The Excluded Volume Effect of Very-long-chain Molecules

Keizo SUZUKI

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

(Received December 26, 1967)

The problem of the excluded volume effect upon the shape of the chain molecule was set twenty years ago[1] and has not been completely solved yet.[2] The approach by Monte Carlo simulation using an electronic computer has led to rather meagre results because of the extraordinarily poor yield of the overlapless form of the long chain; reliable results have been obtained only on chains with a few hundred bonds.[3]

The present author has found a new program to make the overlapless forms in a good yield, producing 8192-bond chains on a diamond lattice. Some results are shown in Table 1, where N is the number of the bonds, r is the radius of the gyration of the chain, a is the bond longth, and α is the exponent in the formula:

$$\langle r^2 \rangle = KN^{\alpha},$$

and is calculated by the equation:

$$\alpha = (\log \langle r^2_{2N} \rangle - \log \langle r^2_N \rangle)/\log 2.$$

TABLE 1

N	$\langle r^2 \rangle / a^2$	α	Yield (%)
1	0.2500	1.052	100
2	0.5185	1.092	100
4	1.105	1.145	94
8	2.444	1.19±0.01	87
16	5.560	1.20±0.01	78
32	12.78	1.20±0.01	71
64	29.31	1.20±0.01	62
128	67.37	1.19±0.01	56
256	153.4	1.19±0.02	50
512	350.3	1.17±0.04	46
1024	787.0	1.15±0.05	40
2048	1740	1.11±0.10	36
4096	3747	1.08±0.13	27
8192	7943		

With the increase in N, α increases at first but gradually decreases after passing a maximum value, 1.20. The previous studies did not find the decrease because they did not reach this region. Theoretically the exponent, α, can not go under 1; it probably approaches 1 very slowly, as previously expected by the present author.[4]

The scheme of the program to make overlapless chains with equal probability is as follows:

1 MAKE AN M-BOND CHAIN AT RANDOM. (M=64, for example)
2 IF THERE IS AN OVERLAP, GO TO 1.
3 $N=M$.
4 IF ANOTHER N-BOND CHAIN IS NOT STORED, STORE THE NEW CHAIN AND GO TO 1.
5 CONNECT THE STORED CHAIN TO THE NEW CHAIN AND MAKE A $2N$-BOND CHAIN.
6 IF THERE IS AN OVERLAP, OUTPUT AND CLEAR BOTH THE N-BOND CHAINS, AND GO TO 1.
7 $N=2N$, AND GO TO 4.

Full programs will appear elsewhere. The last column of Table 1 shows the average yield in getting an overlapless $2N$-bond chain by connecting two N-bond chains. The yield decreases with the increase in N, but it must converge to a finite value of not less than 1/9.

1) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); K. Suzuki, This Bulletin, **22**, 8 (1949).
2) Z. Alexandrowicz, *J. Chem. Phys.*, **46**, 3789 (1967).
3) P. H. Verdier, *ibid.*, **45**, 2118 (1966).
4) K. Suzuki, Thesis, The University of Tokyo (1957).