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## Studies on the Synthesis of Protein Analogus (Part III)

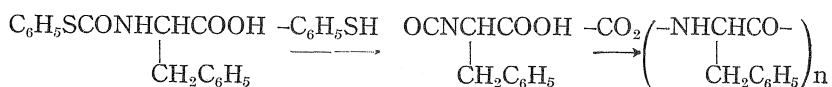
### Polymerisation of DL-phenylalanine\*

By

Junzo NOGUCHI, K. MIYAMORI and Shohei ISHINO

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N-carbothiophenyl-DL-phenylalanine is decomposed slowly at about 120—130°C, swiftly at about 150—160°C, and expells thiophenol and carbondioxide to polymerize. It requires about 16.6 Kcal to release the thiophenol in DL-phenylalanine and finish the following reaction.<sup>1)</sup>



But the polymer obtained by the block method has some colour, and some subreaction is unavoidable. Since it was difficult to get the pure polymer by this method, the polymerisation in solvent was studied at low temperature of below 80°C. Whether it might polymerize by heating for many hours was tested in the various kinds of solvents, benzene, pyridine, dimethyl-aniline, dimethyl-formamide and the mixed solvent of benzene and pyridene etc.. The result of each test is shown in Table I.

Table I

Solvent (10cc)	Sample (g)	Temp. (°C)	Time (hrs.)	Yield (%)	outline
Benzene	0.3	80	1000	38	sticky soln. a little gel-like ppt.
Pyridine	0.3	80	1000	—	a little crystal-like ppt. non-viscous.
Dimethyl aniline	0.3	80	1000	—	very small amount crystal-like ppt. undeveloped polymerisation.
Benzene-Pyridine (7cc) (3cc)	0.3	80	1000	31	sticky soln. glatinous ppt.

In benzene, the reaction was very slow, and in pyridine, only a little crystal-like polymer was made. But in benzene containing a little pyridine, it was promoted. The better result was got in benzene containing a little pyridine, so that we tested the polymerisabilities in the condition of heating at 80°C for about 200 hours at the rates of 0, 1, 2, 4, 10 and 20 moles of pyridine to the sample. The results are shown in Table II.

The most suitable condition of the polymerisations was the use of ten moles pyridine to the sample. The polymerisation of the contents of more or less pyridine was worse than that with ten moles. In benzene only, the polymerisation velocity was so slow

\* It was published in the Jan. of the Chem. Soc. of Japan **75**, 641—642 (1954) (in Japanese).

1) S. Ishino, J. Noguchi, Jan. of the Chem. Soc. of Japan **75**, 639 (1954) Part II.

Table II

Pyridine content in (Benzene-Pyridine) 10cc (cc) moles ratio for sample	Sample (g)	Temp. (°C)	Time (hrs.)	Yield (%)	outline
0	0	80	200	—	no ppt. nonviscous.
0.08	1	80	200	38	a little gel-like ppt. yellow solu.
0.16	2	80	200	38	ibid.
0.32	4	80	200	46	ibid.
0.8	10	80	200	38	almost gelatinized
1.6	20	80	200	31	a little gel-like ppt.

that the reaction by heating for about 200 hours did not give complete polymerisation, but the longer reaction for about 1000 hours. gelatinized the solution uniformly.

The analysis of the sample, which was polymerized in benzene containing ten moles pyridine to the monomer, corresponded to the formula,  $\left( \begin{array}{c} \text{-NHCHCO-} \\ | \\ \text{CH}_2\text{C}_6\text{H}_5 \end{array} \right)_n$ . The polymer

was insoluble in water, mineral acid, alkali, formic acid, acetic acid, alcohol, ether and acetone etc., and sparingly soluble in benzene, and easily soluble in the mixed solvent of acetic acid and monochlor-acetic acid (1 : 1) and in dichlor-acetic acid. The reason of the extremely feeble Biuret's reaction may be that the polymer is almost insoluble in alkali.

We measured the viscosity with Ostwald's viscosimeter at 30°C, and the molecular weight and polymerisation degree by osmotic method in the mixed solvent of glacial acetic acid and monochlor-acetic acid.

Intrinsic viscosity  $[\eta] = 0.068$  (g/100 cc unit),

Molecular weight M. W. = 59,400

Polymerisation degree  $n \approx 400$

#### Experimental

N-carbothiophenyl-DL-phenylalanine (m. p. 56°C) which was used in experiments, was prepared as described in Part I<sup>1)</sup>.

*Poly-DL-phenylalanine*—N-carbothiophenyl-DL-phenylalanine 0.3 g was dissolved in benzene 10 cc containing pyridine 0.8 cc and heated at  $80 \pm 1^\circ\text{C}$  for about 200 hours in a sealed tube. It became gel uniformly. It was centrifuged, washed with a small amount of benzene, absolute alcohol and ether, and dried in vacuum. White powder was obtained. Yield 0.05 g (38% of the theoretical).

Analysis found N=9.47%, H=6.34%, C=73.14%

for  $(\text{C}_9\text{H}_9\text{NO})_n$  calc. N=9.52%, H=6.12%, C=73.50

Molecular weight : It was measured at  $30 \pm 0.01^\circ\text{C}$  by osmotic method with Meshizuka's apparatus.<sup>2)</sup> The sample 0.4092 g was dissolved in the mixture 10 cc of

acetic acid and monochlor acetic acid (1 : 1).

Concentration  $C=4.92$  g/l, Specific gravity  $\rho=1.123$ ,

Osmotic pressure  $\pi=2.08 \times 10^{-3}$  atm.

Molecular weight  $M=59,400$

Polymerisation degree  $\approx 400$

Viscosity : It was measured at  $30 \pm 0.1^\circ\text{C}$  in the mixture of acetic acid and monochlor-acetic acid (1 : 1) with Ostwald's viscosimeter.

intrinsic viscosity  $[\eta] \approx 0.068$ .

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2) G. Meshizuka, *The Chemistry of Highpolymer* **6**, 305 (1949) (in Japanese).