Thermal Homopolymerization of Lysine and Copolymerization with Neutral and Acidic Amino Acids[1]

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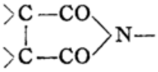
(Received July 15, 1959)

Glutamic acid and aspartic acid characteristically yield copolymers[2,3] with unsubstituted amino acids which fail to form polymers when heated individually. By using an excess of acidic amino acids, it is furthermore possible to copolymerize eighteen common amino acids into a *proteinoid*[4].

The special effects of basic amino acids, particularly lysine, are also interesting. Free DL-lysine was converted to its liquid lactam at 150~170°C with vigorous evolution of water vapor and it homopolymerized at 180~230°C.

The free lysine also copolymerized easily with glycine, alanine and other neutral amino acids, glutamic acid, aspartic acid, caprolactam, succinic acid, terephthalic acid and other carboxylic acids. After acidic hydrolysis, component amino acids were identified by paper chromatography. Infrared absorption spectra of lysine homopolymer, lysine-neutral amino acid copolymers and lysine-glutamic acid copolymer indicated that these are typical polypeptides. The salient maxima at 3080, 3280, 1630 and 1540 $\mathrm{cm^{-1}}$; however, lysine-aspartic acid copolymer shows additional bands at 1720 and 1780 $\mathrm{cm^{-1}}$ which indicate the 5 membered cyclic imide structure[5],



Some of the yield and amino acid composition of typical polymers are as follows:

DL-Lysine homopolymer*

Temp., °C	Yield after dialysis, g.
180	0.07
190	0.15
200	0.17
210	0.18

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[1] Contribution No. 116 of the Oceanographic Institute, aided by Grant C-3971 of the National Institutes of Health, U. S. Public Health Service.

[2] K. Harada and S. W. Fox, *J. Am. Chem. Soc.*, **80**, 2694 (1958).

[3] S. W. Fox, K. Harada and A. Vegotsky, *Experientia*, **15**, 81 (1959).

[4] S. W. Fox and K. Harada, *Science*, **128**, 1214 (1958).

[5] A. Vegotsky, K. Harada and S. W. Fox, *J. Am. Chem. Soc.*, **80**, 3361 (1958).

DL-Lysine-glycine copolymer**

Reaction conditions °C	Reaction conditions hr.	Yield after dialysis g.	Amino acid composition*** Gly %	Amino acid composition*** Lys %
180	2	0.65	77	23
190	1	0.68	62	38
200	1/2	0.64	60	40

DL-Lysine-DL-aspartic acid copolymer****

Temp. °C	Yield after dialysis g.	Amino acid composition*** Asp %	Amino acid composition*** Lys %
170	0.09	33	67
180	0.19	31	69
190	0.99	25	75
200	1.13	24	76
210	1.23	22	78

* DL-Lysine (0.01 mol.) was heated for 2 hr.

** DL-Lysine (0.01 mol.) and glycine (0.01 mol.) were heated.

*** Amino acid compositions were determined by DNP method using column chromatography.

**** DL-Lysine (0.01 mol.) and DL-aspartic acid (0.01 mol.) were heated for 2 hr.

Lysine monohydrochloride did not homopolymerize but did copolymerized with glutamic acid, and with other amino acids in the presence of orthophosphoric acid. Lysine homopolymer was water-soluble (it contained some gel-like material), but it was nondiffusible through cellophane tubing. Lysine-glutamic acid and lysine-glycine copolymers were gel-like materials and lysine-aspartic acid copolymer was sponge-like. The amphoteric polymers of lysine-glutamic acid and also lysine-aspartic acid swelled in alkali and acid, and did not dissolve in either alkali or acid. It is likely that these polymers have a high degree of branching and have a quasi three-dimensional structure. α,ω-Linkage studies of lysine and acidic amino acid residues are now in progress. The lactam formation of lysine is very interesting as is copolymerization of glutamic acid with other amino acids[2]. The lactams serve as reactive intermediates, solvents for the reactions and also basic or acidic catalysts for peptide bond formation. At this time, the studies have revealed a new property of lysine and presented an easy way to prepare lysine-containing polymers.

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