

163. *The Polymerization of 6-Hexanolactam.*

By A. B. MEGGY.

The polymerization of 6-hexanolactam can be interpreted in terms of two equilibrium constants: k_1 determines the ratio of monomer to polymer at equilibrium, and k_2 the chain length of the polymer. From the change of k_1 and k_2 with temperature the approximate values of ΔH and ΔS for the reactions involved can be calculated. The results are used for calculation of the chain length of the polymer in equilibrium with liquid water at 220—280°.

GEE (*Trans. Faraday Soc.*, 1952, **48**, 515) has shown that the marked change in the viscosity and other physical properties of liquid sulphur in the neighbourhood of 170° can be interpreted quantitatively by assuming that S_8 rings are transformed into chains of great length.

Many cyclic organic compounds are readily transformed into linear polymers; among these 6-hexanolactam is of especial interest, since the polyamides obtainable from it have valuable properties for the production of textile fibres. Information on the production and properties of these polymers is contained in B.I.O.S. Report 1472, and the data from that report form the basis for the calculations in this paper.

The polymerization of 6-hexanolactam involves the hydrolysis of 1 mol. to the acid, followed by addition of successive molecules of lactam to the terminal amino-group. In this way chains of any length can be built up: lactam + n -mer \rightleftharpoons ($n + 1$)-mer. Hence,

$$\frac{[\text{lactam}][n\text{-mer}]}{[(n+1)\text{-mer}]} = k_1$$

It may be assumed that all terminal amino-groups will be equally reactive towards the lactam if the chains are more than two or three units long, since the effect of one end of the chain is unlikely to be propagated to the other through more than 15 or 20 bonds. It follows that k_1 will be independent of n , the chain length of the reacting polymer.

If q is the number of hexanolactam units in the chains per terminal amino-group, *i.e.*, the average chain length of the polymer, the weight fraction (w_n) of chain length n is given by (Flory, *Chem. Reviews*, 1946, **39**, 174)

$$w_n = (n/q^2)(1 - 1/q)^{n-1}$$

Hence the molar ratio of n -mer to ($n + 1$)-mer is

$$\frac{w_n}{w_{(n+1)}} \cdot \frac{n+1}{n} = \frac{q}{q-1}$$

For large values of q this expression approaches 1, so that for high degrees of polymerization,

$$[6\text{-hexanolactam}] = k_1 q / (q - 1) = k_1, \text{ approx.}$$

i.e., the equilibrium constant k_1 is approximately equal to the mol.-fraction of monomer in the polymer at equilibrium. The mol.-fraction of hexanolactam as monomer is given by [hexanolactam as monomer]/[total hexanolactam], and as the weight of the end groups (H and OH) is small, it may be neglected; k_1 is then approximately equal to the weight fraction of monomer in the monomer-polymer mixture at equilibrium.

TABLE 1.

T , °K	k_1	$\log k_1$	$\log k_1$ (from eqn. 1)	T , °K	k_1	$\log k_1$	$\log k_1$ (from eqn. 1)
553	0.15	-0.824	-0.824	493	0.10	-1.00	-1.00
523	0.125	-0.903	-0.904	433	0.03 (0.06)	-1.523	-1.224

In Table 1 are given the weight fractions of monomer in equilibrium with polymer at four different temperatures (B.I.O.S., 1472, 14).

It can be seen that the first three points lie on a straight line, given by the equation

$$\log k_1 = 0.624 - 800/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The fourth point lies off this line. As it takes about two months to reach the monomer-polymer equilibrium at this temperature, 160° c, it is possible that equilibrium was not

in fact obtained. The calculated value for k_1 at this temperature is 0.06. The approximate value for ΔH , the heat of reaction, in the temperature range 493—553° K is —3560 cal. mole⁻¹, and the entropy ΔS is —2.85 cal. mole⁻¹ deg.⁻¹.

For a reaction which merely involves the rearrangement of the amide bonds, and does not involve any significant change in the number of bonds or their type, the value of —3560 cal. for the heat of reaction may appear surprisingly large. However, if the polymerization of hexanolactam is catalyzed by alkali so that it takes place rapidly, the temperature may rise as much as 30°. The molecular weight of hexanolactam being taken as 113, and a specific heat of 0.5 being assumed, this indicates a heat of reaction of not less than 1700 cal. per mole to produce the observed temperature rise. A value of 3560 is therefore quite possible. It would appear that in hexanolactam the ring system is slightly strained, and that during polymerization the strain energy is released, the polymer being strainless.

Eqn. (1) gives the proportions of hexanolactam as monomer and polymer, but conveys no information as to the degree of polymerization of the polymer. It is possible for the monomer to be in equilibrium with a few long chains, or many short ones. The number of end groups, CO₂H and NH₂, is determined by the reaction $\text{H}_2\text{O} + \text{—CO}\cdot\text{NH—} \rightleftharpoons \text{—CO}_2\text{H} + \text{—NH}_2$, *i.e.*,

$$\frac{[\text{H}_2\text{O}][\text{—CO}\cdot\text{NH—}]}{[\text{—CO}_2\text{H}][\text{—NH}_2]} = k_2.$$

The activity of water in the system may be defined by the partial pressure of water vapour, $P_{\text{H}_2\text{O}}$.

The mol.-fraction of polymer in an equilibrium mixture of monomer and polymer is given by $(1 - k_1)$, and if the average chain length of the polymer is n , $[\text{—CO}_2\text{H}] = [\text{—NH}_2] = (1 - k_1)/n$. The mol.-fraction of amide groups is $1 - (1 - k_1)/n = (n + k_1 - 1)/n$, whence

$$k_2 = \frac{[P_{\text{H}_2\text{O}}] \cdot n(n + k_1 - 1)}{(1 - k_1)^2}$$

Since k_1 is less than 1, and small compared with n ,

$$k_2 = [P_{\text{H}_2\text{O}}] (n - \frac{1}{2})^2 / (1 - k_1)^2 \quad \dots \quad (2)$$

In Table 2 are given data for the temperature, pressure, and degree of polymerization of hexanolactam (B.I.O.S., 1472, 15). In applying eqn. (2) to the data it will be assumed

TABLE 2.

	$T, ^\circ\text{K}$	$P_{\text{H}_2\text{O}}$	n	k_1	$\log k_2$	$10^3/T$	$\log k_2$ (from eqn. 3)
(1)	541	1.00	180	0.140	4.639	1.848	4.76
(2)	532	0.803	210	0.132	4.672	1.879	4.68
(3)	524	0.645	225	0.125	4.628	1.908	4.61
(4)	513	0.500	220	0.116	4.489	1.949	4.51
(5)	503	0.368	230	0.108	4.387	1.988	4.41
(6)	497	0.283	260	0.103	4.375	2.012	4.35
(7)	480	0.178	500	0.091	4.729	2.084	4.17

that the whole of the vapour pressure is due to water vapour. Col. 4 gives the value of k_1 at the given temperature, calculated from eqn. (1), and col. 5 the value of $\log k_2$ calculated by means of eqn. (2).

When $\log k_2$ is plotted against $1/T$, the points (except the first and last) lie approximately on a straight line, given by the equation

$$\log k_2 = 9.42 - 2520/T \quad \dots \quad (3)$$

For the first reading to lie on this curve, the value of n would have to be 207, and for the last point to fit, n would have to be 263. By almost any test these two points are not consistent with the other five.

From eqn. (3) the heat of reaction is approximately —11,500 cal. per mole, and the change in entropy —43 cal. mole⁻¹ deg.⁻¹. This is for the reaction with water vapour; to obtain the heat of reaction and change in entropy for the reaction with liquid water, it is necessary to deduct the latent heat and entropy of evaporation of water from these figures. At 250°, these are 7370 and 14.1 cal., respectively, so the value for ΔH

for the reaction with liquid water is about -4000 cal. per mole and ΔS is about -29 cal. mole $^{-1}$ deg. $^{-1}$.

If a solution of hexanolactam in water is heated to 250° , polymerization takes place, and the solution separates into two phases, one consisting of lactam in water, the other of lactam in polymer, with possibly some water. Since the polymer is in equilibrium with hexanolactam, the system is one of two components, lactam and water, with two liquid phases and a vapour phase. It will therefore have only one degree of freedom, and the composition of the polymer phase, including the chain length of the polymer, will be a function of the temperature, but will be independent of the amount of water present, so long as there are two liquid phases.

The chain length of the polymer at any temperature can be calculated from eqn. (2), by inserting the appropriate values of k_1 and k_2 , calculated from eqns. (1) and (3), and putting for P_{H_2O} the pressure of steam over pure water at that temperature. Strictly, the fugacity of steam over the system should be used, but the data required to calculate this are not available. The use of the pressure as the best approximation appears reasonable. In Table 3 the values for k_1 , $\log k_2$, and n are calculated for the range $220-280^\circ$.

TABLE 3.

$T, ^\circ\text{C}$	$T, ^\circ\text{K}$	P_{H_2O}	k_1	$\log k_2$	n	$T, ^\circ\text{C}$	$T, ^\circ\text{K}$	P_{H_2O}	k_1	$\log k_2$	n
280	553	63.4	0.15	4.86	29.2	240	513	33.0	0.116	4.51	28.2
260	533	46.3	0.132	4.69	28.7	220	493	22.9	0.10	4.31	27.4

It will be seen that in the presence of an aqueous phase the degree of polymerization is low, and does not alter very rapidly with temperature. The same equilibrium should be obtained on heating an aqueous solution of 6-aminohexanoic acid. It is stated (B.I.O.S., 1472, 18) that when a 60% solution of hexanolactam is heated to 250° , a polymer separates rapidly, having an average chain length of 10. From Table 3 the equilibrium value should be 28, but it is possible that in the process reported equilibrium was not attained.

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DEPT. OF TEXTILE INDUSTRIES, THE UNIVERSITY, LEEDS.

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