

# COMPUTER EXPERIMENT FOR SELECTION OF OPTICAL ISOMER DURING PREBIOTIC POLYMERIZATION

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**Abstract.** Computer experiments simulating prebiotic polymerization were carried out using the Monte Carlo method. A high degree of selection of single optical isomers from racemic monomers occurred by assuming a small asymmetry in their chemical natures, which was included to investigate an amplification of the asymmetry due to parity non-conservation. The asymmetry developed much more slowly than the growth of polymers, and the degree of asymmetry in the polymers increased with the degree of polymerization. Competition between the preferential selection and the disturbance by the statistical fluctuation are discussed.

## 1. Introduction

It is generally accepted that the constituent organic molecules of proteins and nucleic acids such as amino acids, purine and pyrimidine bases, and ribose and deoxyribose were synthesized on the primitive earth via simple organic molecules from the atmospheric gas with energies such as ultraviolet and electric discharges, and that most of them were stored as a primitive soup in the ocean, where the polymers were formed by the dehydration condensation.

However, there is no acceptable answer for the question of how the condensation reaction could proceed steadily in the soup. Although the condensation reaction which leads to an increase of free energy of a system can not occur in an equilibrium state, the existence of a continuously polymerizing process is not impossible in an irreversible process with a continuing supply of energy. The condensation might have proceeded continuously by an effective recycle of the primitive gas, which occurs by the repetition of the formation of condensing agents in the primitive atmosphere exposed to ionizing-energy sources, the fall of the agents into the ocean with rain, and the decomposition of the agents to the original gas components after the dehydration reaction. If the formation of polymers occurs faster than the hydrolysis, steady evolution should be possible. This hypothesis is now being studied with a partial success (Yamagata *et al.*, 1979).

It is still a puzzle why life generated in the one-handed form of biomolecules from the primitive organic soup (Wald, 1957; Ulbricht, 1959; Harada, 1970; Thiemann, 1974; Keszthelyi, 1977), which must have contained the molecules in the racemic form as demonstrated by Miller (1955). After the discovery of parity non-conservation by Lee

and Yang (1956), two different proposals were given on the relation between the origin of optical activity and this fundamental physical phenomena, one by Vester *et al.* (1959) and another by one of the present authors (Yamagata, 1966). The latter proposed that the electromagnetic interaction would slightly violate the parity through a correction of the parity non-conserved weak interaction, and the violation would lead to an intrinsic breakdown of symmetry between D- and L-form of handed molecules, for example, in the wave functions, in the energies, in the chemical reactions. It was also discussed that because of its permanent nature the intrinsic asymmetry should be amplified up to a large extent during polymerization and further evolutionary processes, though the intrinsic asymmetry is so small that it could not be detected in the usual phenomena in physics and chemistry.\* In this paper we wish to report a computer experiment which simulates the polymerization of racemic monomers in aqueous solution and to discuss the relationship between the progress of polymerization and the selection of a single optical isomer resulting from some assumed small asymmetry in the chemical natures between the isomers.

## 2. Computational Procedures

The simulation experiments were carried out in the following procedures. A cubic lattice ( $N^3$ ) is set up in a computer memory. A certain number ( $n$ ) of monomer is distributed at random on the lattice sites with an equal probability for the left-handed (L) and right-handed (D) monomers using the uniform random numbers, so that  $n = n_L + n_D$ . Both  $n_L/n$  and  $n_D/n$  are nominally equal to  $\frac{1}{2}$ , but statistically fluctuate around it. This is a model of a racemic solution of monomers. The monomers are assumed to be surrounded by water molecules, but we can neglect the latter without loss of generality in the simulation experiment.

The lattice is scanned from  $r = (0, 0, 0)$  toward  $r = (N, N, N)$  in the odd numbered scans and with the reverse direction in the even one, so that a flow in one direction is cancelled out. Vacant lattice sites are ignored, whereas if a particle is found at a site it is controlled to behave by the following rules, which simulate Brownian motion, racemization, dehydration condensation and hydrolysis.

(1) Monomers move with an equal probability from the original point  $r_i = (x_i, y_i, z_i)$  to one of 125 lattice points  $r'_i = (x_i + a, y_i + b, z_i + c)$  including the original position, where  $a, b,$  and  $c$  are equal to 0,  $\pm 1,$  or  $\pm 2$ . If the particle collides with the walls of the cube by the movement, the particle is reflected by the wall. If a particle collides with another particle, the former stops at a possible lattice point on the displacement vector  $\Delta r_i(a, b, c) = r'_i(x_i + a, y_i + b, z_i + c) - r_i(x_i, y_i, z_i)$ , and the latter stays at the original point.

(2) The 'residue' in polymers is moved according to Rule (1), if possible, under the constraint that the 'bond length' is kept to the unit length.

\* Recently experiments to search handedness of atoms due to parity non-conservation in weak interaction have been performed by several groups. See the review article; Feinberg, G.: 1978, *Nature* 271, 509.

(3) Monomers 'racemize' with a given probability.

(4) The particles 'condense' with a given probability to form a linear chain polymer when they are present in the nearest sites. The formation of branched polymer is prohibited. When more than two of the nearest sites are occupied by monomers or the end particles of polymer, with which particle it combines is decided by the random numbers.

(5) The bond of a polymer breaks with a given probability.

### 3. Results and Discussions

The probabilities of bonding and hydrolysis are given by parameters in Table I according to the following assumptions.

(i) The rate constant for the bonding between the same isomers is relatively larger than that between opposite isomers. Hydrolysis proceeds with the inverse relation.

This assumption might be justified for the relatively long chains by the experimental results concerning peptides. Blout and Idelson (1956) reported that in the polymerization of  $\gamma$ -benzyl-N-carboxy glutamate anhydride the rate constant for racemic anhydride was much smaller than that for the pure isomers, approximately only one twentieth. Blout *et al.* (1957) also reported that the racemic polymer is much less stable in configuration than the pure polymers. The denatured polymer would be hydrolyzed with much higher probability than that in the stable configuration formed by intramolecular bonds.

(ii) The rate constant for the bonding between L-forms is assumed to be slightly larger than that between D-forms. The hydrolysis proceeds with the inverse relation. This is an expression of the intrinsic molecular asymmetry, but the predominance of L-form is assumed arbitrarily. The latter part of the assumption might be reasonable if the parity non-conserving energy difference between the interaction of L-L and of D-D changes monotonically with their intermolecular distance along the reaction coordinate.

Figure 1 shows an example of the variation of total asymmetry [ $A = (n_L - n_D)/n$ ], and the results of the experiment are given in some detail in Figure 2. The abnormal distribution of 4-, 6-, and 8-mer is probably due to the formation of ring polymers, which is allowed in the present program for polymers of even degree of polymerization over

TABLE I  
Probabilities of bonding and breaking. The probability of 100% for the bonding of L-L is used to accelerate the polymerization.

	Bonding	Breaking
L-L	1	$\gamma$
D-D	$1 - \alpha$	$\frac{\gamma}{1 - \alpha}$
D-L L-D	$1 - \beta$	$\frac{\gamma}{1 - \beta}$

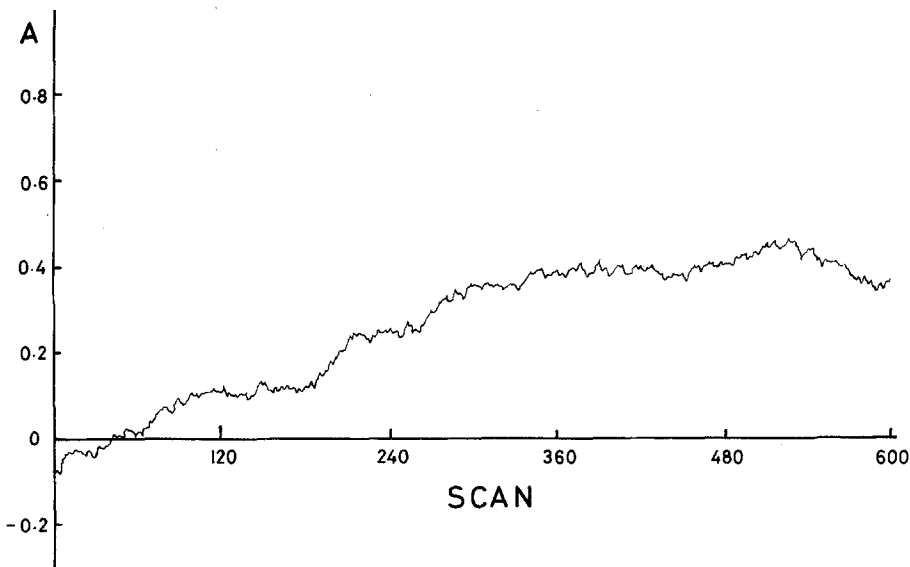


Fig. 1. Variation of total asymmetry [ $A = (n_L - n_D)/n$ ] with scan.  $N = 15$ ,  $n = 1000$ ,  $\alpha = 0.1$ ,  $\beta = 0.8$ ,  $\gamma = 0.05$  and rac (probability of racemization) = 0.2.

4-mer. The results are interesting from the viewpoint of chemical evolution. First, the mean value through the scans of the degree of asymmetry of each polymer increases with the degree of polymerization. The average value for the largest group of polymers reaches about 90%. The yields of the large molecules are very small, but if the program contains a mechanism which freezes the large polymers with high degrees of 'optical' purity, the polymerization of the smaller molecules continues further, and then the yields of the highly asymmetric large polymers are gradually increased. Such freezing mechanisms appear to have existed on the primitive earth, for example, the formation of secondary structures\* such as  $\alpha$ -helix, the formation of macromolecular complex systems like concervate, or the adsorption on clay minerals. Second, the asymmetry develops very slowly compared to polymer growth. There is little difference between the mean distribution of polymers during the first 120 scans and that of the last one, whereas the degrees of asymmetry are much different between them, and this indicates that the system is still in an undeveloped state as to the asymmetry at the first 120 scans.

Figure 3 gives the experimental results in the case of  $\gamma = 0$ , which means no breaking of bonds. This simulates the polymerization in nonaqueous solution, such as that of  $\gamma$ -benzyl-N-carboxy glutamate anhydride discussed above or of N-carboxyanhydride of alanine (Thiemann and Darge, 1974), in which the polymers formed are not exposed to hydrolysis. The result shows a much different pattern of distribution of polymers and no appreciable amplification of the asymmetry. Thus the aqueous system, which allows rearrangements of the units in the polymers through successive condensation and hydro-

\* The effect of the secondary structure will be taken into account in further investigation.

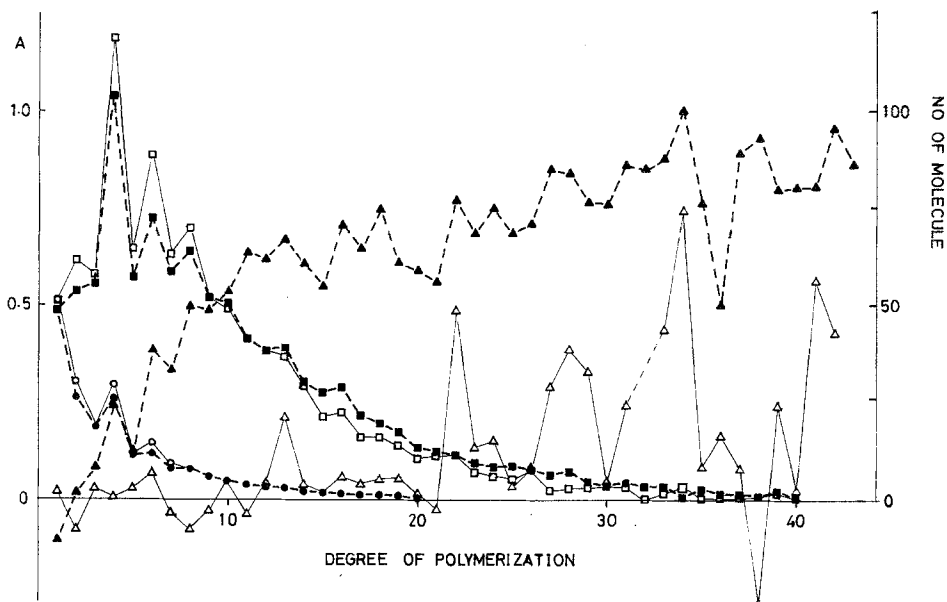


Fig. 2. Dependence of number of polymer and degree of asymmetry on degree of polymerization in the experiment shown in Figure 1.  $\circ$   $\bullet$  number of polymer;  $\square$   $\blacksquare$  number of polymer times degree of polymerization;  $\triangle$   $\blacktriangle$  A (degree of asymmetry). Opened: means through 1st 120 scans. Closed: means through last 120 scans.

lysis, has been demonstrated to be much more advantageous for the selection of single optical isomers (Wald, 1957).

The statistical fluctuation would contribute to the fluctuation of total asymmetry by  $\sqrt{A^2} = 1/\sqrt{n}$  in the order of magnitude. So, if  $\alpha$  is taken to be smaller than a critical value which is presumed to be comparable with  $1/\sqrt{n}$ , the preferential asymmetry would be masked by the statistical fluctuation. In order to test the competition between the preferential selection in the case of  $\alpha = 1/\sqrt{n}$  and the fluctuational disordering, experiments have been performed with a rather small number of particles ( $n = 100$ ) but a very large number of scans (5000). The results (Figure 4) show a high degree of selection of single optical isomers which occurred by overcoming the interruption by the statistical fluctuation. A similar result was also obtained for the experiment with another series of uniform random number. If the freezing mechanism is included in the program, the selection must occur for a much smaller value of  $\alpha$  than  $1/\sqrt{n}$ .

This result can be applied to the prebiotic system. We may assume  $(10 \text{ km})^3$  at least as the volume of the system in which molecules could be well mixed during a geological period. Since the system would have contained  $\sim 10^{40}$  of monomers, the relation  $\alpha \gg 1/\sqrt{n}$  should hold in the system even for a very small value of  $\alpha$ , which is assumed to be of the same order of magnitude as the  $10^{-10}$  estimated by Rein (1974) for the energy difference between optical isomers. Therefore, there would have existed in the prebiotic

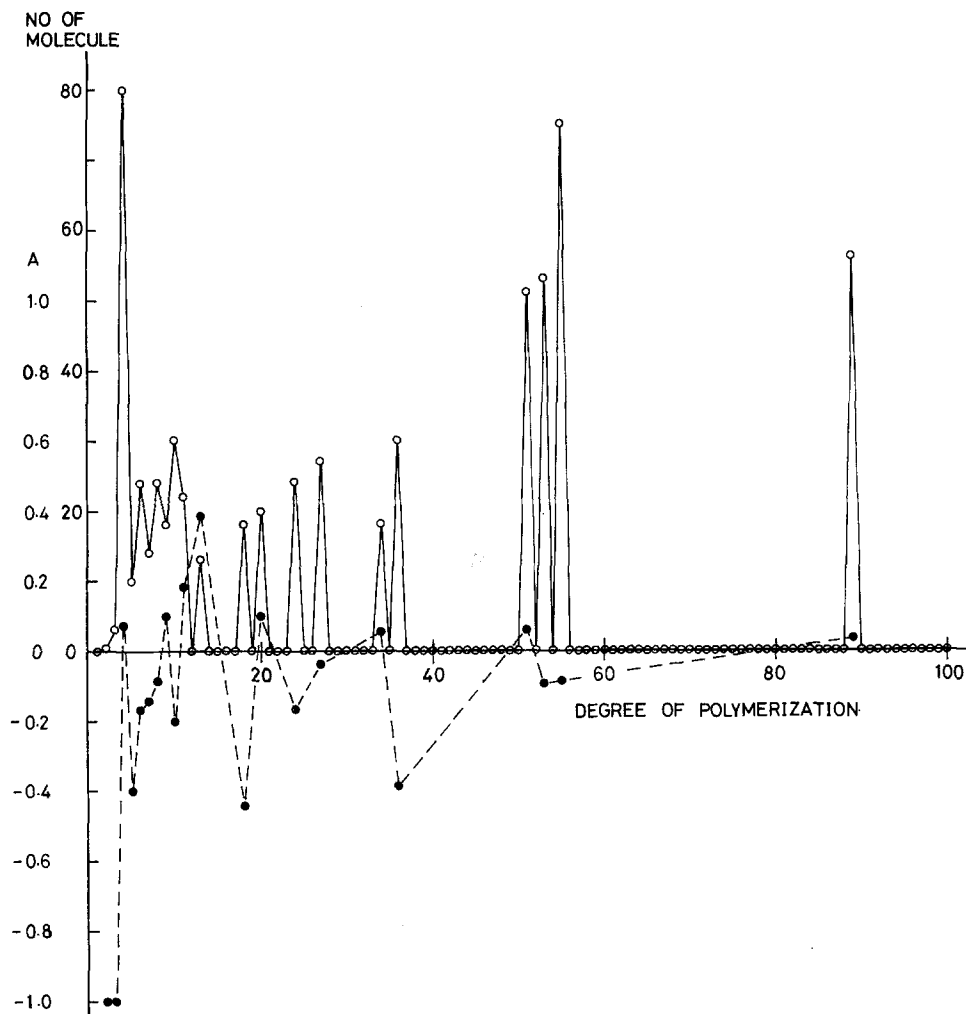


Fig. 3. Dependence of mean number of polymer and mean degree of asymmetry through 91 ~ 120 scan on degree of polymerization in the case of no breaking;  $N = 15$ ,  $n = 1000$ ,  $\alpha = 0.1$ ,  $\beta = 0.5$ ,  $\gamma = 0$ ,  $\text{rac} = 0.2$ . ○ number of polymer times degree of polymerization. ● degree of asymmetry.

system some asymmetry which remained without vanishing by the fluctuational disturbance.

We can conclude that the very small asymmetry arising from the parity violation could overcome the statistical fluctuation and the asymmetry was more concentrated in larger molecules during the growth of polymers with a partial balance between the condensation and the hydrolysis, and that because of the constant nature, the asymmetry could be gradually accumulated through the freezing of polymers. Thus the selection of one-handed molecules would be considered as a result of physical and chemical processes of the system.

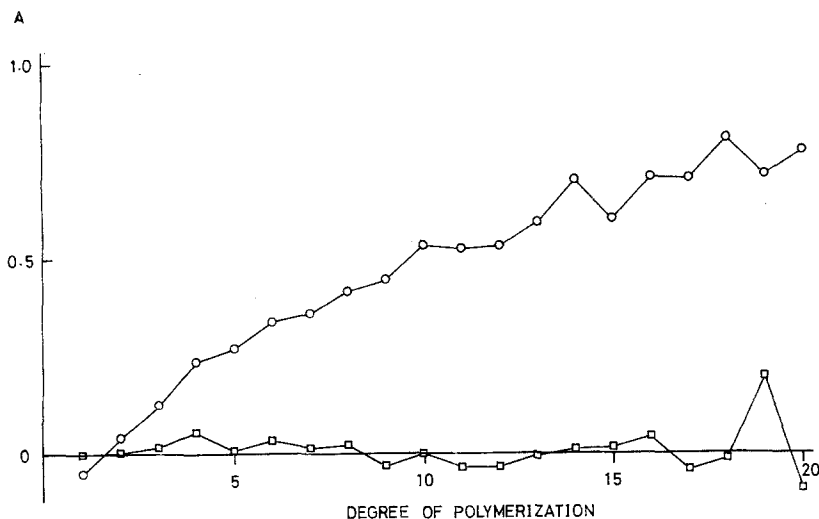


Fig. 4. Mean degree of asymmetry through first 5000 scans for each degree of polymerization. Comparison between two cases;  $\alpha = 1/\sqrt{n}$  ( $\circ$ ) and  $\alpha = 0$  ( $\square$ ).  $N = 8$ ,  $n = 100$ ,  $\beta = 0.8$ ,  $\gamma = 0.15$ ,  $\text{rac} = 0.2$ .

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