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Distribution Function $P(S)$ of Uniform Star Polymers*

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ABSTRACT: In this paper, the probability density distribution function $P(S)$ of the radius of gyration of the unperturbed star polymer chains is investigated using Monte Carlo method. We find that the distribution function $P(S)$ for ideal star-shaped polymer may also expressed in the form of $P(S) - -S^{2a}\exp(-(a+0.5)S^2/\langle S^2\rangle)$, and the parameter a only depends on the number of branches f, which is similar to the Flory–Fisk expression $P(S)$ for ideal linear polymer chain.

KEY WORDS Radius of Gyration / Uniform Star Polymer / Probability Density Function / Monte Carlo Simulation /

Configurational properties of polymer molecules play important roles in the interpretation of many aspects of polymer behavior. Many properties of polymer molecules rely heavily on some knowledge of the average and the distribution of molecular dimensions of the polymer chain. Important in various theories of polymer behavior are the probability density distribution functions $P(\boldsymbol{R})$ and $P(S)$, and the mean-square end-to-end distance $\langle R^2\rangle$ and the mean-square radius gyration $\langle S^2\rangle$ of polymer chains. The mean square $\langle R^2\rangle$ and $\langle S^2\rangle$ can be calculated by

$$\langle R^2\rangle = \int_0^\infty 4\pi R^4 P(\boldsymbol{R})\mathrm{d}R \Big/ \int_0^\infty 4\pi R^2 P(\boldsymbol{R})\mathrm{d}R \quad (1)$$

$$\langle S^2\rangle = \int_0^\infty S^2 P(S)\mathrm{d}S \Big/ \int_0^\infty P(S)\mathrm{d}S \quad (2)$$

In general, the even moments of the $\boldsymbol{R}$ distribution and the S distribution are formally defined by

$$\langle R^{2p}\rangle = \int_0^\infty 4\pi R^{2(p+1)} P(\boldsymbol{R})\mathrm{d}R \Big/ \int_0^\infty 4\pi R^2 P(\boldsymbol{R})\mathrm{d}R \quad (3)$$

$$\langle S^{2p}\rangle = \int_0^\infty S^{2p} P(S)\mathrm{d}S \Big/ \int_0^\infty P(S)\mathrm{d}S \quad (4)$$

Thus, the probability density distribution $P(\boldsymbol{R})$ and $P(S)$ are more important in the study of polymer conformations. Studies of the function $P(R)$ of linear polymer chains have long history,[1-4] and the function $P(R)$ of real polymer chains with a short number of bonds can be given accurately.[5-7] The distribution function $P(S)$ of linear polymer chains was investigated approximately by Fixman and Forsman and Hughes.[8,9] We also study the function $P(S)$ of linear polymer chains using Monte Carlo method.[10] But the function $P(S)$ of star polymer has not yet investigated. In this paper, we study the function $P(S)$ of uniform star polymer chains using Monte Carlo method.

CALCULATION METHODS

If C_n is the number of samples and $f_n(S)\Delta S$ is the number of walks whose radius gyrations lie between S and $S+\Delta S$, we have

$$\int_S^{S+\Delta S} P(S)\mathrm{d}S = C_n^{-1} f_n(S)\Delta S \quad (5)$$

If C_n is large enough, ΔS small enough, and $P(S)$ decrease or increase monotonously, the left of eq 5 may be written

$$\int_S^{S+\Delta S} P(S)\mathrm{d}S = P(S+\Delta S/2)\Delta S \quad (6)$$

thus,

$$P(S+\Delta S/2) = C_n^{-1} f(S) \quad (7)$$

ΔS is equal to $0.025\langle S^2\rangle^{1/2}$ in our calculation. In the region of maximum of $P(S)$, ΔS must be more small. In this paper, the region is from $S=0.90\langle S^2\rangle^{1/2}$ to $S=1.0\langle S^2\rangle^{1/2}$, and ΔS is equal to $0.01\langle S^2\rangle^{1/2}$ in the region. The unperturbed uniform star polymer chains are generated using the body-centred cubic lattice model. The uniform star chain consists of f branches, and each of the branches has n beads.

RESULTS AND DISCUSSION

Simulations are carried out for stars of $f=3$, 5, and 7 with length per branch from $n=100$ to $n=400$ beads, and we use 1000000 samples in each case. All computations are performed on VAX8350 computer using FORTRAN source codes. We calculate the probability density distribution function $P(S)$ using eq 7, and the results are given in Figures 1—6. We first calculated probability function $P(S)\Delta S$ of uniform star chains of 5 branches with different branch chain length $n=200$ and $n=400$ in order to perform the effects of branch chain length n on distribution function $P(S)\Delta S$, and the results are given in Figure 1. In Figure 1, we find the probability $P(S)\Delta S$ is independent of branch chain length n, and only depends on f and $S/\langle S^2\rangle^{1/2}$. In Figure 2, we also calculate probability $P(S)\Delta S$ of star chains of various branch number f with constant chain length $n=200$. In Figure 2, $P(S)\Delta S$ decreases with increasing branch number f for small S or large S, but the maximum of $P(S)\Delta S$ increases with increasing f. In order to investigate the form of probability density distribution function $P(S)$, we show

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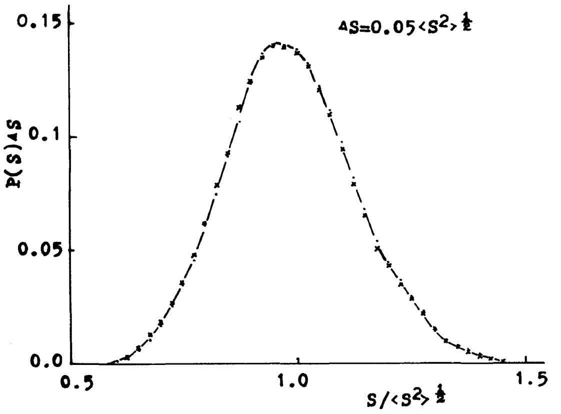

Figure 1. Probability $P(S)\Delta S$ *vs.* $S/\langle S^2\rangle^{1/2}$ for uniform star chains of $f=5$ with different length of branch chain. (–·–) $n=200$, $\langle S^2\rangle=265.8$; (–*–) $n=400$, $\langle S^2\rangle=531.2$.

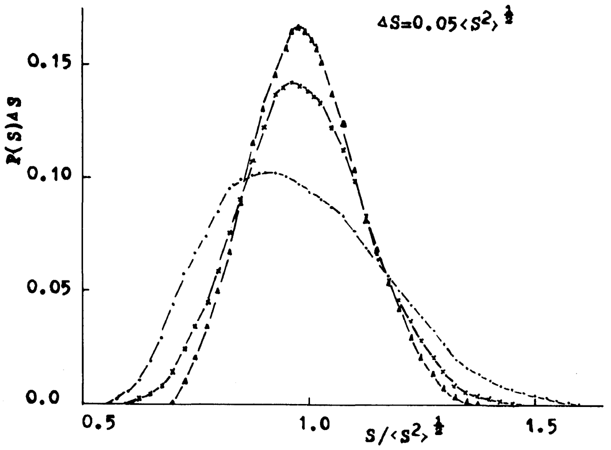

Figure 2. Probability $P(S)\Delta S$ *vs.* $S/\langle S^2\rangle^{1/2}$ for uniform star chain of $n=200$. (–·–) $f=3$, $\langle S^2\rangle=237.0$; (–×–) $f=5$, $\langle S^2\rangle=265.8$; (–▲–) $f=7$, $\langle S^2\rangle=276.5$.

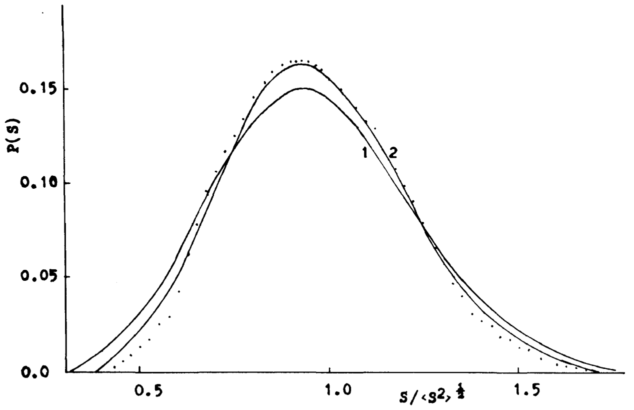

Figure 3. Probability density function $P(S)$ *vs.* $S/\langle S^2\rangle^{1/2}$ for a linear chain of $n=200$ ($\langle S^2\rangle=101.2$). 1, ref 11; 2, eq 8 with $a=7.0$, $b=4.0$; (·) Monte Carlo.

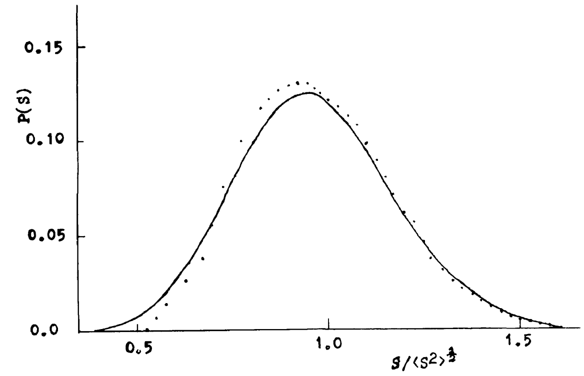

Figure 4. $P(S)$ *vs.* $S/\langle S^2\rangle^{1/2}$ for a uniform star chain of $f=3$ and $n=200$ ($\langle S^2\rangle=237.0$). (—) eq 8 with $a=5.0$; (·) Monte Carlo.

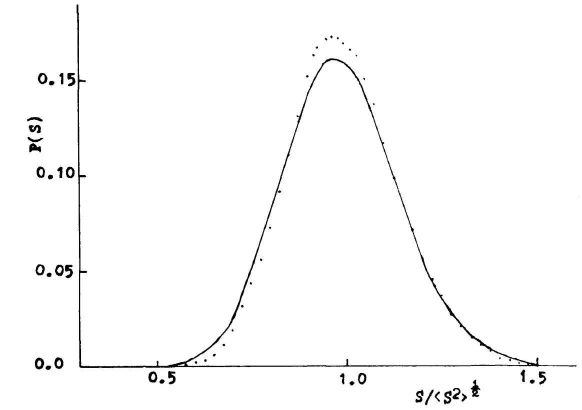

Figure 5. $P(S)$ *vs.* $S/\langle S^2\rangle^{1/2}$ for a uniform star chain of $f=5$ and $n=200$ ($\langle S^2\rangle=265.8$). (—) eq 8 with $a=10.0$; (·) Monte Carlo.

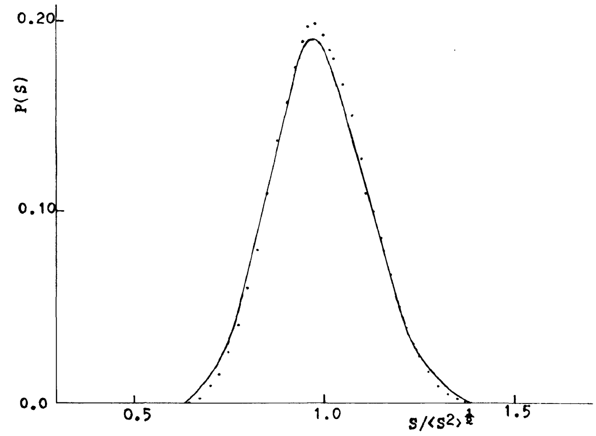

Figure 6. $P(S)$ *vs.* $S/\langle S^2\rangle^{1/2}$ for a uniform star chain of $f=7$ and $n=200$ ($\langle S^2\rangle=276.5$). (—) eq 8 with $a=12.0$; (·) Monte Carlo.

plots of $P(S)$ against S, and the results are given in Figures 3—6. Here, $P(S)$ of linear polymer chain is also calculated, and the results are shown in Figure 3. In Figures 3—6, we find that the simulation values of $P(S)$ can be written in the form of

$$P(S)=C\cdot S^{2a}\exp(-(a+0.5)S^2/\langle S^2\rangle) \quad (8)$$

where

$$c=\int_0^{\infty} S^{2a}\exp(-(a+0.5)S^2/\langle S^2\rangle)\mathrm{d}S \quad (9)$$

and $\langle S^2\rangle$ is the mean-square radius of gyration. The parameter a only depend on f, and the value is 3.5 for $f=1$, 5.0 for $f=3$, 10.0, for $f=5$, and 12.0 for $f=7$, respectively. We find that our function $P(S)$ of the unperturbed uniform star polymer chain is similar to the Flory–Fisk expression $P(S)=C'\cdot S^6\exp(-3.5S^2/\langle S^2\rangle)$ for the ideal linear polymer chain.[11] Although the Flory–Fisk expression for $P(S)$ was reproduced only from the ratios of moments,[11] not from experimental data or theory, our computer simulation supports that the ex-

Table I. Values of $\langle S^{2p}\rangle/\langle S^2\rangle^p$ under different conditions

$2p$	f	Monte Carlo	Theory[a]	Deviation	$\langle S^2\rangle$
−2	1	1.256	1.286	0.023	102.1
	3	1.160	1.201	0.034	237.0
	5	1.090	1.105	0.014	265.8
	7	1.067	1.071	0.0037	275.6
−1	1	1.081	1.094	0.012	
	3	1.061	1.075	0.013	
	5	1.031	1.037	0.0058	
	7	1.024	1.030	0.0058	
1	1	0.9746	0.9727	−0.0019	
	3	0.9814	0.9696	−0.012	
	5	0.9903	0.9882	−0.0022	
	7	0.9940	0.9921	−0.0019	
3	1	1.078	1.081	0.0028	
	3	1.054	1.066	0.011	
	5	1.029	1.035	0.0058	
	7	1.021	1.021	0	
4	1	1.220	1.222	0.0016	
	3	1.156	1.182	0.022	
	5	1.078	1.081	0.0028	
	7	1.056	1.061	0.0047	

[a] Values of $\langle S^{2p}\rangle/\langle S^2\rangle^p$ calculated by eq 4 and 8.

pression for the unperturbed linear polymer chain is remarkably good, and $P(S)$ of the ideal star-shaped chain is also expressed in the form of modified Flory–Fisk expression. To examine $P(S)$, we also calculate the ratio $S^{2p}/\langle S^2\rangle^p$ using eq 4 and our function $P(S)$, and the results are given in Table I. The ratio $S^{2p}/\langle S^2\rangle^p$ using Monte Carlo method is also obtained, and the results are also given in Table I. In Table I, we find the maximum deviation is only 3.4%, thus our function $P(S)$ is reasonable.

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