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Monte Carlo Simulations of a Semi-Flexible Polymer Solution

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We performed Monte Carlo simulations of semi-flexible polymer solutions in the good solvent limit for various concentration and flexibility by using new method. This method is composed of two parts: one is the usual enrichment algorithm and the other is a new algorithm that represents polymerization. This new algorithm enabled us to get useful samples for high concentration solution, which could not be obtained by means of the usual enrichment algorithm only. We discussed the gyration-radius exponent [ν] from the relation [$\ln(R_g)\sim\nu\ln(l)+C$] between the chain length [l] and the gyration radius [R_g] of polymers for various concentration and flexibility. The results are as follows: In extra high flexibility (45%~85%) regions, we obtained $\nu\sim0.5$ (the value of ideal chain). In the high flexibility (5%~15%) and low concentration (3%~15%) region, ν varied from 0.59 (the value of flexible chain) to 0.5 with increasing concentration. In the low flexibility (3%~5%) and low concentration (3%~10%) region, ν varied from 1.0 (the value in the stiff chain limit) to 0.59 with increasing chain length.
Key words: Monte Carlo simulation, semi-flexible polymer, polymerization, gyration radius

1. INTRODUCTION

The Monte Carlo simulations on a lattice have been extensively used as an important theoretical approach in the physics of polymer solutions. Among them, the solutions of flexible polymers in good solvents at relatively low concentration have been successfully studied by means of the enrichment algorithm [1-3]. In this algorithm, however, it is difficult to simulate the solutions at relatively high concentration.

The solutions of semi-flexible polymer chains have attracted increasing interest since their conformational properties are characterized as neither the flexible chains nor the stiff chains. Recently, Kasabo, *et al.* [4] reported an interesting experimental result of the conformations of the semi-flexible polymer solutions which exhibits the crossover behavior between the flexible and stiff chains.

In the present study, we simulate the solutions of the semi-flexible polymers by using the lattice Monte Carlo method and study their conformational properties in global range of concentration and flexibility. For this purpose, we make it possible to simulate high concentration solutions by combining the enrichment algorithm and a new algorithm that represents polymerization. In particular, we study the gyration radius [R_g] and the associated exponent [ν] for various concentration and flexibility.

2. SIMULATION METHOD

We assume that we are dealing with the athermal solution, i.e., the good solvent limit. All polymer chains are simulated as the self-avoiding walks (SAWs). We generate various polymer conformations on a simple cubic lattice (330x330x330) by using the new method combining (1) the enrichment algorithm (Fig. 1) and (2) the polymerization algorithm (Fig. 2).

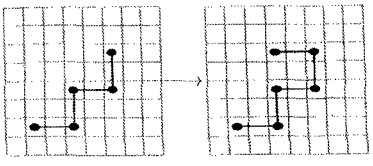

Fig. 1 : Explanation of the enrichment algorithm. A polymer is elongated from an endpoint to the nearest neighbors.

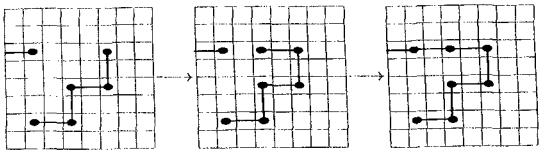

Fig. 2 : Explanation of the polymerization. Two polymers are joined if two endpoints meet each other.

We measure afterwards the concentration and flexibility for each solution sample that we generated. Here, we assume that the concentration is equal to (the number of occupied lattice points) divided by (the number of all lattice points), and flexibility is equal to (the number of turns) divided by (the number of joints).

We estimate the gyration-radius exponent [ν] from the relation [$\ln(R_g)\sim\nu\ln(l)+C$] between the chain length and the gyration radius [R_g] of polymers for various concentration and flexibility. Then, we discuss the dependence of [ν] on the concentration and flexibility.

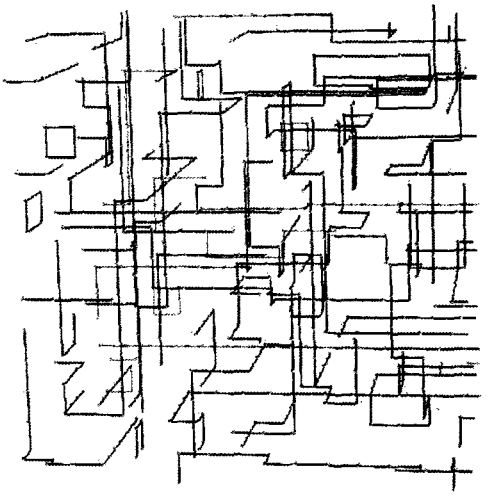

Fig. 3 : Sample of this simulation. (low concentration)

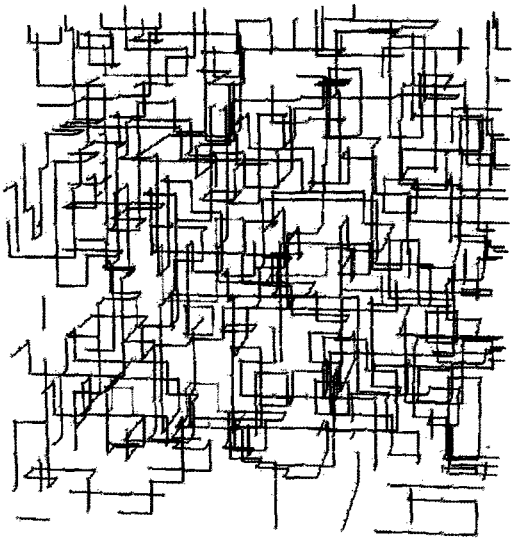

Fig. 4 : Sample of this simulation. (high concentration)

concentration(%) / flexibility(%)	3~5	5~10	10~15	15~25	25~35	35~45
3~5	depend on chain length (0.6~1.0)		0.580	——	——	——
5~10	0.590	0.541	0.548	——	——	——
10~15	0.531	0.521	0.514	——	——	——
45~55	0.502	0.511	0.507	0.506	0.514	0.514
75~85	0.509	0.505	0.516	0.529	0.532	——

Table 1 : ν in various concentration and flexibility.

3. RESULT

Figures 3 and 4 represent resulting samples. Table 1 lists the values of ν that were obtained in various concentration and flexibility. ν depends on the chain length in the low flexibility (3%~5%) and low concentration (3%~10%) region [A]. ν does not depend on the chain length in the high flexibility (5%~15%) and low concentration (3%~15%) region [B] and in the extra high flexibility (45%~85%) region [C]. We describe the detail of each region in the following:

A. low flexibility (3%~5%) and low concentration (3%~10%) region

We obtained the data as shown in Figs. 5 and 6 in the low flexibility and low concentration region. Figures 5 and 6 show the graphs of the chain length versus the gyration radius with double logarithmic plot. From these figures, we find that ν depends on the chain length. That is, ν varies from 1.0 to 0.6 with increasing chain length. This behavior resembles the experimental result by Kasabo, *et al.* [4]. It seems that the vending of long chains cause this character.

B. high flexibility (5%~15%) and low concentration (3%~15%) region

We obtained the data as shown in Figs. 7 and 8 in the high flexibility (5%~15%), low concentration (3%~15%) region. Figures 7 and 8 show the graphs of the chain length versus the gyration radius with double logarithmic plot. We find that ν does not depend on the chain length in this case. The value of ν in Fig. 7 (concentration: 3%~5%) is 0.590 which is the same value of the flexible real chain. The value of ν in Fig. 8 (concentration: 10%~15%) is 0.548. We know that a polymer in the high concentration solution behaves like an ideal chain due to the lack of the excluded volume effect which is caused by a screening effect, so the value of ν in the high concentration region is 0.5. It seems that the value of ν varies from 0.59 to 0.5 with increasing concentration.

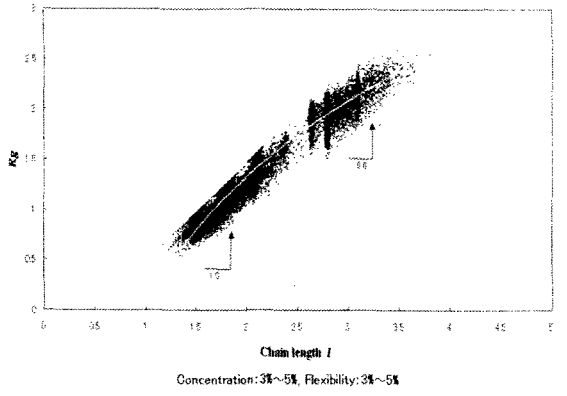

Fig. 5 : Chain length versus gyration radius.

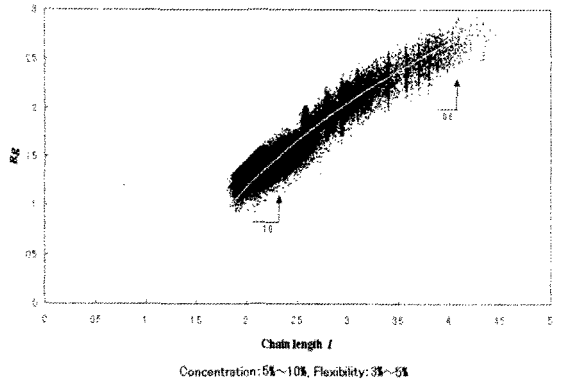

Fig. 6 : Chain length versus gyration radius.

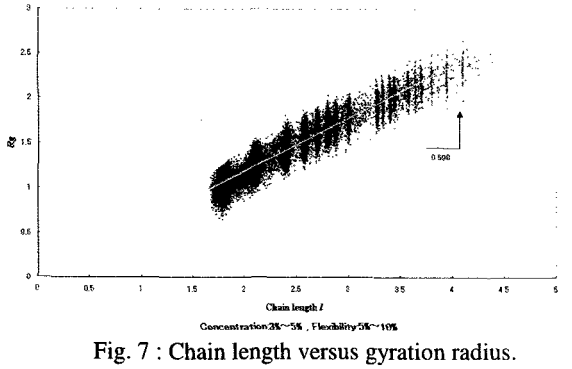

Fig. 7 : Chain length versus gyration radius.

C. extra high flexibility (45%~85%) region

We obtained the data as shown in Fig. 9 in the extra high (45%~85%) flexibility region. Figure 9 shows the graph of the chain length versus the gyration radius with double logarithmic plot. We find that ν does not depend on the chain length either. The value of ν in Fig. 9 is 0.509 which is close to 0.5 ; the value of an ideal chain. The others in the same region are almost the value close to 0.5. We can explain the reason of this interesting result as follows: In this region, polymers are bent extremely, so polymers become like a ball. The concentration of the solution is not so high, but the concentration in a part that is close to polymer chain (ball) becomes high. So polymer behaves like an ideal chain and the value of ν is close to 0.5.

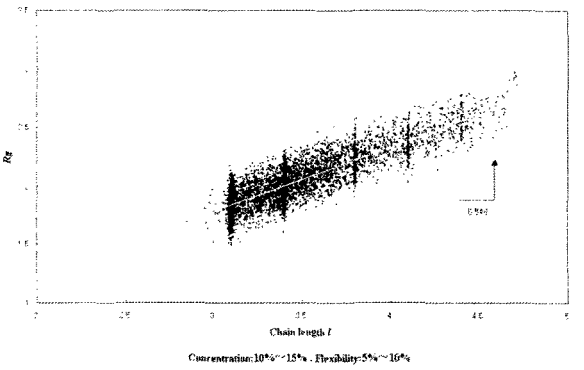

Fig. 8 : Chain length versus gyration radius.

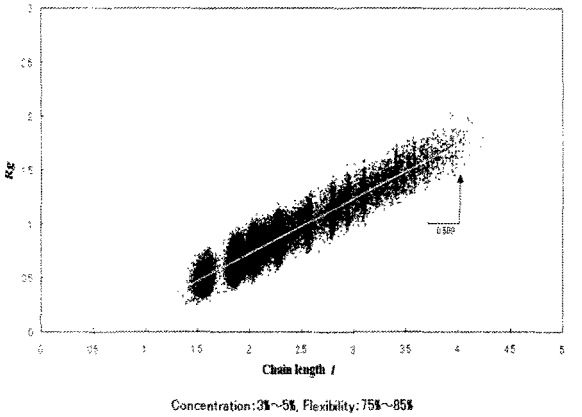

Fig. 9 : Chain length versus gyration radius.

4.SUMMARY

We have performed Monte Carlo simulations of semi-flexible polymer chains by means of a new method combing the enrichment algorithm and the polymerization, and found the following results. In the low flexibility (3%~5%) and low concentration (3%~10%) region, ν varies from 1.0 to 0.6 depending on the chain length. In the high (75%~85%) flexibility and low concentration (3%~15%) region, ν is independent of the chain length and concentration. ν is close to 0.59 in the low concentration side, and close to 0.5 in the high concentration side. In the extra high flexibility (45%~85%) region, ν is independent of the chain length and concentration. ν is close to 0.5. The behavior in the low flexibility and low concentration region is similar to that observed experimentally.

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