is the center-of-mass coordinate:

$$\vec{R}_{CM} = (1/N) \sum_{i=1}^{N} \vec{R}_i$$

The internal energy is the total potential energy, (1), while the specific heat is the fluctuation of the internal energy. Before beginning a simulated annealing sequence, we did a "melting run" of about 80 000 steps. During this stage, the temperature was set very high ($k_B T = 10^6$ kcal/mol) to allow the chain to sample all parts of configuration space. In doing this, we allowed the segments to pass each other by setting $U_{ij}(R_{ij} = 0) = L$, where L is a large but finite number (generally $L = 10^6$ kcal/mol).

The temperaure was decreased according to a predefined annealing schedule. At each temperature, the system was equilibrated (using multiple reptation steps) until the energy became nearly constant. The criteria for equilibration was

$$\bar{E}_n - 2C \leq \bar{E}_m \leq \bar{E}_n + 2C$$

where $\bar{E}_m$ is the average energy of the previous m steps, and C is the energy fluctuation (standard deviation) of the last n steps. For $N = 32$, n was chosen as 3000 and m was chosen as 900 000. For $N = 16$ and $N = 64$, n was chosen as 2000 and m was chosen as 400 000. For $N = 8$, n and m were chosen as 1000 and 100 000.

The annealing schedule involved a temperature decrease of 100 K per step for higher temperatures, which was decreased to 50 K per step when the energy fluctuations (specific heat) became large (near the globularization transition temperature, T_c).

Results and Discussion

A. Radius of Gyration versus Temperature. The temperature dependence of the radius of gyration $\langle S^2 \rangle$ is shown in Figure 2 for differing numbers of carbon atoms (N). In the case of $N = 8$ (Figure 2a), the radius of gyration becomes larger as the temperature is decreased, leading to an all-trans structure at low temperature. In the case of $N = 16$ (Figure 2b), $\langle S^2 \rangle$ becomes larger as the temperature is decreased to about 400 K and suddenly drops for temperaures below 300 K. In the case of $N = 32$ (Figure 2c), $\langle S^2 \rangle$ starts dropping below 1050 K, becoming a constant at about 300 K. In the case of $N = 64$ (Figure 2d), $\langle S^2 \rangle$ starts dropping below 1500 K, becoming a constant at about 400 K. End-to-end length versus temperature exhibits very similar tendencies.

To analyze the results, we used rotational isomeric state (RIS) theory[10] to calculate the radius of gyration as a function of temperature, as shown in Figure 2 (dotted line). In RIS theory, only nearest-neighbor interactions between atoms are considered, and no long-range interactions are taken into account. Also, the torsional angles of each bond are assumed to take only three discrete values: (1) trans (t, torsional angle $\phi = 0°$); (2) gauche plus (g^+, $\phi = 112.5°$); (3) gauche minus (g^-, $\phi = -112.5°$). The energy difference between trans and gauche is set to be $E_g - E_t = 0.5$ kcal/mol, and the energy difference between $g^{\pm}g^{\mp}$ and $g^{\pm}g^{\pm}$ is set to be $E(g^{\pm}g^{\pm}) - E(g^{\pm}g^{\mp}) = 2.7$ kcal/mol. Also, the C–C bond lengths are set to be 1.53 Å, and the C–C–C angles are set to be 112°. With the above two assumptions, RIS theory leads to analytic results for all N.

In the case of $N = 8$, the result of the simulation is described well by RIS theory except at high temperature. In the high-temperature region, the dimension of the chain is larger in the simulation than in RIS theory. This is due to the volume exclusion effect, which is neglected in RIS. When $N = 16$ and larger, the chains collapse in the low-temperature region. This is not explained by RIS theory due to the lack of long-range attractive
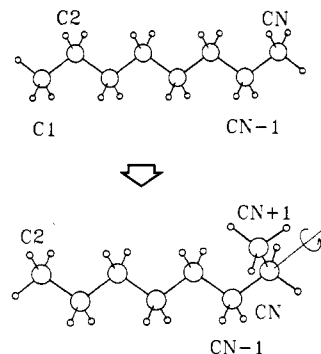
(10) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.

Figure 1. Trial movements used in this study. Here C_8H_{18} ($N = 8$) is shown.

interactions. In addition, the volume exclusion discrepancy at high temperature increases as the chain becomes larger.

In analyzing the results of the simulations, we find it useful to define an expansion factor α^2:

$$\alpha^2 = \langle S^2 \rangle / \langle S^2 \rangle_0 \quad (8)$$

as the ratio of the radius of gyration for the real chain $\langle S^2 \rangle$ to that of the free chain, $\langle S^2 \rangle_0$ (as given by RIS theory).

B. Comparisons of Lattice and Nonlattice Models. In polymer simulations it is common to use a lattice model in which all carbon atoms must be at sites on a diamond lattice. This considerably simplifies the programming and reduces the calculation time. In this model, all angles are tetrahedral, and the C–C and C–H bond lengths are set to be 1.53 and 1.10 Å, respectively (our calculation treated hydrogen atoms explicitly). We used the same potential energy parameters as for the continuously variable chain (nonlattice), but extra energy was added to each gauche conformation relative to a trans conformation to reproduce the same gauche-trans energy difference. To make a direct comparison with the lattice model, we did nonlattice calculations for a model with free torsional angles (as in section A) but with only three allowed torsional angles ($\phi = 0°$, $\pm112.5°$) as in the diamond lattice (and RIS theory).

The temperature dependence of the radius of gyration for a lattice model and nonlattice models for the case $N = 64$ is shown in Figure 3. The temperature dependence of $\langle S^2 \rangle$ with a lattice model shows a globular transition as for the nonlattice models, but $\langle S^2 \rangle$ in the lattice model is smaller than in the nonlattice models, especially in the high-temperature region. On the other hand, the temperature dependence of $\langle S^2 \rangle$ in both nonlattice models is very similar. This suggests that the discrepancy in the lattice model is not due to the discreteness of the torsional angles allowed but rather to the effect of discreteness on the entropies of extended versus globular configurations.

C. Specific Heat versus Temperature. The temperature dependence of specific heat is shown in Figure 4 for differing values of N. In the case of $N = 32$ (Figure 4c) and $N = 64$ (Figure 4d), sharp peaks in the specific heat (at $T = 400$ and 600 K, respectively) mark the transition from random coil to globule. In the case of $N = 16$ (Figure 4b), a sharp peak is observed at $T = 150$ K, indicating the globular transition. The transition temperature increases as N becomes larger, as expected from the increased favorability of intermolecular interactions. However, for $N = 8$ (Figure 4a) no globular transition is observed, and the specific heat increases monotonically as the temperature is decreased to 100 K.

D. Estimation of the Flory Θ Temperature. The mean-field theory predicts the following scaling behavior for a flexible chain molecule as $N \rightarrow \infty$:[1]

$$T > \Theta, \quad \langle R^2 \rangle \propto \langle S^2 \rangle \propto N^{2\nu}, \quad \text{where } \nu = \tfrac{3}{5}, \langle R^2/N \rangle \propto N^{0.2}$$

$$T = \Theta, \quad \langle R^2 \rangle \propto \langle S^2 \rangle \propto N^{2\nu}, \quad \text{where } \nu = \tfrac{1}{2}, \langle R^2/N \rangle \propto N^0$$

$$T < \Theta, \quad \langle R^2 \rangle \propto \langle S^2 \rangle \propto N^{2\nu}, \quad \text{where } \nu = \tfrac{1}{3},$$
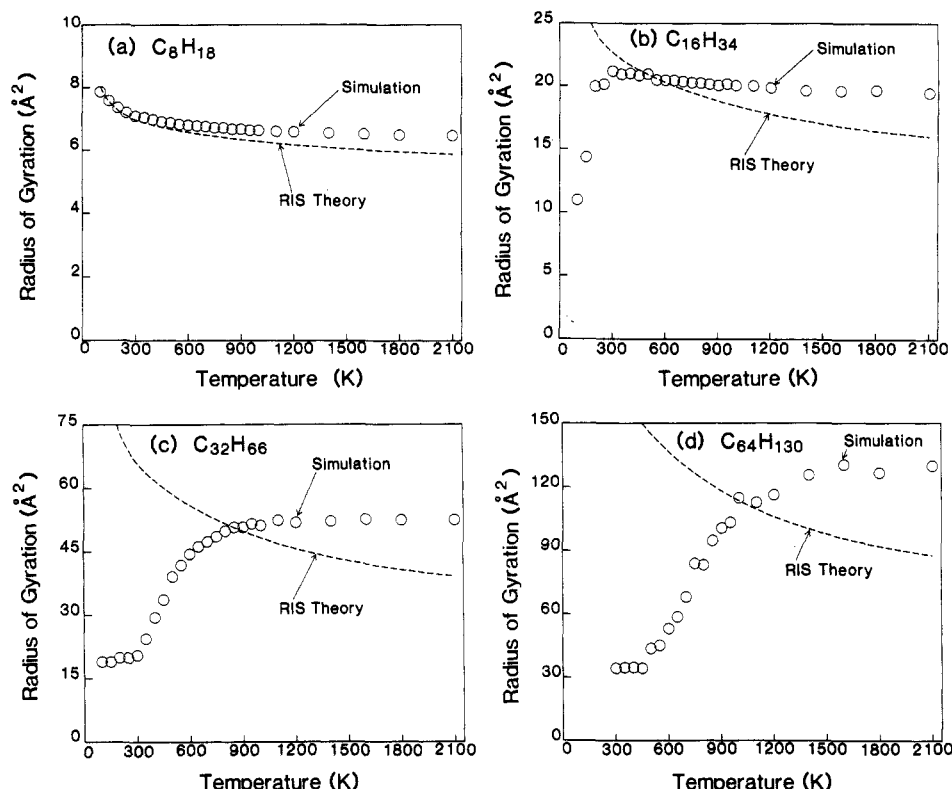
$$\langle R^2/N \rangle \propto N^{-0.33}$$

Figure 2. Radius of gyration, $\langle S^2 \rangle$, as a function of temperature (nonlattice, free torsion). Dashed line shows RIS theory.
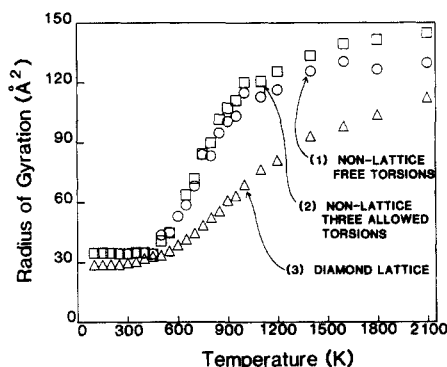

Figure 3. Temperature dependence of radius of gyration, $\langle S^2 \rangle$, for $C_{64}H_{130}$ with use of three different models: (1) nonlattice, free torsions; (2) nonlattice, three allowed torsions ($\phi = 0°$, $\pm112.5°$), (3) diamond lattice.

where the Flory temperature Θ is a measure of interatomic interactions versus rigidity.

To determine the value of Θ from our simulations, we plot $\langle R^2 \rangle / N$ and $\langle S^2 \rangle / N$ versus N in Figure 5. The expected slope at high temperature is indicated by the $N^{0.2}$ line. For 1600 K we see that $N = 32$ and 64 lead to results close to this slope. The expected slope at low temperature is indicated by the $N^{-0.33}$ line. Here we see that $N = 32$ and 64 give the correct trend but greater deviation. At the Θ temperature, both plots should have zero slope as $N \rightarrow \infty$. From Figure 5 we see the $\Theta \approx 1100$ K. In these simulations, interactions with solvent are ignored, so that our model assumes a *very* poor solvent in which polymethylene is immiscible. This leads to a high Θ and a high globularization temperature. When the chain is in a good solvent, the attractive energy *between* different polymer units will stabilize more extended structures and decrease the Θ temperature.

Including the excluded volume effect and attractive interactions of nearest-neighbor lattice sites on the diamond lattice model, Kremer et al.[7] obtained $k_B\Theta/\epsilon_a = 2.25 \pm 0.10$, where ϵ_a is the attractive nearest-neighbor energy. In our model, the attractive interaction is not between nearest neighbors as in these lattice simulations; rather we include a larger range corresponding to

the tail of the van der Waals interaction. Consequently the effective ϵ_a is not just the depth of C–C van der Waals interaction (0.1 kcal/mol) but rather is $\epsilon_a \approx 0.5$ kcal/mol. This ϵ_a is obtained by calculating the total nonbonded attractive interaction between carbons and dividing by 2. Using $\epsilon_a = 0.5$ for Kremer's lattice simulation would lead to $\Theta = 570$ K, much smaller than our estimated value of 1100 K. The same lattice model was used by Kolinski et al.[6] but included the gauche–trans energy difference ϵ_g. For $N = 200$ they estimated Θ for differeing values of the chain flexibility parameter $|\epsilon_g/\epsilon_a|$. They obtained $k_B\Theta/\epsilon_a = 2.22$ when $|\epsilon_g/\epsilon_a| = 1$ and $k_B\Theta/\epsilon_a = 2.50$ when $|\epsilon_g/\epsilon_a| = 4$. Using Θ from their simulation with $|\epsilon_g/\epsilon_a| = 4$ and assuming $\epsilon_a = 0.5$ kcal/mol lead to $\Theta = 630$ K. This value is also smaller than our value (our calculations use $|\epsilon_g/\epsilon_a| \sim 5$). Both of these lattice estimations of Θ ignored H–H and C–H attractive interactions, whereas they are included in our studies. Also, the number of pairs of units attracting each other in lattice models is smaller than that in our model. These effects would both tend to make the estimated Θ temperature smaller than ours.

Experimentally, the Θ temperature of polymethylene in diphenyl ether solvent is $\Theta = 434$ K,[11] and this is considerably smaller than our estimated value. The main reason for this discrepancy is the stabilization of extended structures because of attractive energy between polymethylene and solvent.

E. Comparison with Mean-Field Theory. Using mean-field theory, Sanchez[1] has shown that in the limit of large N, the expansion factor α^2 of (8) is given by

$$(7\phi_\alpha/3N)(1 - \alpha^2) = \frac{1}{2}(\Theta/T)\phi_\alpha^2 + \ln(1 - \phi_\alpha) + \phi_\alpha \quad (9)$$

where

$$\phi_\alpha = \phi_0/\alpha^3$$

$$\phi_0 = (19/27)^{1/2}N^{-1/2}$$

In the derivation of this equation, the chain is assumed to be completely flexible, and long-range interactions between atoms (volume exclusion and van der Waals attraction) are taken into

(11) Seymour, R. B. *Introduction to Polymer Chemistry*; Robert E. Krieger: New York, 1978; p 41.
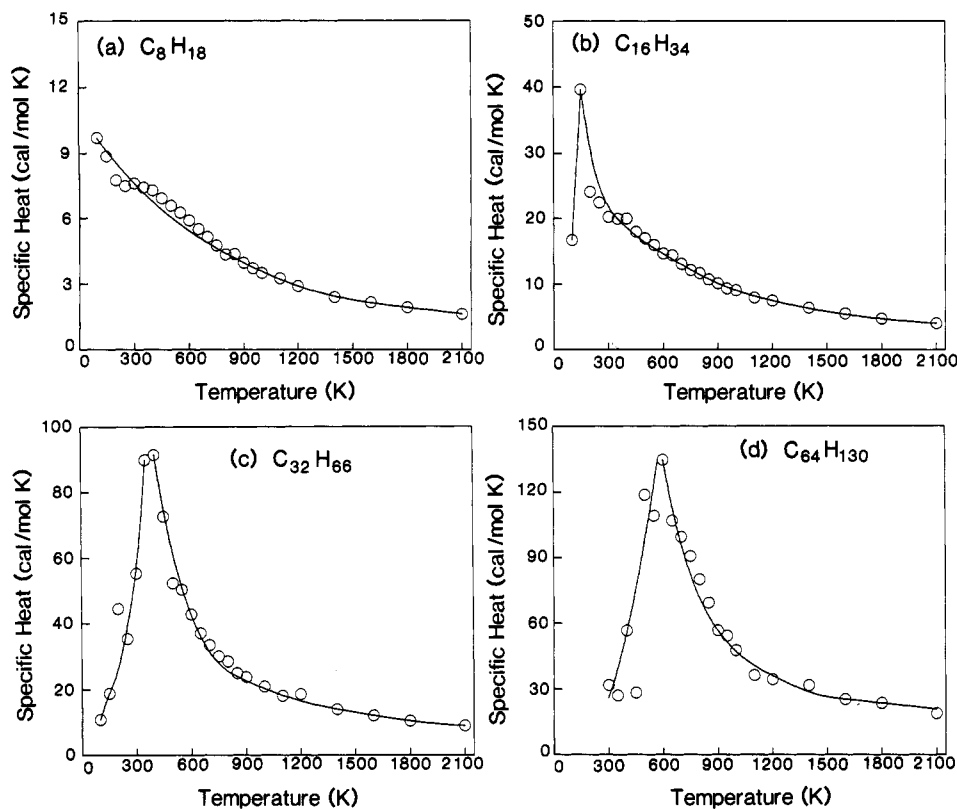
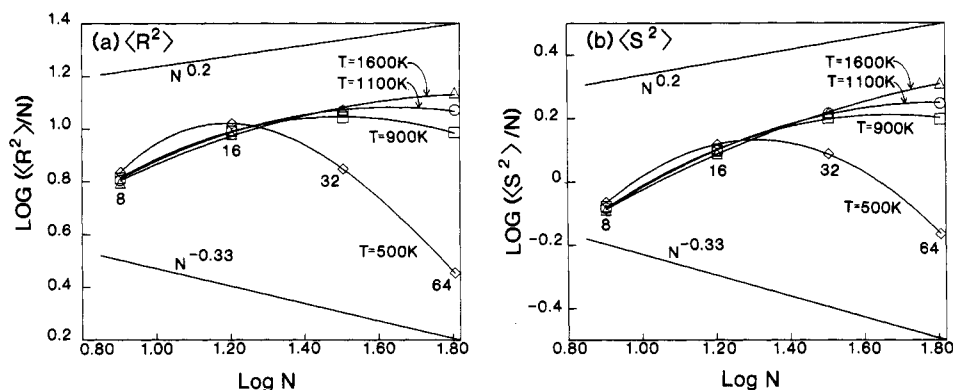**Figure 4.** Temperature dependence of specific heat. Solid lines are visual fits of the data.

Figure 5. Dependence of radius of gyration, $\langle S^2 \rangle$, and end-to-end distance, $\langle R^2 \rangle$, upon chain length for various temperatures. The Θ temperature is determined by requiring zero slope for large N.
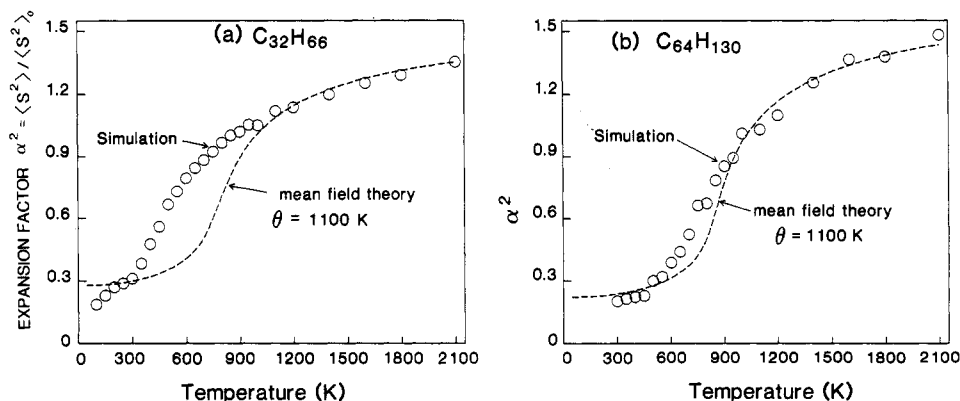

Figure 6. Relative size of (a) $C_{32}H_{66}$ and (b) $C_{64}H_{130}$ as a function of temperature. The expansion factor α^2 is the ratio of the calculated radius of gyration to that expected for a random coil. The dotted line shows how well the simulations are fit in terms of a one-parameter mean-field theory.

account by using average values (average density of atoms and average energy between atoms). Therefore, no correlation effects are considered. It is valid in the limit of large N and, as indicated in Figure 6, provides a good fit to the results of the simulations for $N = 64$. For $N = 32$, the fit is good at high temperature but

not at low temperature. For smaller chains ($N = 8, 16$), the fit is poor (as expected, since N is not large).

F. Most Stable Structure of the Chain. During the simulation, the actual conformation of the chain is sampled periodically and displayed by using the BIOGRAF molecular modeling package[12]
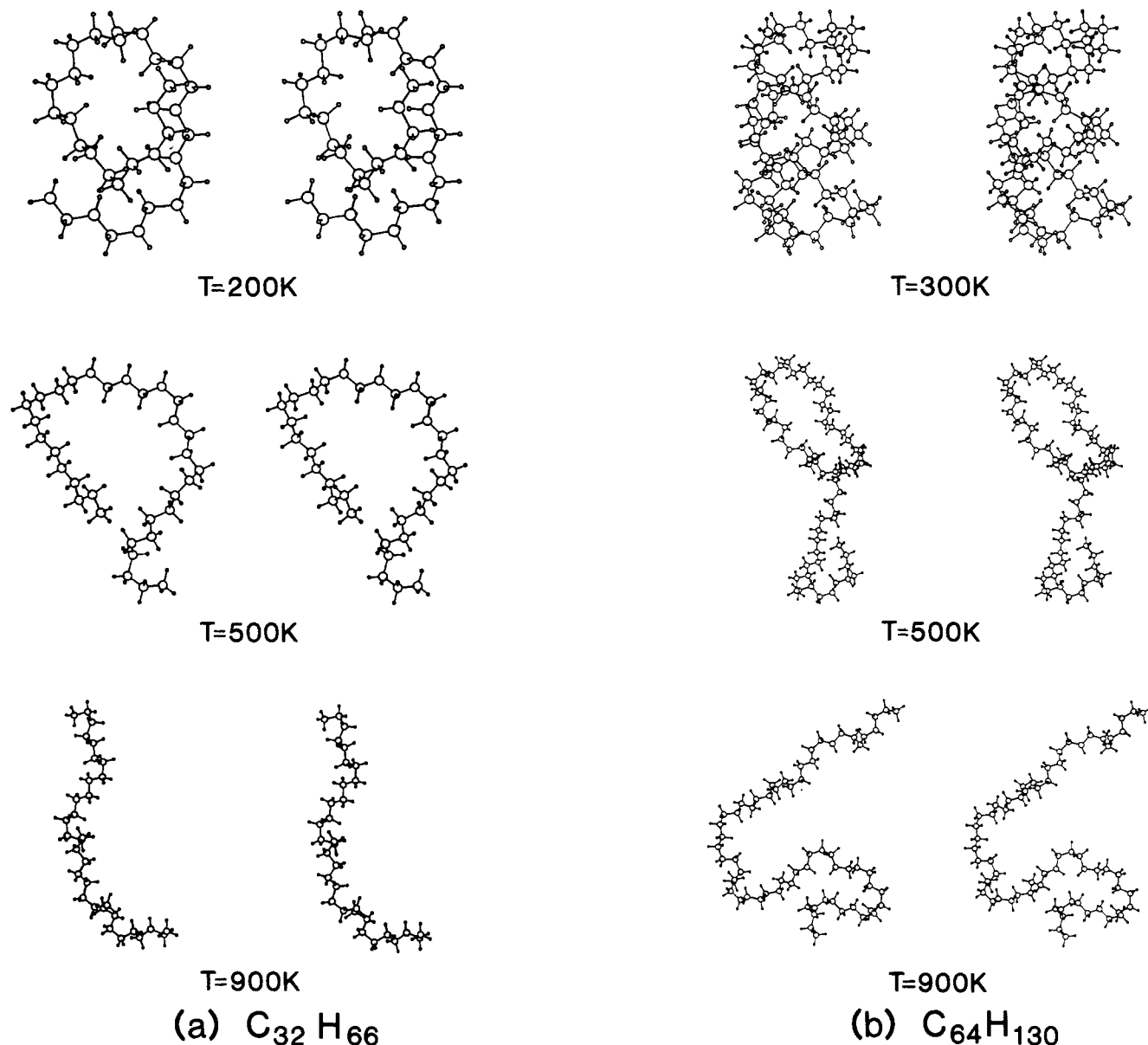
T=200K

T=300K

T=500K

T=500K

T=900K

T=900K

(a) $C_{32}H_{66}$

(b) $C_{64}H_{130}$

Figure 7. Stereoplots of the equilibrated conformations of polymethylene at various temperatures (selected randomly from the equilibrated set of configurations): (a) $C_{32}H_{66}$; (b) $C_{64}H_{130}$.

on an Evans and Sutherland PS 330 graphics system. This is a useful aid to understanding the conformation changes in the systems under study. Snapshots of conformations at various temperature are shown in Figure 7 for $N = 32$ and $N = 64$. Simulations are carried out at each temperature until thermal equilibrium is reached; the temperature is then lowered, and the system reequilibrated (this process can be thought of as simulated annealing[13]). We find that this procedure leads at low temperature to the most stable structure. As shown in Figure 7, the stable structure is folded or pseudoglobular. To make a globular structure, the chain must have multiple gauche interactions causing unfavorable local interactions. For sufficiently long chains, this unfavorable conformation is compensated by the favorable van der Waals interactions between chains, leading to globular formation.

Summary

Computer simulations of realistic isolated polymethylene chains have been used to characterize the transitions between random coil at high temperature and globular conformations at low temperature. For longer chains, the random coil–globularization transition is well characterized in terms of a single-parameter mean-field theory. We find that lattice models lead to significant errors in characterizing this system.

(12) BIOGRAF is an interactive molecular simulation three-dimensional graphics program from BioDesign Inc., Pasadena, CA.

(13) Kirkpatrick, S.; Gelatt, Jr., C. D.; Vecchi, M. P. *Science (Washington, D.C.)* **1983**, *220*, 671.