on the history of the sample. The unconditioned samples displayed the lowest sorption and dilation values while the exchange-conditioned samples displayed the largest, presumably due to the lowered energy requirements for penetrant sorption. In addition, the largest enhancements of sorption of dilation over unconditioned values, at a given conditioning level, were noted for PC, with the smallest enhancements occurring for TMHFPC. This trend reflects larger enhancements for materials with larger percentage increases in fractional free volume and correspondingly smaller values of T_g as seen in the series PC, TMPC, and TMHFPC.

Acknowledgment. The authors gratefully acknowledge the PC samples provided by General Electric Co., the TMPC samples provided by Dow Chemical Co., and the TMHFPC synthesized by Mark Hellums of The University of Texas at Austin. Additionally, support by NSF Grant No. CBT-8516148 is acknowledged.

References and Notes

(1) Jordan, S. M.; Koros, W. J.; Fleming, G. K. *J. Membr. Sci.* **1987**, *30*, 191.
(2) Enscore, D. J.; Hopfenberg, H. B.; Stannett, V. T.; Berens, A. R. *Polymer* **1977**, *18*, 1105.
(3) Berens, A. R.; Hopfenberg, H. B. *Polymer* **1978**, *19*, 489.
(4) Fleming, G. K. Ph.D. Dissertation, University of Texas at Austin, Austin, TX, 1987.
(5) Jordan, S. M.; Koros, W. J.; Beasley, J. K. *J. Membr. Sci.* **1989**, *43*, 103.
(6) Tsai, B. C.; Wachtel, J. A. In *Barrier Polymers and Barrier Structures*; Koris, W. J., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, in press.
(7) Fleming, G. K.; Koros, W. J. *Macromolecules* **1986**, *19*, 2285.
(8) Wonders, A. G.; Paul, D. R. *J. Membr. Sci.* **1979**, *5*, 63.
(9) Chan, A. H.; Paul, D. R. *J. Appl. Polym. Sci.* **1979**, *24*, 1539.
(10) Barrer, R. M.; Barrie, J. A.; Slater, J. *J. Polym. Sci.* **1958**, *27*, 177.
(11) Koros, W. J.; Chan, A. H.; Paul, D. R. *J. Membr. Sci.* **1977**, *2*, 165.
(12) Chern, R. T.; Koros, W. J.; Sanders, E. S.; Chan, A. H.; Hopfenberg, H. B. In *Industrial Gas Separations*; Whyte, T. E., Yon, C. M., Wagner, E. H., Eds.; ACS Symposium Series No. 233; American Chemical Society: Washington, DC, 1983.
(13) Hellums, M. W.; Koros, W. J.; Husk, G. R.; Paul, D. R. *J. Membr. Sci.*, in press.
(14) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(15) Koros, W. J. Ph.D. Dissertation, University of Texas at Austin, Austin, TX, 1977.
(16) Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1903.
(17) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2497.
(18) Vrentas, J. S.; Wu, W.-T. *J. Membr. Sci.* **1987**, *31*, 337.
(19) Jones, W. M.; Isaac, P. J.; Phillips, D. *Trans. Faraday Soc.* **1959**, *55*, 1953.
(20) Berens, A. R.; Hopfenberg, H. B. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1757.
(21) van Krevelen, D. W.; Joftyzer, P. J. *Properties of Polymers*, 2nd ed.; Elsevier: New York, 1976.
(22) Moe, M. B.; Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 1931.
(23) Pilato, L.; Litz, L. M.; Hargitay, B.; Osbourne, R. C.; Farnham, A. G.; Kawakami, J.; Fritze, P. E.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1975**, *16*, 42.
(24) Maeda, Y.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 957.

Quasi-Scaling for Finite Lattice Polymers with Pair and Triplet Interactions

Yoshinobu Watanabe, Motoshi Katoh, and Hiroshi Okamoto*

Department of Systems Engineering, Nagoya Institute of Technology, Gokisomachi, Shouwaku, Nagoyashi, 466, Japan

Received August 22, 1989; Revised Manuscript Received December 6, 1989

ABSTRACT: To extract the sealing for finite polymers, we present general relations directly derived from the context of the renormalization group and examine their validity. The context asserts that, in the two-parameter model, any of the reduced moments is described solely by an arbitrary reduced moment. In the three-parameter model, it is described by two arbitrary reduced moments. Our basic relations are free from the artificial theoretical models and involve no specific reference point such as Θ-point. For finite polymers, the concepts of *scaling*, *master curve*, and *master surface* should be replaced by those of *quasi-scaling*, *master belt*, and *master shell*, respectively. The relations were critically examined by numerical experiments of lattice polymers with the nearest-neighbor pair and triplet intrachain interactions. In a restricted regime, we could identify universal master belts in two-dimensional plottings. In three-dimensional plottings, we could identify universal master shells, within which many of the two-dimensional non-quasi-scaling points fall. The convergence to the expected quasi-scaling is varied by the combinations of the reduced moments.

1. Introduction

Although the scaling concept for single polymers has been constructed in several ways, the correspondence of the theoretical models with actual and/or lattice polymers is not entirely clear. The model used in the conformational renormalization group (RG)[1] is a Gaussian molecule with two-body (and three-body) δ-function-like intrachain interaction. However, the polymer intrachain interaction is actually never so.[2] The correspondence of a self-avoiding walk with the zero-dimensional spin system[3] is merely mathematical. The polymer model used in the classical mean-field theory is much like a preaveraged monomer cloud rather than a string of monomers.[4] To legitimate these models, we have to conceive extremely long, unpractical molecules. Then what hap-

0024-9297/90/2223-2994$02.50/0

pens in the scaling for polymers of practical finite lengths? Further, the authors have often encountered difficulties in following the sophistication in constructing the theories and in assessing the approximation involved. Even if experiments exhibit deviations from the theories' predictions, we cannot answer the question of which of the three, the model itself, the mathematics in the theories, or the polymer length in the experiments, is responsible for it.

This motivates us to investigate the polymer scaling without referring to the theoretical predictions based upon the artificial models such as mentioned above. In this paper, to extract the scaling for finite polymers, we exclusively use the RG premise.[5] In handling the finite polymers, we have to admit some deviations from the true scaling. We note that the concepts of *scaling*, *master curve*, and *master surface* should be replaced by those of *quasi-scaling*, *master belt*, and *master shell*, respectively. The validity of the equations is critically examined by numerical experiments of lattice polymers. Any invalidity of the equations can be ascribed solely to the invalid application of the RG context to polymer statistics. The examination proceeds through two steps in the increasing order of the number of the RG parameters involved.

In the first step, the lattice polymers with the nearest-neighbor pair intrachain interaction were investigated. The finite polymer statistics in some restricted range certainly obey the quasi-scaling, but at the same time there were many experimental non-scaling points.

In the second step, another parameter, the nearest-neighbor triplet intrachain interaction was introduced. We expect that it serves to widen the range to which the RG is applicable.[6] It should be mentioned that Oono et al.[7] showed that an RG operation on the polymer model of the Gaussian molecule with the δ-function-like pair intrachain interaction yields the δ-function-like triplet intrachain interaction. The success in the quasi-scaling, however, depends on the correlations involved.

Our basic eq 2.6 and 2.7 (see below) involve no specific reference point such as the Θ-point. This enables us to undertake analysis through direct comparison of measured quantities only. This is in sharp contrast with many of the previous simulations[8] and experiments,[9] in which the polymer scaling is treated by the scaling variable constructed by the distances from the Θ-point. Freed has already emphasized the importance of an analysis of this kind.[1]

Our data were mainly from polymers embedded in the simple cubic (SC) lattice. The points from the face center cubic (FCC) polymers were limited in number but demonstrated the coincidence. This supports our conjecture that the master belts or shells are universal. The reptation Monte Carlo method[10] was used throughout. We also used the exact enumeration method. Though the feasible polymerization degree by the latter was very limited, its highest reliability was a key in obtaining the conclusions.

2. Renormalization Group and Course of Analysis

The renormalization group has been used as a tool to extract the critical exponents and the scaling for spin systems and for polymer systems. In a polymer language, the operation of the RG transformation onto a single polymer statistic is equivalent to seeking the combinations of the polymerization degree, n, and the intrachain interaction parameter, η, satisfying

$$\Gamma(1/n, \eta; \vec{r}) = \lambda^a \Gamma'(1/n', \eta'; \vec{r}') \tag{2.1a}$$

with

$$1/n < 1/n' \tag{2.1b}$$

$$r = \lambda r' \quad \lambda > 1 \tag{2.1c}$$

In the above, Γ describes the correlation between two polymer segments separated by a vectorial distance $\vec{r}$, with λ, the length scale factor, being a number larger than 1. The exponent a should be appropriately chosen.[6] (2.1a) describes the connection between the polymer system in the left-hand side, which is before the RG operation, and the right-hand side, the one after the operation. (2.1c) means that the unit length in the right-hand side systems should be compared to λ times of the unit length in the left-hand side. The transformation of the parameters by an RG

$$1/n \to 1/n' \tag{2.2a}$$

$$\eta \to \eta' \tag{2.2b}$$

should be unique irrespective of the correlations. Iteration of the infinitesimal RG ($\lambda \sim 1$) yields a series of parameter values, which pictures a "flow line" in the coordinate space spanned by the parameters $1/n$ and η. This paper does not concern with the fixed point and related problems.

There are several variations equivalent to (2.1a). Analytical polymer RG theories solving (2.1a) with respect to $1/n'$ and η', or its equivalents, have to handle the artificial models but inevitably introduce the confusion mentioned in the Introduction.

To eliminate the confusion, we must first check the validity of the RG premise (eq 2.1a). For that purpose, we convert it into a more convenient form (eq 2.6) in which the discreteness of the lattice is averaged out. Define the mth moment by

$$\langle r^m \rangle_\Gamma = \int \mathrm{d}^d\vec{r}\, r^m\, \Gamma(1/n, \eta; \vec{r}) \tag{2.3}$$

Equation 2.1 tells us that the reduced moment $M_\Gamma{}^{m,n}$

$$M_\Gamma{}^{m,n} = \langle r^m \rangle_\Gamma / \langle r^n \rangle_\Gamma{}^{m/n} \tag{2.4}$$

is invariant by an RG operation.

$$M_\Gamma{}^{m,n} = M_{\Gamma'}{}^{m,n} \tag{2.5}$$

Thus, any of the reduced moments is held constant along a flow line. A flow line in the two-dimensional parameter space is identified by assigning a value to a particular reduced moment. Thus, any reduced moment is a function of the particular reduced moment M_{ref}

$$M_\Gamma{}^{m,n} = M_{\Gamma'}{}^{m,n}(M_{\mathrm{ref}}) \tag{2.6}$$

Equation 2.6 asserts that the plottings $M_\Gamma{}^{m,n}$ vs M_{ref} for polymers with various $1/n$ and η construct a single curve (i.e., a master curve in the ($M_\Gamma{}^{m,n}$, M_{ref}) space). We expect that the master curve would be independent of the lattice structure (i.e., universal).

But (2.6) involves a contradiction. The points plotted as (2.6) from the polymers with a constant $1/n$ but various η will form a curve in the ($M_\Gamma{}^{m,n}$, M_{ref}) space. Likewise, we can construct another curve for polymers with a different n. Since the two curves are essentially different, we cannot accept that (2.6) holds strictly for an interval. This contradiction may vanish for infinite polymers. For finite polymers we have to admit some small deviations from (2.6). The experimental points do not fall on a single curve but within a width of a beltlike zone. The concepts of *scaling* and *master curve* should be replaced by those of *quasi-scaling* and *master belt*,

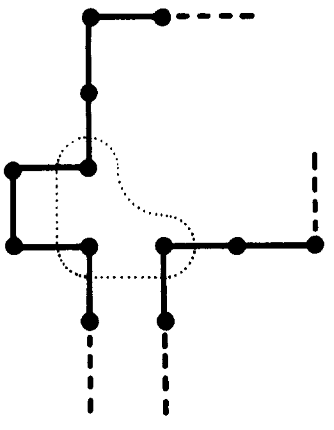

Figure 1. Illustration of the nearest-neighbor triplet intrachain interaction. The configuration in which an element neighbors two arbitrary nonbonded elements contributes an energy ϵ_3 in addition to the usual pair intrachain interaction energy, ϵ_2.

respectively. The width of a master belt is somewhat arbitrary, but we assume it to be of the same order as the experimental resolution.

Freed derived (2.6) through manipulating the theoretical model and the explicit dependences of polymer properties on his scaling variable ζ.[1] We, however, regard it simply as a direct consequence of the polymer RG premise (2.1). Equation 2.6 asserts that the direct effects of n and η on $M_\Gamma{}^{m,n}$ are absorbed in a variable M_{ref}. Since it involves no specific reference point (e.g., the Θ-point), the analysis can proceed by connecting the measurable quantities. This is in contrast with the previous simulation works[8] and experiment[9] as mentioned before.

If (2.6) is not satisfied by polymer statistics and if we still adhere to the polymer scaling, then we should introduce a third parameter in (2.1) (Appendix 1). We use the nearest-neighbor triplet intrachain interaction for this parameter. To define a parameter flow in the three-dimensional parameter space, it is sufficient to set the values of two arbitrary reduced moments. Then, any reduced moment is a function of the two particular reduced moments $M_{\text{ref,u}}$ and $M_{\text{ref,2}}$.

$$M_\Gamma{}^{m,n} = M_\Gamma{}^{m,n}(M_{\text{ref,1}}, M_{\text{ref,2}}) \tag{2.7}$$

Equation 2.7 asserts that the three-dimensional plottings $M_\Gamma{}^{m,n}$ vs $M_{\text{ref,1}}$ and $M_{\text{ref,2}}$ fall on a single surface (i.e., a master surface). However, by a consideration similar to that in the two-parameter scaling, we have to admit some deviations from the true scaling (eq 2.7) and replace the concepts of *scaling* and *master surface* by those of *quasi-scaling* and *master shell*, respectively. The experimental points do not fall on a surface but within a thickness of a master shell. We assume the thickness to be the same order as the experimental resolutions.

3. Procedures

A polymer molecule is simulated by a self-avoiding chain of n elements, each occupying contiguous lattice sites (n-mer) on a simple cubic (SC) lattice. A nearest-neighbor nonbonded-element pair contributes an energy ϵ_2 to the conformation. In the same way, a nearest-neighbor nonbonded-element triplet contributes an energy ϵ_3 (see Figure 1). The interaction parameters η and ξ are defined by $\eta = \exp[-\epsilon_2/kT]$ and $\xi = \exp[-\epsilon_3/kT]$, respectively.

The usual reptation Monte Carlo (MC) method[10] combined with Metropolis algorithms[11] assuring the canonical distribution was adopted. The method, which had been repeatedly explained,[5] was modified so as to account for the triplet interaction. The details are omitted here because there was no essential change in spite of the modification. The polymerization degree, n, covered the range from 20 to 225. Simulation with the FCC lattice polymers ($12 \leq n \leq 100$) was also performed. The number of samples ranged from 10 000 to 50 000 for each of the specific conditions.

To overcome the statistical uncertainty inherent in the MC method, we also adopted the exact enumeration. The method definitely limited the feasible polymerization degree ($n \leq 15$), but its highest reliability was very helpful in obtaining our conclusions.

The measured quantitites were various even order moments averaged over end to end distances, radii of gyrations, and quasi-radii of gyrations.[12] They were, respectively, defined by

$$\langle h^m \rangle = \langle \{\vec{r}(n) - \vec{r}(1)\}^m \rangle \tag{3.1}$$

$$\langle r^m \rangle = \langle \{(1/n)\sum_i s(i)^2\}^{m/2} \rangle \tag{3.2}$$

$$\langle s^m \rangle = \langle (1/n)\sum_i s(i)^m \rangle \tag{3.3}$$

where m is an even integer, $\vec{r}(i)$ is the position vector of the ith element, and $s(i)$ is the distance of the ith element measured from the mass center. To accommodate (3.2) and (3.3), the correlation Γ in (2.1) should be appropriately defined (Appendix 2). The reduced moments $M_x{}^{m,n}$ were calculated by

$$M_x{}^{m,n} = \langle x^m \rangle / \langle x^n \rangle^{m/n} \tag{3.4}$$

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

4. Results and Discussion

Although in the following our results are illustrated only graphically, all the numerical data are available in the supplementary material (see below).

4.1. Two-Dimensional Parameter Space. 4.1.1. Results. At first, we check (2.6) in which the triplet interaction parameter, ξ, is fixed at 1. We plot $M_x{}^{m,n}$ against M_{ref} for polymers with various $1/n$ and η, checking whether M_{ref} really determines $M_x{}^{m,n}$ as (2.6) claims. We choose arbitrarily $M_r{}^{4,2}$ as M_{ref}.

Figure 2 illustrates the plotting of $M_r{}^{8,6}$ against $M_r{}^{4,2}$ for the SC and the FCC polymers with various $1/n$ and η. Then η values employed are listed in Table I. The figure includes the point for Gaussian polymers and the one for the infinite polymers at the Θ-point at which the second virial coefficient vanishes ($A_2 = 0$). The latter (Bruns point) was given by Bruns.[12] The locus of the points for an n-mer, say 13-mer, looks like the letter U. Its upper branch corresponds to strongly collapsed molecules ($\eta > 2.2$), and the lower branch, to coiled or slightly collapsed molecules. Each lower branch converges to a master belt extending from the left edge of the figure to the upper right edge. If we admit a deviation of 0.005 parallel to the $M_r{}^{8,6}$ axis, the points from the polymers with n not less than 9 and η not larger than $\eta_\Theta(n)$ or so fall within a master belt where $\eta_\Theta(n)$ means the η at the n-mer Θ-point. According to Bruns, $\eta_\Theta(9) = 1.267$ and $\eta_\Theta(129) = 1.298$.[12] In the figure, the master belt is shown by the shaded zone. It is noteworthy that the FCC polymer locus converges to the same master belt. It may indicate the master belt is universal.

Figures 3–5 show the similar plottings $M_h{}^{6,4}$ vs $M_r{}^{4,2}$, $M_s{}^{6,4}$ vs $M_r{}^{4,2}$, and $M_h{}^{6,4}$ vs $M_h{}^{4,2}$, respectively.

We have plotted many other combinations of $M_x{}^{m,n}$ vs $M_r{}^{4,2}$ and others, although they are omitted here to save space.

4.1.2. Discussion. The plottings reveal that the quasi-scaling (2.6) is certainly valid in an appropriate interval. These plottings may be classified into two groups. The first group is the one shown in Figures 2 and 3, in which the the loci of n-mers do not cross each other. The plottings $M_r{}^{m,n}$ vs $M_r{}^{p,q}$, $M_s{}^{m,n}$ vs $M_s{}^{p,q}$, and $M_h{}^{m,n}$ vs $M_r{}^{p,q}$

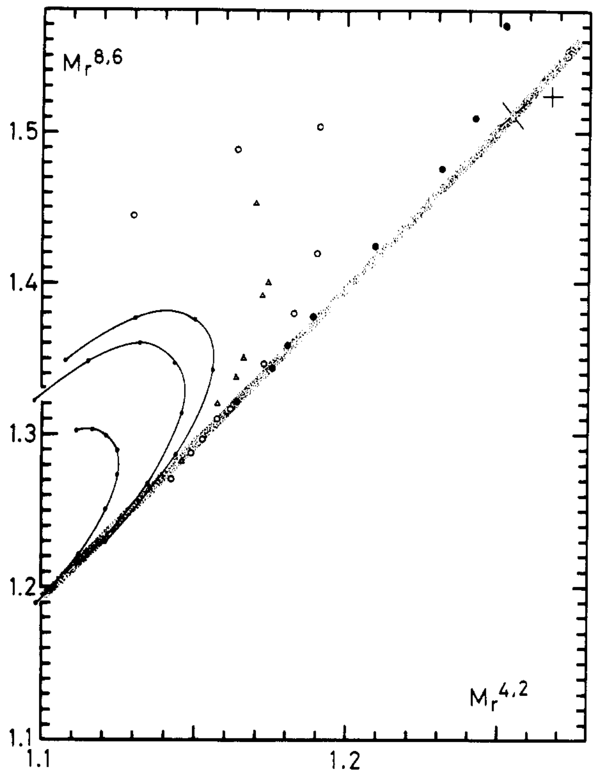

Figure 2. Plots of $M_r^{8,6}$ vs $M_r^{4,2}$ for the SC and the FCC polymers with various polymerization degree n and the nearest-neighbor pair interaction η (=exp[$-\epsilon_2/kT$]). The nearest-neighbor triplet interaction ξ (=exp[$-\epsilon_3/kT$]) is fixed at 1. (–•–) The exact enumeration points for the SC polymers with n = 9, 13, and 15 from left to right, respectively. (○ and ●) The MC points for the SC polymers with n = 31 and 100, respectively. (△) The MC points for the FCC polymers with n = 20. The η value for each point is listed in Table I. (+) The point for the Gaussian polymer. (×) The Bruns point. The shaded zone means the master belt.

Table I
Values of the Nearest-Neighbor Pair Interaction, η = exp[$-\epsilon_2/kT$], Employed in Figures 2–5[a]

n	η
9, 13, 15	1.0, 1.40, 1.80, 2.20, 2.60, 3.0, 3.40, 3.80, 4.20, 4.60
30	1.0, 1.05, 1.10, 1.15, 1.20, 1.30, 1.40, 1.50, 1.80, 2.0, 2.20
100	1.0, 1.05, 1.10, 1.15, 1.20, 1.30, 1.40, 1.45, 1.50
FCC 20	1.0, 1.10, 1.15, 1.20, 1.25, 1.30, 1.40

[a] This table lists the respective η values for points, from the leftmost of the lower branch of the U-like or half-U-like locus to the right in each figure, in the order demonstrated. An exception is the 9-mer locus in Figure 5. Its leftmost point is for η = 1.4.

belong to this group. The second group is the one shown in Figure 4 and 5 in which the loci cross each other. The plottings $M_s^{m,n}$ vs $M_r^{p,q}$ and $M_h^{m,n}$ vs $M_h^{p,q}$ belong to this group.

The master belt formation is easily confirmed in the first group. For the second group, we can still figure the master belt, but the convergence of the loci is not so well established. The convergence to (2.6) is established, but by variant manners by the correlations.

Each master belt starts from shorter polymer points, passes through near the Bruns point and/or the Gaussian point, and further extends infinitely although points of relatively small number fall on the second and the third regions at present.

At this juncture, we recall the Freed's crossover theory based on the model of Gaussian molecule with the δ-functionlike pair interaction. According to the theory, polymer properties are uniquely described by a scaling variable, ζ, in the regime from the scaling limit to the vanishing pair interaction. The theories' prediction translated to our system is the existence of a master curve extending from a point for infinite polymers in a good

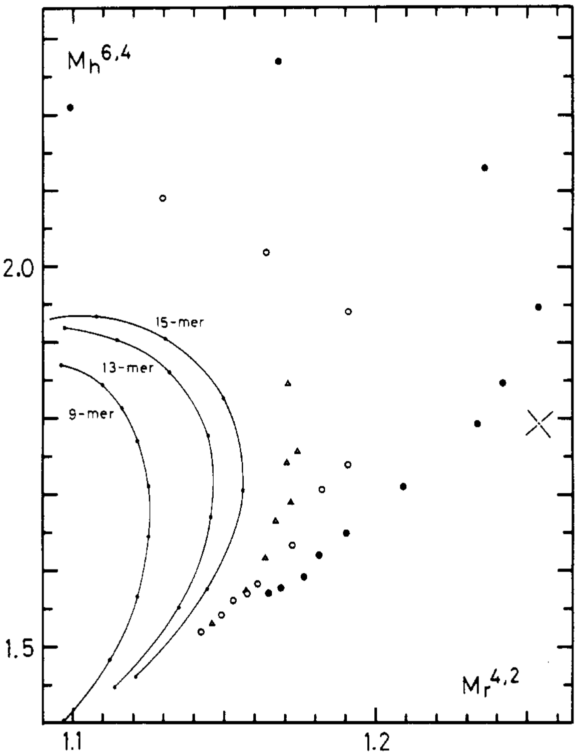

Figure 3. Plots of $M_h^{6,4}$ vs $M_r^{4,2}$ for the SC and the FCC polymers with various n, η, and a fixed ξ (=1.0). For symbols, see the caption to Figure 2.

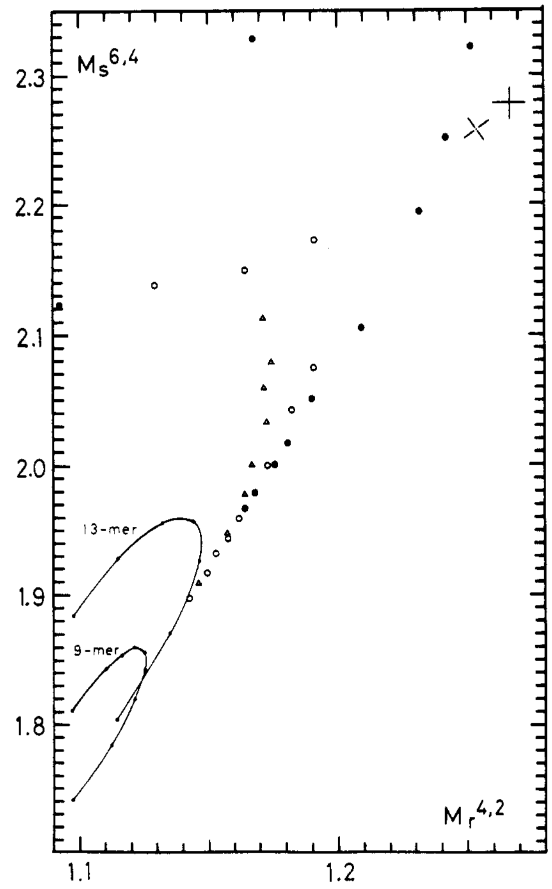

Figure 4. Plots of $M_s^{6,4}$ vs $M_r^{4,2}$ for the SC and the FCC polymers with various n, η, and a fixed ξ (=1.0). For symbols, see the caption to Figure 2.

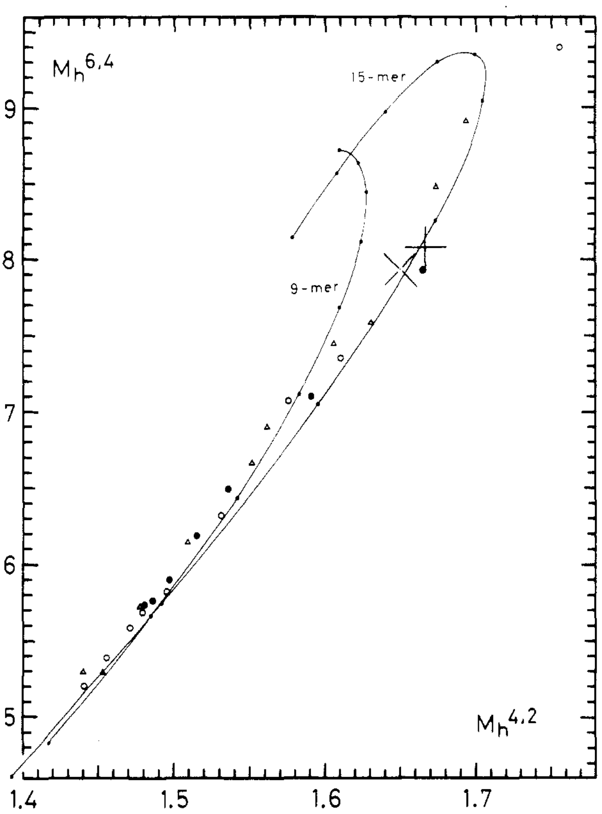

Figure 5. Plots of $M_h^{6,4}$ vs $M_h^{4,2}$ for the SC and the FCC polymers with various n, η, and a fixed ξ (=1.0). For symbols, see the caption to Figure 2.

solvent regime, which is perhaps a point upper right of the point for 100-mer with $\eta = 1$, to the point for Gaussian polymers. Our numerical experiments on finite polymers reveal that the quasi-scaling is obeyed in a regime more extended than the theoretical prediction. Our experimental points were not enough for determining whether the Bruns point or the Gaussian point lies in the master belt. Cherayil et al. attributed the incoincidence of the Bruns point with the Gaussian point to the contribution of the triplet interaction.[13] Several experiments on polystyrene solutions have reported the single variable scaling below the Θ-point.[9c]

4.2. Three-Dimensional Parameter Space. 4.2.1. Results. Our next problem is to examine whether the introduction of a third parameter establishes the two-variable quasi-scaling including the points not satisfying (2.6). The choice of $M_{\mathrm{ref},1}$ and $M_{\mathrm{ref},2}$ in (2.7) is arbitrary. We first examine (2.7) by the combinations of the reduced moments from the same correlations, i.e., $M_h^{8,6}$ vs ($M_h^{6,4}$ and $M_h^{4,2}$), etc., and then the other combinations of different correlations such as $M_h^{8,6}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$). To visualize the three-dimensional plottings suggested by (2.7), we show their cross sections by constant $M_x^{m,n}$ planes. The points were determined by the interpolation of the experimental points.

Figure 6 shows the several cross sections of the $M_h^{8,6}$ vs ($M_h^{6,4}$ and $M_h^{4,2}$) by constant $M_h^{8,6}$ planes. In the figure, each frame represents the error bars roughly estimated. Its center represents the most probable value. The frameless points are from exact enumeration. In the plot (a), all the points except one are from exact enumeration and are most reliable. Remarkably, the points are nearly on a line regardless of ξ and the lattices. Indeed, the thickness of the master shell which should be admitted is as small as 0.001. In the plot (b), the exact enumeration points from $\xi = 1$ and $\xi = 1.1$ are clearly on different curves. But we can see the convergence of the points for longer SC and FCC polymers from the MC method. In the plots (c) and (d), the points from different ξ and the lattices are on different U-like loci, but their lower branches converge with each other.

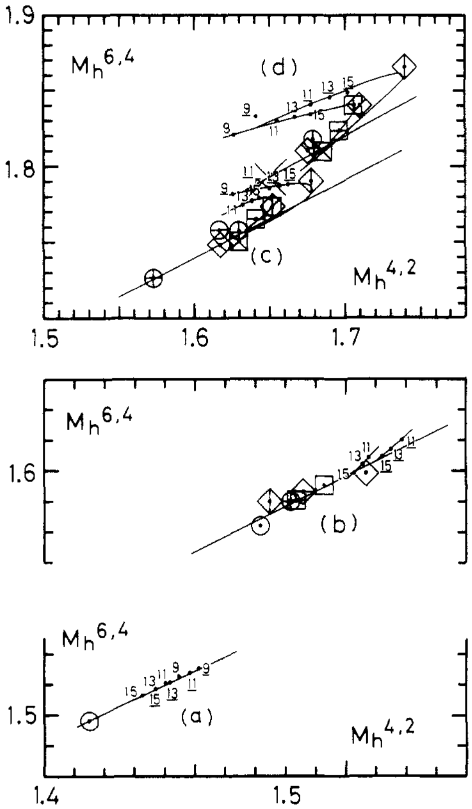

Figure 6. Cross sections of $M_h^{8,6}$ vs ($M_h^{6,4}$, $M_h^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by the planes of $M_h^{8,6}$ = 1.549 (a), 1.649 (b), 1.849 (c), and 1.9225 ($M_h^{8,6}$ value for the Bruns point; (d). The points were evaluated through interpolation of the experimental points. (●) Points from the exact enumeration for the SC polymers with n as indicated in the figure. The nonunderlined number means that the corresponding point is for the condition $\xi = 1$ and the underlines mean $\xi = 1.1$. (⊡, ⧄, ◫, ⊟, and ⊠) Points from the MC for the SC polymers with $\xi = 1$ and $n = 20, 45, 67, 100$, and 225, respectively. (⟐, ⬘, ⬙, ⬗, ⬖, and ◈) Points from the MC for the SC polymers with $\xi = 1.1$ and $n = 20, 31, 45, 67, 100$, and 225, respectively. (⊙, ⊖, ⦶, and ⊕) Points from the MC for the FCC polymers with $\xi = 1$ and $n = 12, 20, 30$, and 100, respectively. The center of a symbol is the most probable point, and the size of the symbol frame means the error bar. (×) The Bruns point. The lines are merely visual guides.

Figure 7 shows the cross sections of the radius of gyration reduced moments relation $M_r^{8,6}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$) by constant $M_r^{8,6}$ planes. Compared to the end-to-end reduced moments, the points better obey (2.7). The plot (b) shows that even the points for the strongly collapsed polymers, which form the left half of the plotting, are on a common curve, that is, within a thin master shell. The plot (c) may indicate that the points for polymers with $\xi = 1.1$ are not on the surface including the Bruns point. The master shell is like a plate but may be slightly convex and twisted.

Figure 8 illustrates the cross sections of $M_s^{8,6}$ vs ($M_s^{6,4}$ and $M_s^{4,2}$). The situation is similar to the one in Figure 7.

We next examine (2.7) by combinations of the reduced moments of different correlations.

Figure 9 shows the cross sections of $M_h^{8,6}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$) by planes of constant $M_h^{8,6}$ planes. The plots (a) and (b) appear to confirm (2.7). However, in the plot (c), a few points near the Bruns point may deviate from the quasi-scaling.

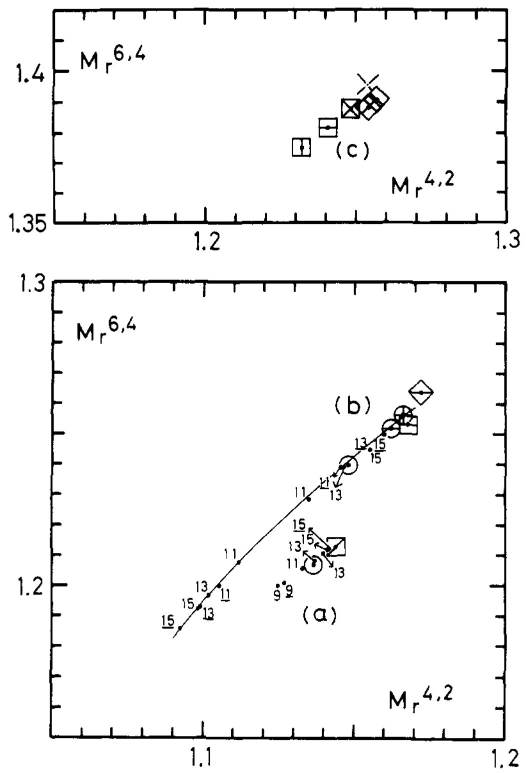

Figure 7. Cross sections of $M_r^{8,6}$ vs ($M_r^{6,4}$, $M_r^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by the planes of $M_r^{8,6}$ = 1.274 (a), 1.330 (b), and 1.5125 (value of $M_r^{8,6}$ at the Bruns point, c). The points were evaluated through the interpolation of the experimental points. (⊠) Points from the MC for the SC polymer with n = 31 and ξ = 1. For the other symbols and the line, see the caption to Figure 6.

Figure 10 shows the similar cross sections of $M_h^{6,4}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$).

Figure 11 shows the cross sections of $M_s^{8,6}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$) by planes of constant $M_s^{8,6}$. We can again figure the master shell, but the plot (a) indicates the breakdown of (2.7) in the regime giving $M_s^{8,6}$ = 1.858 or less. (It is roughly in the range $n \leq 13$ and $\eta \leq 1.5$ for polymers with $\xi = 1$ and the range $n \leq 11$ and $\eta = 1.1$ for polymers with $\xi = 1.1$).

Figure 12 shows the cross sections of $M_s^{6,4}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$) by planes of constant $M_s^{6,4}$ and of constant $M_r^{6,4}$. In the plots (a) and (d), the exact enumeration points for polymers with $\xi = 1$ are on curves different from those for polymers with $\xi = 1.1$. The plots (b) and (c) may not provide a very firm evidence for (2.7). Contrary to the cases described heretofore, no appreciable improvement of the quasi-scaling of $M_s^{6,4}$ vs $M_r^{6,4}$ is exhibited.

4.2.2. Discussion. The quasi-scaling (2.7) is valid for a far wider regime than (2.6) is. Most of the points that are not within the master belt, the points for polymers with different ξ and for the FCC polymers, fall within the same master shell.

The satisfaction of $M_h^{8,6} = M_h^{8,6}$ ($M_h^{6,4}$, $M_h^{6,4}$), $M_h^{8,6} = M_h^{8,6}$ ($M_r^{6,4}$, $M_r^{4,2}$), and $M_r^{8,6} = M_r^{8,6}$ ($M_r^{6,4}$, $M_r^{4,2}$) results in $M_h^{4,2} = M_h^{4,2}$ ($M_r^{6,4}$, $M_r^{4,2}$), though it was not shown graphically.

The satisfaction of $M_s^{8,6} = M_s^{8,6}$ ($M_s^{6,4}$, $M_s^{4,2}$) and $M_s^{8,6} = M_s^{8,6}$ ($M_r^{6,4}$, $M_r^{4,2}$) and the failure of $M_s^{6,4} = M_s^{6,4}$ ($M_r^{6,4}$, $M_s^{4,2}$) in the short-chain region results in the failure of $M_s^{4,2} = M_s^{4,2}$ ($M_r^{6,4}$, $M_r^{4,2}$) in the same region. It also means $M_s^{m,n}$ does not scale in the same way as $M_h^{p,q}$ and $M_w^{p,q}$ in the short-chain region.

The U-like loci in the plots (b)-(d) in Figure 6 or the plots (a) and (d) in Figure 12 reveal that the corresponding surfaces are folded. The quasi-scaling seems to be affairs on one of the leaves of the folded surfaces. The folding reflects the crossing of the loci in the second group of the two-dimensional plottings such as in Figures 4 and 5.

In a wide range the quasi-scaling (2.7) is obeyed but variantly by the correlations. The theories are suspicious of the existence of the two-variable scaling includ-

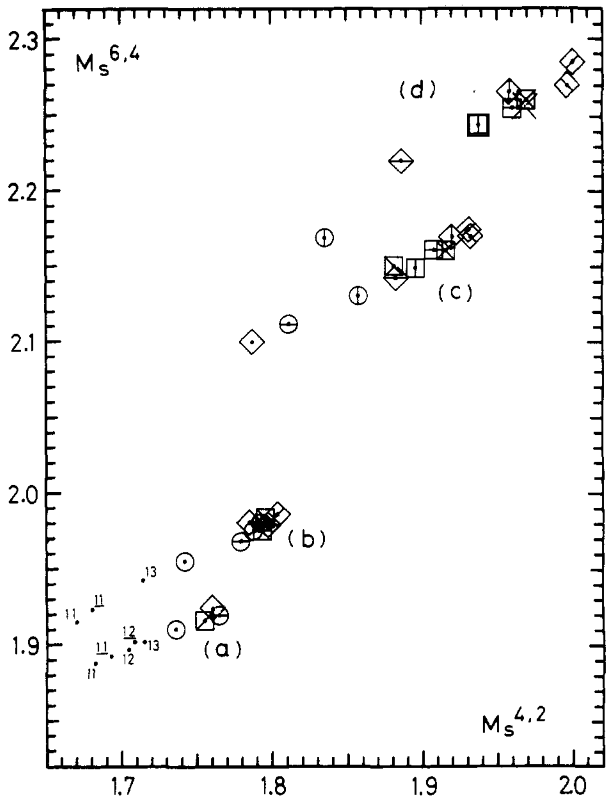

Figure 8. Cross sections of $M_s^{8,6}$ vs ($M_s^{6,4}$, $M_s^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by the planes of $M_s^{8,6}$ = 2.0 (a), 2.020 (b), 2.30 (ce, and 2.425 (value of $M_s^{8,6}$ at the Bruns point; (d). The points were evaluated through the interpolation of the experimental points. For symbols, see the captions to Figures 6 and 7.

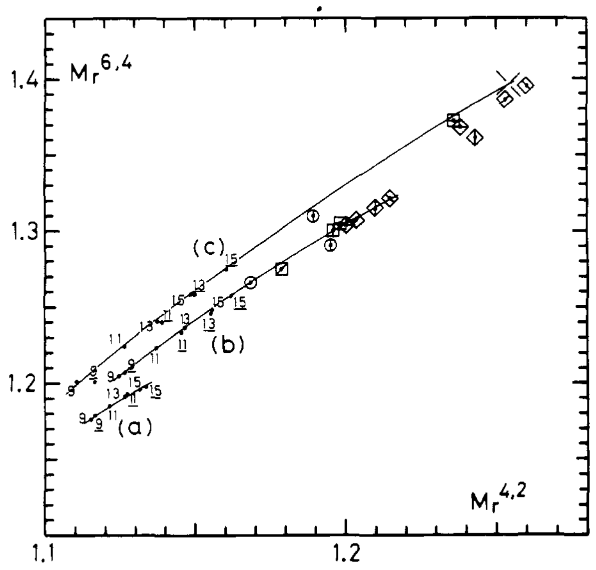

Figure 9. Cross sections of $M_h^{8,6}$ vs ($M_r^{6,4}$, $M_r^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by the planes of $M_h^{8,6}$ = 1.549 (a), 1.750 (b), and 1.9225 (value of $M_h^{8,6}$ at the Bruns point; c). The points were evaluated through the interpolation of the experimental points. For symbols and lines, see the captions to Figures 6 and 7.

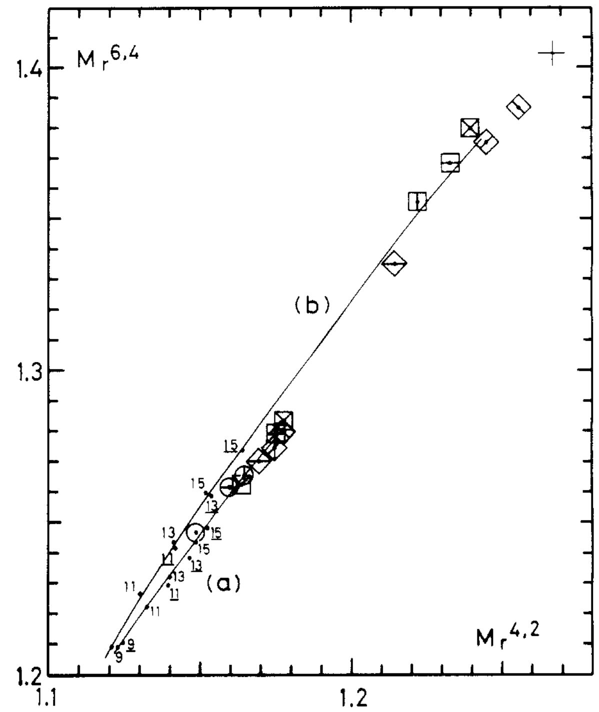

Figure 10. Cross sections of $M_h^{6,4}$ vs ($M_r^{6,4}$, $M_r^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by planes of $M_h^{6,4} = 1.60$ (a), and 1.807 (value of $M_h^{6,4}$ at the Bruns point; b). The points were evaluated through the interpolation of the experimental points. (+) The point for Gaussian polymers. For symbols and lines, see the captions to Figures 6 and 7.

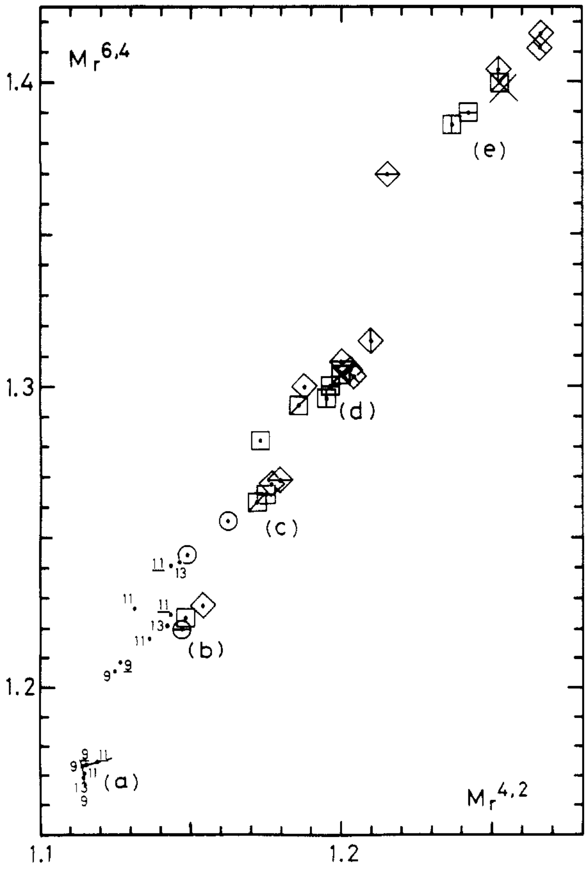

Figure 11. Cross sections of $M_s^{8,6}$ vs ($M_r^{6,4}$, $M_r^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by the planes of $M_s^{8,6} = 1.858$ (a), 2.0 (b), 2.10 (c), 2.190 (d), and 2.425 (value of $M_s^{8,6}$ at the Bruns point; e). The points were evaluated through the interpolation of the experimental points. For symbols, see the captions to Figures 6 and 7.

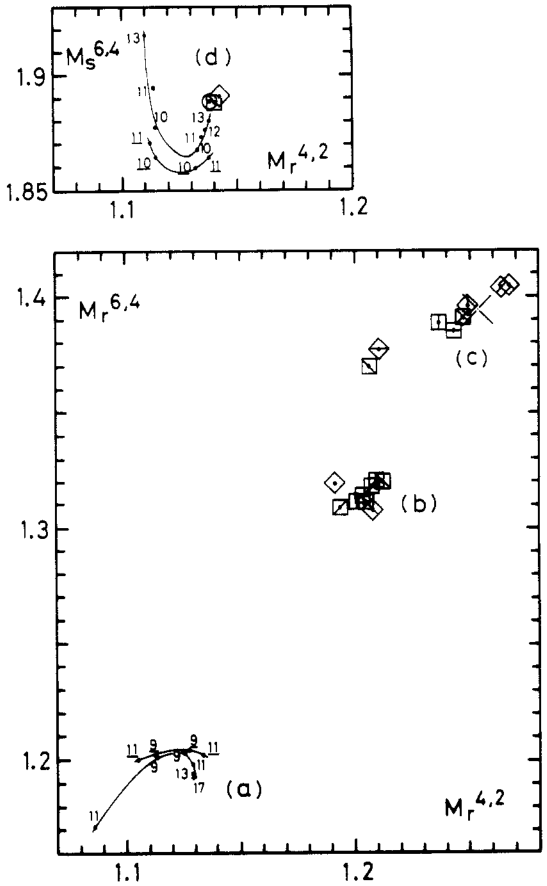

Figure 12. Cross sections of $M_s^{6,4}$ vs ($M_r^{6,4}$, $M_r^{4,2}$) for the SC and the FCC polymers with various n, η, and ξ by the planes of $M_s^{6,4} = 1.850$ (a), 2.089 (b), 2.10 (value of $M_s^{6,4}$ at the Bruns point; c), and the plane of $M_r^{6,4} = 1.210$ (d). The points were evaluated through the interpolation of the experimental points. For symbols and lines, see the captions to Figures 6 and 7.

ing collapsed polymers.[14] Our experiment shows that it depends on the correlations. Our finding in the quasi-scaling of $M_h^{8,6}$ vs ($M_h^{6,4}$ and $M_h^{4,2}$) is parallel to the theoretical. Contrary to this, our results of $M_r^{8,6}$ vs ($M_r^{6,4}$ and $M_r^{4,2}$) indicate the quasi-scaling involving collapsed polymers.

5. Summary

A formal application of the RG premise (2.1) to the finite lattice polymer statistics provides us with a way to investigate the polymer scaling without referring to the existing theories constructed from the artificial models. For finite polymers, the terms *scaling*, *master curve*, and *master surface* should be replaced by the terms *quasi-scaling*, *master belt*, and *master shell*, respectively, which admit small deviations from the true scaling.

(1) We first examine the quasi-scaling for the SC and the FCC lattice polymers with various chain length n and the nearest-neighbor pair interactions, η. The RG premise leads to the single variable scaling (2.6). In conformity with this, our numerical experiments showed a relation of a reduced moment vs an arbitrary reference reduced moment constructing a universal master belt in an appropriate regime. The regime is much more extended than the one that the crossover theory predicts, but naturally there are many points that are not on the master belts.

(2) The RG premise further expects that, by introducing a third parameter, we can construct a master shell in a space spanned by three reduced moments (eq 2.7). It will include the two-dimensional non-quasi-scaling points. Our numerical experiments showed that points

from the SC lattice polymers with various n, η, and the intrachain triplet interactions, ξ, as well as FCC lattice polymers, fall within the universal master shell. In a few cases, no appreciable improvement of the quasi-scaling by the third parameter was exhibited. The convergence to the quasi-scaling is varied by the correlations concerned.

(3) The theory is suspicious of the scaling extending from coiled to collapsed polymers.[14] In our experiments, the master shell for three end-to-end reduced moments certainly excludes the collapsed molecules. On the other hand, the master shell for three radius of gyration reduced moments, as well as the one for three quasi-radius of gyration reduced moments, does include both coiled and collapsed molecules.

Acknowledgment. The computer system HITAC M-680H in the Computer Center of the Institute of Molecular Science was employed throughout this work.

Appendix

1. The three-parameter RG premise is then

$$\Gamma(1/n, \eta, \xi; \vec{r}) = \lambda^a \Gamma'(1/n', \eta', \xi'; \vec{r}') \qquad \text{(A1)}$$

The two-parameter RG may be conceived as the case in which ξ is constrained at a fixed value. It is expected that the applicability of the RG could be widened by the release of the constraining and by appropriate control of the values of the newly introduced parameter.[6] The choice of this parameter is somewhat arbitrary,[6] but we prefer to use the triplet interaction. This coice arises from Oono et al.'s theory[7] asserting that an operation of the RG on the Gaussian molecules with δ-functionlike pair interaction yields the triplet interaction. The blob model RG with triplet interaction by de Gennes is well-known.

2. The end-to-end reduced moments are from correlations of end to end correlations. The quasi-radius of gyration reduced moments are from chain element distribution around the mass center. The radius of gyration reduced moments are from the radius of gyration distributions among samples. Although the last ones are not from the correlations but rather a simple size distribution, it does not affect (2.6) or (2.7).

Supplementary Material Available: Table II listing all the numerical data of the reduced moments vs n, η, and ξ along with the extra data that were not used in the text, including the intrachain element to element distance reduced moments (MC) and the reduced moments of short polymers with even polymerization degree (exact enumeration) (33 pages). Ordering information is given on any current masthead page.

References and Notes

(1) See, for example: Freed, K. F. *Renormalization Group Theory of Macromolecules*; John Wiley & Sons Inc.: New York, 1987.
(2) Freed, K. F. *J. Phys. A* **1985**, *18*, 871.
(3) See, for example: de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(4) de Gennes, P.-G. *J. Phys. Lett.* **1975**, *36*, L55.
(5) Okamoto, H. *J. Chem. Phys.* **1988**, *88*, 5095.
(6) See, for example: Ma, S. K. *Modern Theory of Critical Phenomena*; W. A. Benjamin, Inc.: Reading, Massachusetts, 1976.
(7) Oono, Y.; Freed, K. F. *J. Chem. Phys.* **1981**, *75*, 993.
(8) See, for example: (a) Curro, J. G.; Schaefer, D. W. *Macromolecules* **1980**, *13*, 1199. (b) Kremer, K.; Baumgärtner, A.; Binder, K. *J. Phys. A* **1981**, *15*, 2879.
(9) See, for example: (a) Miyaki, Y.; Fujita, H. *Polym. J.* **1981**, *13*, 749. (b) Perzynski, R.; Adam, M.; Delsanti, M. *J. Phys.* **1982**, *43*, 129. (c) Park, I. H.; Wang, Q. W.; Chu, B. *Macromolecules* **1987**, *20*, 1965.
(10) Wall, F. T.; Mandel, F. *J. Chem. Phys.* **1975**, *63*, 4592.
(11) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E.; Teller, J. *J. Chem. Phys.* **1953**, *21*, 1087.
(12) Bruns, W. *Macromolecules* **1984**, *17*, 2826.
(13) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 3089.
(14) Douglas, J. F.; Freed, K. F. *Macromolecules* **1985**, *18*, 2445.