Vanishing of the Chain Length Dependence of the Second Virial Coefficient Zero Point for Lattice Polymers

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ABSTRACT: We have succeeded in finding a unique solvent condition (Θ*-point) at which the second virial coefficients of lattice polymers of various chain lengths vanish simultaneously. This was accomplished by introducing the nearest-neighbor triplet interaction into the lattice polymers with the traditional nearest-neighbor pair interaction. The finite lattice polymers at this point are not Gaussian, which contrasts with the Gaussian behavior of the continuous model polymers with two- and three-body δ-function interactions at the corresponding point. Ignoring this unfixed issue, we constructed a map providing the relations of the parameters of the two polymers which were established from the penetration function behaviors.

Introduction

In spite of the continuing and extensive study of the polymer Θ-point,[1,2,6,12] we believe that a clear-cut understanding of its physical meaning has not yet been attained. This is partly because of the large difference between the theoretical models and the real polymers or the lattice polymers in simulation.

The Θ-point has two definitions:[3] (1) the solvent condition at which an isolated polymer behaves in a Gaussian manner and (2) the solvent condition at which the second virial coefficient A_2 vanishes. Contrary to early expectation,[2] the two definitions are not necessarily consistent.

We start from the second definition and recall the lattice polymer simulations by Janssens and Bellemans[4] and Bruns.[3] Both studies utilized lattice polymers in the simple cubic (SC) lattice with the nearest-neighbor element pair interaction. According to Janssen and Bellemans,[4] the solvent condition η at the Θ-point, η_Θ, depends on the number of elements in a polymer molecule n as

$$\eta_\Theta = 1.309(1 - 0.096/n^{1/2}) \tag{1}$$

where $\eta \equiv \exp(-\epsilon_2)$, with ϵ_2 the potential energy associated with a nearest-neighbor nonbonded element pair in units of kT (see below). Bruns' work[3] with respect to η_Θ almost coincided with Janssen and Bellemans, but he also found that isolated polymers at the Θ-point are not Gaussian. This is so even for infinite polymers.

In this paper, we try to find a unique solvent condition where the second virial coefficient vanishes irrespective of the chain length. We seek to accomplish this by introducing the nearest-neighbor triplet interaction[5] (see below) into the traditional SC lattice polymers with the nearest-neighbor pair interaction. We call the solvent condition of this kind the Θ*-point. Previously, we examined precisely the quasi-scaling for the finite lattice polymers with the nearest-neighbor pair and triplet interactions.[5]

After determining the Θ*-point, we examined whether the lattice polymers at that point are Gaussian as is the case for continuous model polymers. This work should be viewed as one of the steps to attain a good understanding of the relation between the two polymers by controlling the triplet interaction.

The continuous model considers a polymer molecule to be a Gaussian molecule with several multibody δ-function interactions. A conformation of a polymer chain is specified by a continuous position vector $\vec{c}(\tau)$, with τ being the contour distance along the chain. After some transformation, its Hamiltonian involving up to the three-body interaction[6] is

$$H(\vec{c}(\tau))/kT = (1/2)\int_0^N d\tau \{d\vec{c}(\tau)/d\tau\}^2 + (\upsilon_2/2!)\int_0^N d\tau_2 \int_0^N d\tau_1\, \delta\{\vec{c}(\tau_1) - \vec{c}(\tau_2)\} + (\upsilon_3/3!)\int_0^N d\tau_3 \int_0^N d\tau_2 \int_0^N d\tau_1\, \delta\{\vec{c}(\tau_1) - \vec{c}(\tau_2)\}\delta\{\vec{c}(\tau_2) - \vec{c}(\tau_3)\} \tag{2}$$

where N is the chain length, the constraint $|\tau_1 - \tau_2| \geq a$ (with a the cutoff) applies to the integral in the second term, the constraints $|\tau_1 - \tau_3|, |\tau_3 - \tau_2|, |\tau_2 - \tau_1| \geq a$ apply to the integral in the third term, and υ_2 and υ_3 are the strengths of the two- and the three-body interactions. Although the polymer Hamiltonian (2) should involve the four-body and higher body interaction terms, they are neglected because the higher order terms are diminished with negative powers of N.[6]

According to the model (2), the inconsistency of the two definitions of the Θ-point and its chain length dependence arises from the existence of the three-body term υ_3. At the Θ*-point, υ_2 and υ_3 are zero and the polymers are Gaussian.

Procedure

The second virial coefficient A_2 is connected with the interchain excluded volume $\langle V \rangle$ by[7]

$$A_2 = \langle V \rangle/(2n^2) \tag{3}$$

The interchain excluded volume $\langle V \rangle$ is evaluated through

$$\langle V \rangle = \Omega\{Z_1^2 - Z_{1,2}\}/Z_1^2 \tag{4}$$

where Z_1 is the partition function of a single polymer confined in a volume Ω and $Z_{1,2}$ is the distinguishable two-chain partition function of polymers in the same volume.

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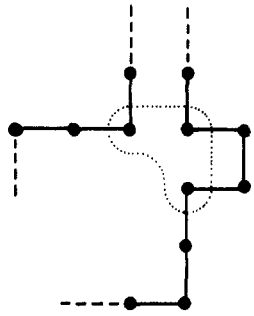

Figure 1. Illustration of a nearest-neighbor triplet configuration in which an element is a neighbor to two nonbonded elements.

In this work, each polymer molecule (n-mer) is simulated by a self-avoiding chain of elements occupying n sites in the SC lattice. As usual, we assume that each nearest-neighbor nonbonded element pair contributes an energy ϵ_2 (in units of kT) to the polymer. We also assume that each nearest-neighbor nonbonded element triplet contributes an energy ϵ_3 (in units of kT) (Figure 1). This is an artifice first introduced in the lattice systems to rescue the off-scaling[5] and to simulate the three-body term in the continuous model (2). The contribution of the three-body interaction cannot be controlled by experiments on real polymers but only through numerical experiments such as this. It will, in turn, contribute to the understanding of real polymers. The solvent condition is thus specified by the combination of ϵ_2 and ϵ_3, or η and ξ, where

$$\eta = \exp(-\epsilon_2) \tag{5a}$$

$$\xi = \exp(-\epsilon_3) \tag{5b}$$

First we generated many n-mer conformations with the realization probability governed by canonical statistics under a specified solvent condition of $\epsilon_2 = \epsilon_{2,0}$ and $\epsilon_3 = \epsilon_{3,0}$ or of $\eta = \eta_0$ and $\xi = \xi_0$. Our Monte Carlo simulation adopted Wall and Mandell's reptation method[8] combined with Metropolis et al.'s algorithm[9] for the purpose. The method, which has been repeatedly described,[10] should be modified so as to include the energy contribution from the triplet interaction if $\xi_0 \neq 1$.

The second virial coefficient A_2 at the reference solvent condition was evaluated by using the conformation samples generated. The interchain excluded volume $\langle V \rangle$ in our lattice polymers is rewritten as

$$\langle V \rangle = \frac{\sum_i \sum_j [\sum_{\vec{r}} \{1 - \exp(-W_{i,j}(\vec{r}))\}] \exp\{-W_1(i) - W_2(j)\}}{[\sum_i \exp\{-W_1(i)\}][\sum_j \exp\{-W_2(j)\}]} \tag{6}$$

In eq 6, $W_1(i)$ and $W_2(j)$ are the intrachain potential energies (in units of kT) of polymer 1 with conformation i and that of polymer 2 with conformation j, respectively, and $W_{i,j}(\vec{r})$ is the interchain potential energy between the same polymers which are at a relative distance $\vec{r}$. The summation over i and j extends over all conformations of the two polymers. The summation over $\vec{r}$ covers all relative positions of the two chains.

In our simulation, the conformation summation was performed for over 10 000 pairs, whereas the $\vec{r}$ summation was performed exactly. Since our conformation samples were generated with the realization probability proportional to $\exp[-W_\alpha(i,\epsilon_{2,0},\epsilon_{3,0})]$ (α = 1, 2), the arithmetic average of the $\vec{r}$ summation over the sample pairs is expected to approach the excluded volume $\langle V \rangle$ at the reference solvent condition. Therefore, to a good approximation

$$\langle V(\eta_0,\xi_0) \rangle = \langle \sum_{\vec{r}} [1 - \exp\{-W_{i,j}(\vec{r},\eta_0,\xi_0)\}] \rangle_{i,j} \tag{7}$$

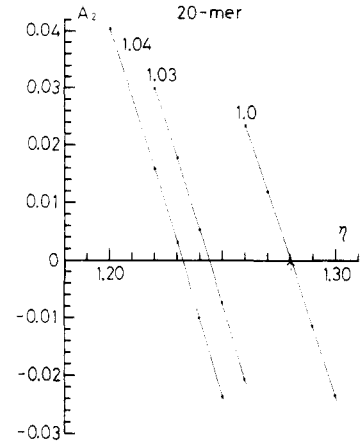

Figure 2. Second virial coefficient A_2 vs η with ξ as a parameter for 20-mer. The values of ξ are indicated. The arrow indicates the estimation for the Θ-point by Janssens and Bellemans[4] for the polymer with $\xi = 1$.

At an arbitrary solvent condition ϵ_2, ϵ_3 such as

$$\epsilon_2 = \epsilon_{2,0} + \Delta\epsilon_2 \tag{8a}$$

$$\epsilon_3 = \epsilon_{3,0} + \Delta\epsilon_3 \tag{8b}$$

the intrachain energy is

$$W_\alpha(i) = n_{\alpha,2}(i)\epsilon_2 + n_{\alpha,3}(i)\epsilon_3 = W_{\alpha,0}(i) + \Delta W_\alpha(i) \tag{9a}$$

$$W_{\alpha,0}(i) = n_{\alpha,2}(i)\epsilon_{2,0} + n_{\alpha,3}(i)\epsilon_{3,0} \tag{9b}$$

$$\Delta W_\alpha(i) = n_{\alpha,2}(i)\Delta\epsilon_2 + n_{\alpha,3}(i)\Delta\epsilon_3 \tag{9c}$$

where $n_{\alpha,2}(i)$ is the number of nearest-neighbor nonbonded element pairs of the ith conformation of polymer α, $n_{\alpha,3}(i)$ is the number of nearest-neighbor nonbonded element triplets of the same conformation, and α = 1, 2. By introducing (9) in (6) and by the same reason deriving (7), the excluded volume at the solvent condition ϵ_2,ϵ_3 or η,ξ is calculated by

$$\langle V(\eta,\xi) \rangle = \frac{\langle \exp\{-\Delta W_1(i) - \Delta W_2(j)\} \sum_{\vec{r}} [1 - \exp\{-W_{i,j}(\vec{r})\}] \rangle_{i,j}}{\langle \exp\{-\Delta W_1(i)\} \rangle^2} \tag{10}$$

where the angular brackets in the denominator on the right-hand side mean the arithmetic average over samples.

Equation 10 is correct for any η,ξ pair, but with increasing deviation from the reference point, we need more samples to obtain a good estimation. The reference solvent condition near the Θ*-point is preferable. Our choice was $\eta_0 = 1.27$ and $\xi_0 = 1.0$, which is the Θ-point for 99-mer according to (1).

The second virial coefficients at and near the reference point were calculated for 20-, 40-, 80-, and 120-mers. Through interpolation the second virial coefficient zero points were estimated. The existence of the Θ*-point was then investigated.

Results and Discussion

Figures 2–5 show plots of A_2 vs η with ξ as a parame-

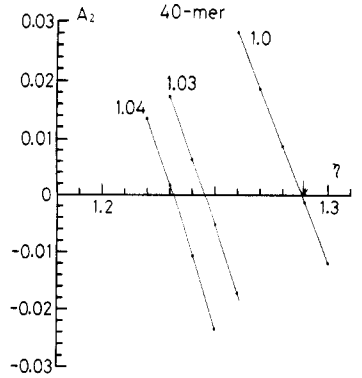

Figure 3. Second virial coefficient A_2 vs η with ξ as a parameter for 40-mer. The values of ξ are indicated. The arrow indicates the estimation for the Θ-point by Janssens and Bellemans[4] for the polymer with $\xi = 1$.

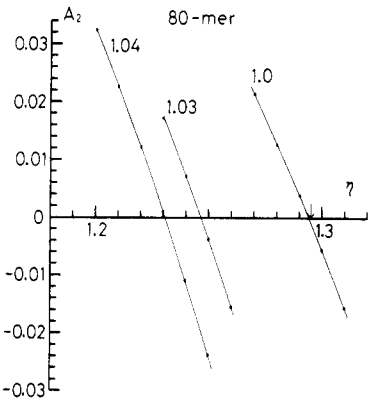

Figure 4. Second virial coefficient A_2 vs η with ξ as a parameter for 80-mer. The values of ξ are indicated. The arrow indicates the estimation for the Θ-point by Janssens and Bellemans[4] for the polymer with $\xi = 1$.

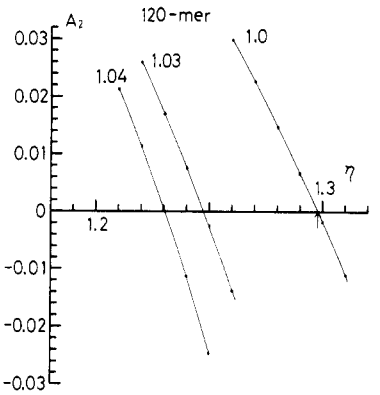

Figure 5. Second virial coefficient A_2 vs η with ξ as a parameter for 120-mer. The values of ξ are indicated. The arrow indicates the estimation for the Θ-point by Janssens and Bellemans[4] for the polymer with $\xi = 1$.

ter for 20-, 40-, 80-, and 120-mers, respectively. In the figures, Janssens and Bellemans' estimation[4] for polymers with $\xi = 1$ is indicated by the arrows.

The second virial coefficient zero points $(\eta_\Theta(n),\xi_\Theta(n))$ were read off from the figures by interpolation. They are plotted in the (η_Θ,ξ_Θ) coordinate with n as a parameter as shown in Figure 6. The plots cross one another within a very small area, which is the same order with the experimental scattering. We consider that we have found the Θ*-point. Our estimation is

$$\eta_\Theta^* = 1.2356 \pm 0.0007 \quad (11a)$$

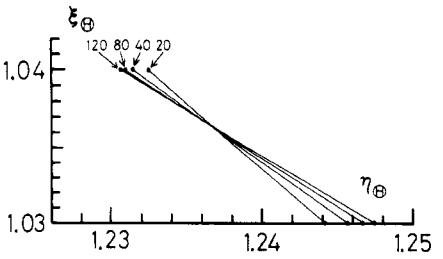

Figure 6. ξ_Θ vs η_Θ relations with the chain length n as a parameter. The values of n are indicated.

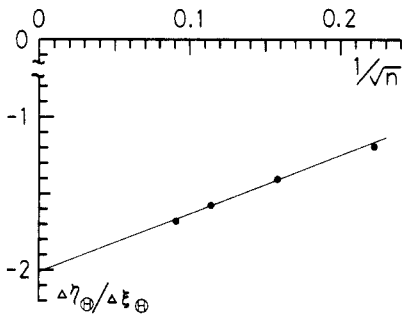

Figure 7. Plot of $\Delta\eta_\Theta/\Delta\xi_\Theta$ vs $1/n^{1/2}$, with $\Delta\eta_\Theta = \eta_\Theta - \eta_\Theta^*$ and $\Delta\xi_\Theta = \xi_\Theta - \xi_\Theta$. The points with a common $1/n^{1/2}$ but different combinations of η_Θ and ξ_Θ fall within a single symbol.

$$\xi_\Theta^* = 1.0370 \pm 0.0005 \quad (11b)$$

Figure 7 shows a plot of the ratio $\Delta\eta_\Theta(n)/\Delta\xi_\Theta(n)$ vs $1/n^{1/2}$ for various combinations of $\eta_\Theta(n)$ and $\xi_\Theta(n)$, where $\Delta\eta_\Theta = \eta_\Theta(n) - \eta_\Theta^*$ and $\Delta\xi_\Theta = \xi_\Theta(n) - \xi_\Theta^*$. The points with a common $1/n^{1/2}$ but from different combinations of $\Delta\eta_\Theta$ and $\Delta\xi_\Theta$ fall well within a single symbol in the figure. The linear approximation with the least-squares method gives

$$\Delta\eta_\Theta = \{-2.013 \pm 0.027 + (3.79 \pm 0.22)/n^{1/2}\}\Delta\xi_\Theta \quad (12)$$

Then for infinite polymers

$$\Delta\eta_{\Theta,\infty} = (-2.013 \pm 0.027)\Delta\xi_{\Theta,\infty} \quad (13)$$

According to Freed,[6] the second virial coefficient A_2 of the continuous model polymers in the first-order perturbation approximation[6] is

$$A_2 = (4\pi)^{3/2}N_A(Nl/3)^{3/2}(2M^2)^{-1}[v_2N^{1/2}/(2\pi)^{3/2} - (v_3/\pi^3)\{1 - (N/4a)^{1/2}\}] \quad (14)$$

where N_A is Avogadro's number, l is the step length, and M is the molecular weight. Then at the Θ-point, where, $v_2 = v_{2,\Theta}$ and $v_3 = v_{3,\Theta}$

$$v_{2,\Theta} = 8(2\pi)^{-3/2}v_{3,\Theta}\{(1/N^{1/2}) - (1/4a)^{1/2}\} \quad (15)$$

For infinite polymers

$$v_{2,\Theta,\infty} = -4(2\pi)^{-3/2}a^{-1/2}v_{3,\Theta,\infty} \quad (16)$$

Relations 15 and 16 are very similar in form to relations 12 and 13 of our lattice polymers.

The continuous model polymer (2) asserts the existence of the Θ*-point at

$$v_2 = v_{2,\Theta}^* = 0 \quad (17a)$$

$$v_3 = v_{3,\Theta}^* = 0 \quad (17b)$$

together with the Gaussian behavior at this point. Obviously, this arises from the neglect of the higher body terms in the Hamiltonian (2).

To examine whether our lattice polymers at the Θ*-point behave in a Gaussian manner as the continuous model polymers, we calculated the reduced moments which are

Table I
Comparison of the Reduced Moments of the Lattice Polymers at the Θ*-Point with Those of the Gaussian Polymers

	$M_h^{4,2}$	$M_h^{6,4}$	$M_r^{4,2}$	$M_r^{6,4}$	$M_s^{4,2}$	$M_s^{6,4}$
lattice polymer						
$n = 20$	1.502	1.582	1.157	1.235	1.762	1.933
$n = 40$	1.543	1.642	1.185	1.278	1.822	2.024
$n = 80$	1.592	1.706	1.207	1.316	1.872	2.098
$n = 120$	1.596	1.724	1.215	1.326	1.894	2.134
gaussian polymer	1.667	1.807	1.267	1.404	2.000	2.278

dimensionless ratios of the moments of the polymer sizes. Following Bruns,[3] they are

$$M_x^{m,n} = \langle x^m \rangle / \langle x^n \rangle^{m/n} \tag{18}$$

$$x \in \{h, r, s\}$$

$$\langle h^{2k} \rangle = \langle |r(n) - r(1)|^{2k} \rangle \tag{19}$$

$$\langle r^{2k} \rangle = (1/n) \langle \{ \sum_{i=1}^{n} s(i)^2 \}^k \rangle \tag{20}$$

$$\langle s^{2k} \rangle = (1/n) \langle \{ \sum_{i=1}^{n} s(i)^{2k} \} \rangle \tag{21}$$

where $\vec{r}(i)$ is the position vector of the element i and $s(i)^2$ is its squared distance from the center of mass.

The conformation samples at the Θ*-point were generated by the scheme mentioned in the previous section for polymers at the reference point with $\xi \neq 1$. The reduced moments were then directly calculated from the samples. They are listed in Table I and compared with the Gaussian values. There is some difference between the two. Our lattice polymers with $n \leq 120$ are not Gaussian at the Θ*-point. Of course, there remains the possibility that infinte polymers at the Θ*-point are Gaussian.

A continuous polymer is different from a lattice polymer. The correspondence of the two polymers, if there is such a correspondence, will be established after coarse-graining[6] or for quantities averaged over a range of the very long lattice polymer conformations.

The calculation of A_2 or $\langle V \rangle$ requires the integration or the averaging of the interchain interaction over all conformations and the mutual vectorial separation. The vanishing of A_2 or $\langle V \rangle$ is the result of compensation in the integration.

In considering the single-chain polymer statistics, we divide a polymer chain into a certain number of subchains.[12] The polymer will be Gaussian when the intersubchain excluded volume vanishes. Two subchains are not mutually independent but constrained because they are connected through the molecular backbone. The vanishing of the intersubchain excluded volume is expected as a result of the integration over the constrained mutual separation.

We found a good correspondence of the lattice polymers with the continuous model polymers concerning the existence of the Θ*-point and the manner of the chain length dependence of the Θ-point (cf. (12) with (14)). The above argument suggests that the correspondence does not assure the same thing between the two concerning the single-chain behavior. At present, we are not sure whether a full correspondence can be established by infinite polymers.

The penetration function R defined by

$$R = \langle V \rangle / \langle r^2 \rangle^{3/2} \tag{22}$$

is dimensionless and one of the renormalization group (RG) invariants discussed before.[5,6,13] We found in our previous study[13] that the R value at the RG good-solvent fixed point of the lattice polymers with $\xi = 1$ (10.3) agrees well with the theoretical value from the continous model polymers without the three-body term (10.3).[14,15] (We found several misprints[16] in that paper.[13]) The RG good-solvent fixed point of the lattice polymers is at $\eta = \eta_g^* = 1.13$ (and $\xi = \xi_g^* = 1$).[13]

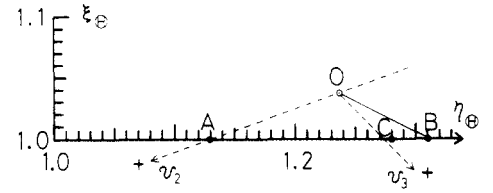

Figure 8. Correspondence of the (η,ξ) coordinate of the lattice polymers with the (v_2,v_3) coordinate of the continuous model polymers. The penetration functions of both polymers at the point O are zero irrespective of the chain length. The penetration functions of both polymers of infinite length are 10.3 at point A and zero along line OB.

The penetration functions at the Θ-point are zero.

Figure 8 provides a map indicating the relation between the parameters (η,ξ) of the SC lattice and (v_2,v_3) of the continuous model on the (η,ξ) rectangular coordinate. Along the quoted lines or at the points, the penetration functions of the two differently defined polymers assume the same values. Although it ignores the unfixed items in the single-chain behavior mentioned above, it will give a perspective in understanding the relations of the two polymers.

The point $O(\eta_\Theta^*,\xi_\Theta^*)$ is the origin of the (v_2,v_3) coordinate. The point A $(\eta_g^*,1)$ must be on the v_2 axis. We simply assume the v_2 axis coincides with the line OA. On the line OB satisfying (12), the penetrations of infinite lattice polymers are zero. The v_3 axis should be chosen and scaled so that the penetrations of the continuous model polymers are zero along the line OB, which should satisfy (16) with respect to the (v_2,v_3) coordinate. Of course, it requires the scaling of the v_2 axis together with the cutoff a. In any case, the v_3 axis is in the area bounded by the v_2 axis and the line OC, where C is the Θ-point of the shortest lattice polymers with $\xi = 1$ satisfying (12).

Cherayil et al.'s crude estimation[11] of the three-body parameter z_3 $(=(2\pi)^{-3}v_3)$ at the Θ-point of the infinite lattice polymers ($\xi = 1$) was 5×10^{-3}. The converted v_3 value is 1.2. This may be an approximation to the v_3 component of point B. From (16), the v_2 component of the same point is $-0.3a^{-1/2}$.

Freed had developed a theory treating the relations between the two polymers in a general way.[17]

We argued before[13] that the RG poor-solvent fixed point, if there is such a point, is not on the η-axis. The Θ*-point is just the poor-solvent fixed point if we exclusively use the penetration for the RG operation device. To obtain a complete picture, however, we have to examine whether the reduced moments of infinite polymers are constant along the line OB.[14]

We expect the simulation for polymers embedded in other lattices perhaps to yield similar results, but this is

beyond the scope of the present work.

Summary

The second virial coefficient zero point (Θ-point) of traditional lattice polymers with nearest-neighbor pair interactions varies with the inverse square root of the chain length. We have succeeded in finding a unique solvent condition (Θ*-point) at which the second virial coefficients of the lattice polymers of various chain lengths vanish simultaneously. This was accomplished by associating an appropriate energy to each nearest-neighbor triplet in a polymer conformation. The Θ-point behavior of our lattice polymers is much like those of the continuous model polymers with two- and three-body δ-function interactions. On the other hand, the reduced moments of the lattice polymers at the Θ*-point are not Gaussian, in contrast to the continuous model polymers at the same point. Ignoring this last inconsistency, we have constructed a map providing the relations of the parameters of the two polymers, which were established from the consistency in the penetration function.

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References and Notes

(1) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293.

(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York, 1953.

(3) Bruns, W. *Macromolecules* **1984**, *17*, 2826.

(4) Janssens, M.; Bellemans, A. *Macromolecules* **1976**, *9*, 303.

(5) Watanabe, Y.; Katoh, M.; Okamoto, H. *Macromolecules*, in press.

(6) E.g.: Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987.

(7) E.g.: Hill, T. L. *Statistical Mechanics*; McGraw-Hill: New York, 1956.

(8) Wall, F. T.; Mandell, F. *J. Chem. Phys.* **1975**, *63*, 4592.

(9) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

(10) E.g.: Curro, J. G.; Schaefer, D. W. *Macromolecules* **1980**, *13*, 1199.

(11) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 3089.

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

(13) Okamoto, H. *J. Chem. Phys.* **1988**, *88*, 5096.

(14) Oono, Y.; Freed, K. F. *J. Phys. A* **1982**, *15*, 1931.

(15) The penetration function R in this paper is connected with ψ in Oono and Freed's paper[14] by $R = 8(\pi^{3/2})\psi$.

(16) We found several misprints in numerical factors in Okamoto's paper.[13] In the 10th line on p 5103, -2ψ should be replaced by $-\psi/2$. In the 12th line on the same page, $-A_2/2\langle S^2\rangle^{3/2}$ should be replaced by $-2A_2/\langle S^2\rangle^{3/2}$. In the second line on p 5104, 2ψ should be replaced by $-\psi$ ($=R$).

(17) Freed, K. F. *J. Phys. A* **1985**, *18*, 871.

A Normal Vibrational Analysis of Syndiotactic Polystyrene

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ABSTRACT: A normal vibrational analysis has been performed for the all-trans conformation of syndiotactic polystyrene. In this analysis a set of nonredundant symmetry coordinates and force constants has been employed for the phenyl ring. The other force constants needed for the chain have been transferred from studies of alkanes and have been applied to many polymers such as polyethylene and polypropylene. Observed infrared and Raman data, including polarization characteristics, have been satisfactorily assigned. Several localized ring modes that are also present in atactic and isotactic polystyrene as well as in toluene have been identified. Other conformation-sensitive features, which are unique to the syndiotactic isomer, are identified. Polarized infrared data show that coextruded samples have nearly perfect orientation of the trans sequences with the plane of the rings normal to the chain axis. The orientation is seen to increase upon annealing at 200 °C due to an increase in crystallinity. Upon higher temperature annealing a melting point of 285 °C is observed. The theoretical modulus is calculated from the slope of the dispersion curve of the longitudinal acoustic vibration near the Brillouin zone center. A value of 67 GPa was obtained.

Introduction

Recently, syndiotactic polystyrene (sPS) has been a subject of great interest.[1-9] Only quite recently has the synthesis been developed to produce nearly 100% syndiotactic polymer.[1,2,7] This material has several interesting physical characteristics: (1) a melting temperature of ca. 270 °C, although with annealing at gradually higher temperatures we have observed a melting point as high as 285 °C; (2) a variety of chain conformations, including a fully trans-planar zigzag backbone in addition to a helical conformation observed for solution-cast films; and (3) the presence of a solid–solid phase transition at ~190 °C involving changes in both chain conformation and packing.[1,3-7] Because of its inherent backbone stiffness and strong intermolecular interactions, macroscopic properties such as modulus and strength and their insensitivity to temperature are expected to exceed those of most polymers.

The structure of sPS is complex. Diffraction and spectroscopic studies have revealed that this polymer exists in a helical conformation upon casting from dilute solution and can easily transform to the all-trans conformation upon annealing or drawing.[3,5,6,10,11] The differences in the infrared and Raman spectra observed for different forms of sPS are striking. From the spectra obtained from samples of different tacticity and from pre-

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