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The Capacity of Lactams for Polymerisation as a Function of Their Structure

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The capacity of lactams of different structures for polymerisation is considered from thermodynamic and kinetic standpoints. It is shown that the significant differences between the enthalpies of polymerisation can be accounted for by the presence of intramolecular hydrogen bonds and also by the resonance stabilisation of the cyclic amide. The probability of the polymerisation of lactams is determined kinetically by the chemical structure of the monomer, namely the conformation of the molecules (the presence of *cis*- and *trans*-isomers), the stabilisation of the amide group by the inductive, mesomeric, and hyperconjugation effects, the polarity of the molecules (the presence of hydrogen bonds or the occurrence of dipole-dipole interactions), and the basicity of the monomer.
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I. INTRODUCTION

Synthetic heterochain polyamides constitute a class of macromolecular compounds comprising an enormous number of examples and having considerable theoretical and practical importance[1]. Together with the polycondensation reaction, the polymerisation of lactams (cyclic amides) is very important for the synthesis of polyamides. During the last decade, considerable advances have been made in the field of the polymerisation and synthesis of lactams: new methods for their polymerisation have been developed and the range of lactams used to synthesise industrial polyamides (β-lactams, α-pyrrolidinone, α-piperidinone, and ω-dodecalactam) has been extended.

The anionic polymerisation of lactams, on the basis of which a procedure has been developed for the synthesis of polyamide articles by chemical moulding[2,3], which is a great achievement in the synthesis and processing of polymers, has developed particularly in recent years. The use of the ionic polymerisation of lactams made it possible to extend the scope of the synthesis of polyamides having different structures. The method has been used to synthesise both homopolyamides (with linear, branched, and cross-linked structures[4-8]) and copolymers (statistical[9-12], block[13,14], and graft[15-19]), the properties of which vary within wide limits as a function of their structure and the initial monomers.

In connection with the expansion of the range of lactams used to synthesise various types of polyamides, the problem of the dependence of their reactivity on structure has become important. Extensive experimental data have accumulated in the literature on the reactivity of lactams, treated from both thermodynamic and kinetic standpoints, and a number of reviews have been published on the mechanism and kinetics of polymerisation in the presence of various catalytic systems[20-23]. However, the problem of the extent to which the differences between the reactivities of lactams are a consequence of thermodynamic factors and to what extent they are determined by the kinetic conditions arising during these reactions still cannot be regarded as solved.

Examination of the general characteristics of the polymerisation of cyclic amides containing different numbers of units in the ring from thermodynamic and kinetic standpoints is the subject of the present review.

II. THERMODYNAMIC APPROACH

The thermodynamics of polymerisation is known to be determined solely by the propagation stage, since the initiation and chain-termination stage are single steps, while the chain propagation stage involves a large number of addition reactions. The sharp differences in the behaviour of different lactams can probably be accounted for primarily by the sign and magnitude of the free energies of polymerisation:

$$\Delta G = \Delta H - T\Delta S = \Delta G^{\circ} + RT \ln K,$$

where ΔH is the change in the heat content of the system or the heat of reaction, ΔS the change in the entropy of the system, T the absolute temperature, K the equilibrium constant of the reaction, and ΔG° the standard change in free energy on polymerisation referred to the pure monomer and the polymer. If $\Delta G < 0$ for polymerisation, i.e. the free energy of the system decreases, the process is thermodynamically feasible.

The enthalpy of polymerisation of cyclic compounds is associated with the strain of their rings, which depends on the distortion of the valence angles and the interaction of atoms within the ring; the enthalpy depends both on ring size and the presence of substituents. For cyclic amides, ΔH can depend also on (1) the different resonance stabilisations of the monomer and polymer owing to the unequal conjugation or hyperconjugation and (2) the differences between the energies of hydrogen bonds or dipole–dipole interactions in the monomer and polymer.

The entropy of polymerisation depends on the probability of the existence of the monomer in the cyclic form or in the form of the elementary unit of the linear polymer.

1. ΔH for the Polymerisation of Lactams

The first attempt at a thermodynamic treatment of the reversible ring ⇌ polymer reaction was made in 1950 by Strepikheev[24], who outlined a correct and rigorous procedure for the thermodynamic treatment of the problem of the polymerisation of cyclic compounds. A similar treatment of the thermodynamic stability of cyclic compounds was achieved independently in 1955 by Dainton et al.[25] in connection with the estimation of the free energy of the system. The values of ΔH for the hypothetical polymerisation reaction of cycloalkanes were found as the differences between the heats of formation of the polymer units (these heats were calculated from the contributions of the corresponding groups to the heat of formation) and the experimental heats of formation of cycloalkanes.

The heat of polymerisation can be found in different ways.

1. By direct calorimetric measurements on the polymerisation reaction, which make it possible to determine ΔH. However, the polymerisation process hinders calorimetric measurements, which naturally affects the accuracy of the determination.

2. By calculating ΔH from a comparison of the heats of combustion of the monomer and polymer. The latter quantity is calculated per polymer unit. The accuracy of this method is also low, since a small value of ΔH is calculated from [the difference between] large quantities.

3. By determining the difference between the experimental heats of combustion of the lactams and the heats of combustion calculated additively from the increments for the corresponding groups: 155.85 kcal mole^{-1} for CH_2(liq.), 79.4 kcal mole^{-1} for CONH(liq.), 156.3 kcal mole^{-1} for CH_2(solid), and 77.2 kcal mole^{-1} for CONH(solid).

Table 1. Heats of combustion and ring strain in cycloalkanes[26].

No. of ring units n	Heat of combustion per methylene group, kcal mole^{-1}	Ring strain* per methylene group, kcal mole^{-1}	No. of ring units n	Heat of combustion per methylene group, kcal mole^{-1}	Ring strain* per methylene group, kcal mole^{-1}
3	166.6	9.2	9	158.8	1.4
4	164.0	6.6	10	158.6	1.2
5	158.7	1.3	11	158.4	1.0
6	157.4	0.0	12	157.7	0.3
7	158.3	0.9	13	157.8	0.4
8	158.6	1.2	n-alkane	157.4	0.0

* Ring strain is defined as the difference between the heats of combustion per methylene group of the given cycloalkane and the [corresponding?] n-alkane (157.4 kcal mole^{-1}).

We shall consider initially the thermodynamic stability of cycloalkanes. Comparison of the heats of combustion per methylene group in such cyclic compounds and linear alkanes yields a general estimate of a thermodynamic stability of rings of different size.[26] Table 1 shows that the differences between the heats of combustion of cycloalkanes and n-alkanes per methylene group demonstrate a decrease of thermodynamic stability with increase in ring strain. The strain in three- and four-membered rings is very high, diminishing subsequently on passing to five-, six-, and seven-membered rings, after which it again increases for eight to eleven-membered rings, and finally falls once more on passing to rings of still greater size.

Two components of ring strain are distinguished: angular strain and repulsion due to the presence of substituents. Rings containing less than five atoms are highly strained through high angular strain, i.e. the considerable distortion of their valence angles compared with the normal tetrahedral angle. In five-membered and larger rings, there is no distortion of the valence angle, since the rings can exist in a non-planar form. In rings with more than eight units, the strain due to the distortion of the valence angle is virtually absent, but they are nevertheless thermodynamically unstable, because the hydrogen atoms or other substituents are contained within the ring at distances such that they repel one another. On this basis, it is possible to set up the following sequence of cycloalkanes as a function of ring size in order of increasing thermodynamic stability:

$$3,4 < 8-11 < 7,12,13 < 5 < 6.$$

Rings containing certain other atoms or groups of atoms instead of methylene groups fall in the same sequence. Although the data for cyclic compounds such as ethers, lactones, and lactams are inadequate, the general postulates have been confirmed[27]. Thus Small[28] attempted to extend Dainton's calculations[25] for cycloalkanes to certain series of saturated heterocyclic compounds (cyclic ethers and imines). He showed that the difference between the values of ΔS for the polymerisation reactions of cycloalkanes and the corresponding cyclic ethers and imines is small. The ΔH for the polymerisation reaction show greater differences.

Hall and Schneider[29] confirmed the validity of Dainton's[25] and Small's[28] findings and reached the following conclusions concerning the capacity of various heterocyclic compounds for polymerisation on the basis of their own experimental data.

1. Four-, seven-, and eight-membered cyclic compounds polymerise most readily; the capacity of five- and six-membered carbonyl monomers for polymerisation depends on the class of compound.

2. Substitution of cyclic hydrocarbons by a heteroatom has an insignificant influence on their capacity for polymerisation.

3. Substituents (alkyl or aryl) always decrease the capacity of cyclic compounds for polymerisation.

Other workers[30] also established that the substitution of a CH_2 group by O or NH causes little alteration in the capacity of cyclic compounds for polymerisation. In this case, substitution has hardly any influence on the valence angles in cyclic structures. The ring strain caused by the repulsion of substituents diminishes when the methylene group is replaced by the less bulky carbonyl group or an oxygen atom, which leads to an increase of the thermodynamic stability of the ring. It has also been shown[27] that, in contrast to hydrogen, other substituents in cyclic structures as a rule increase their stability, although the cause of this is not altogether clear.

We shall now consider the variation of the heats of polymerisation of lactams with different numbers of units in the ring. Skuratov and Strepikheev and coworkers[31-38, 43-45] have played a leading role in the study of this problem. Table 2 presents the values of ΔH for the polymerisation of lactams containing between 5 and 13 units in the ring and obtained in different ways. Column A lists the ΔH for the polymerisation of lactams measured experimentally with the aid of a double calorimeter using a

compensation technique; column *B* lists the ΔH estimated by another procedure—by comparing the experimental heats of combustion of lactams and the corresponding polymers: the ΔH calculated from the enthalpies of cyclisation of different lactams are given in column *C*.

Table 2. Heats of polymerisation of lactams.

Lactam	No. of ring units *n*	ΔH, kcal mole^{-1} *A*	Refs.	ΔH, kcal mole^{-1} *B*	Refs.	ΔH, kcal mole^{-1} *C*	Refs.
α-Pyrrolidinone	5	—	—	+1.3	32,33	−1.1	33
				−1.3	41,42		
α-Piperidinone	6	—	—	−1.1	32,33	−2.2	33
ε-Caprolactam	7	−3.3	34	−3.0	32,33	−3.8	33
		−3.5	39		38,39		
ξ-Oenantholactam	8	−5.2	35	−5.7	32,33,38,42	−5.3	33
η-Caprylolactam	9	−7.8	33	−9.6	38,42	—	—
Pelargolactam	10	—	—	—	—	−5.5	38
Decanolactam	11	—	—	—	—	−2.8	38
Undecanolactam	12	—	—	—	—	+0.5	38
Laurolactam	13	~0	33,38	−1.5	41,42	—	—

It was to be expected that the ΔH for the polymerisation of lactams estimated in different ways should be different, depending on the temperature and the phase state of the monomers and polymers to which they refer. However, Table 2 shows that the values of ΔH are similar. Therefore, in order to calculate ΔH for polymerisation, it is quite admissible to adopt the average of these values (Fig. 1). The ΔH for the polymerisation of lactams have been calculated in this way[38]. Fig. 1 shows that ΔH for the polymerisation of lactams containing between 5 and 9 units in the ring decreases and then rises for lactams containing between 9 and 13 units in the ring to values close to zero.

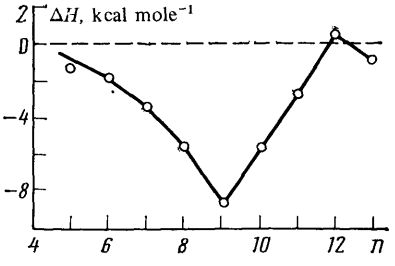
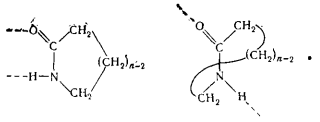


Figure 1. The heats of polymerisation of lactams (ΔH) as a function of the number of units in the ring (n).

Comparison of the heats of polymerisation of lactams and the corresponding cycloalkanes shows that the enthalpies of lactam ring formation are smaller than the values for their hydrocarbon analogues (Table 3).

Some workers believe[46-50] that such a significant difference between the enthalpies of polymerisation of lactams and cycloalkanes can be accounted for by the presence of intermolecular hydrogen bonds in the lactams†. A comparative study of the free and associated NH groups by infrared spectroscopy led to conclusions about the isomerism and conformations of the rings of the test compounds:



cis-conformation *trans*-conformation

Table 3. Comparison of the enthalpies of polymerisation of cycloalkanes and cyclic amides.

No. of ring units *n*	ΔH, kcal mole^{-1} cycloalkane (Ref.25)	lactam (Ref.33)
5	5.2	1.1
7	5.2	3.8
8	8.3	5.3

The energy of formation of intermolecular hydrogen bonds is expressed in terms of quantities of the same order of magnitude as the heat of ring opening and can vary within wide limits depending on the structure of the lactam (Table 4). Table 4 shows that α-pyrrolidinone exists exclusively in the form of the *cis*-isomers. Lactams containing between 6 and 9 units in the ring exist in both *cis*- and *trans*-forms, while (10–13)-membered lactams exist in the thermodynamically more stable ($\Delta H_{av} = -4.0$ kcal mole^{-1}) isomeric *trans*-form.

Table 4. Thermodynamic characteristics of the hydrogen bonds in lactams[47].

No. of ring units *n*	$-\Delta H$, kcal mole^{-1} *cis*-	*trans*-
5	8.35	—
6	7.30	3.90
7	7.10	4.20
8	6.95	3.70
9	7.05	5.05
10	—	3.82
11	—	3.82
12	—	3.80
13	—	3.75
	mean 7.35	mean 4.00

According to Ogata's data[50], the *cis*-form is characteristic of (6–7)-membered lactams, ζ-oenantholactam contains equivalent amounts of the *cis*- and *trans*-isomers, and the nine-membered lactam exists preferentially in the *trans*-form. On the basis of Ogata's data, one can calculate, subject to a major assumption and without allowance

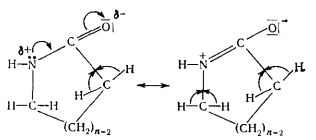
† The intermolecular interaction in the polymer does not play an appreciable role owing to steric factors[27].

for resonance stabilisation, the maximum degree of association of lactam molecules. If it assumed arbitrarily that ΔH for cyclo-octane is approximately equal to ΔH_{tot} for ζ-oenantholactam, then the degree of association of the molecules x can be found as follows:

$$\Delta H_{\text{cyclo-octane}} \simeq \Delta H_{\zeta\text{-oenantholactam}} + \frac{x}{2}(\Delta H_{cis.} + \Delta H_{trans.});$$

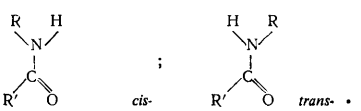
$x = 56.3\%$. We believe that this value is very much too high.

Thus the reduced enthalpy of polymerisation of lactam rings compared with the hydrocarbon analogues cannot be fully accounted for by the energy of formation of intermolecular hydrogen bonds in lactam molecules. Evidently the lower isothermal heat of polymerisation (negative ΔH) of lactams compared with the corresponding [hydrocarbon] ring is also associated with the resonance stabilisation of the lactam, since resonance is possible only in the monomer[27]:

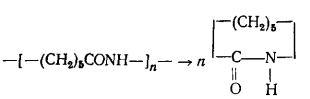


Other workers hold the same view[48-51]. Furthermore, owing to the hyperconjugation of the methylene group with the C=O and C=N bonds, ΔH for the polymerisation of lactams is reduced.

A novel method for the empirical calculation of ΔH for lactams from the change in the number of the so called "*gauche*-interactions" of the butane type on ring closure is discussed by Cubbon[52] in connection with the estimation of the influence of substituents on the polymerisation of lactams. He also believes that, when a seven-membered lactam cyclises, four new *gauche*-interactions occur (two involving CH_2/CH_2 groups, one involving the CH_2/CO group, and one involving the CH_2/NH group). The energy of a single interaction is 0.8 kcal mole^{-1}, so that the total contribution to the enthalpy of cyclisation of ε-caprolactam is 3.2 kcal mole^{-1}. A ^{1}H NMR study of methylacetamide has shown that the *trans*-form of the amide group is more stable than the *cis*-form at least to the extent of 1.4 kcal mole^{-1}.[52]



On the other hand, the overall enthalpy of the reaction



is approximately 4.6 kcal mole^{-1}. We believe that this value is not altogether correct, since it is difficult to accept that ε-caprolactam exists exclusively in the *cis*-form (see above).

2. Estimation of ΔS for the Polymerisation of Lactams (under Standard Conditions)

One of the methods for the calculation of ΔS is based on the determination of the equilibrium constant within the limits of a certain temperature range. However, this method cannot be always applied, because it is difficult to measure the quantity

$$K = \frac{[M_{n+1}^-]}{[M_n^-][M]} .$$

Owing to the presence of a range of molecular weights, the number of terms (n) varies within wide limits.

The method for the determination of the entropy of polymerisation by means of the formula

$$\Delta S^0 = \Delta H^0 / T_{\lim} .$$

is promising. The scope of this method is limited only by the accuracy of the measurement of the heat of polymerisation and of the limiting temperature ($T_{\lim}$).

Another, perhaps the most widely used method of calculation is based on the knowledge of the entropies of the monomer and polymer:

$$\Delta S^0 = \frac{1}{n} \cdot S^0_{(n)} - S^0_{(1)} ,$$

where $S^\circ_{(n)}$(polymers) and $S^\circ_{(1)}$(monomers) are calculated from the experimental true heat capacities of these substances at low temperatures.

There exists a method for the calculation of ΔS° using the relation

$$\Delta S^0 = R \ln \frac{k_p}{k_{p^1}} ,$$

which follows directly from the expressions for the propagation (k_p) and depolymerisation (k_{p^1}) rate constants.

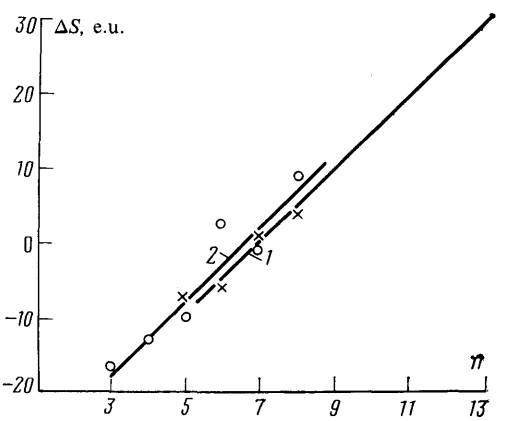


Figure 2. Variation of ΔS for the polymerisation of lactams and cycloalkanes as a function of the number of units in the ring under standard conditions: 1) lactams[38]; 2) cycloalkanes[25].

ΔS can also be obtained by a statistical procedure. In this case one uses the relation according to which the overall entropy of reaction consists of ΔS_{trans}, ΔS_{rot}, and ΔS_{vibr}.

There are very few literature data for the entropies of lactams with different numbers of units in the ring and the corresponding polymers, while for (9–13)-membered lactams there are no data at all.

Skuratov[32,38,44,45], who carried out the most systematic studies on this problem, estimated the entropies of polymerisation of five-, six-, seven-, and eight-membered cyclic amides. The ΔS were calculated from the absolute entropies $S_{298.16}$ and the true heat capacities of these substances in the temperature range 62–328 K. The values of ΔS for (9–13)-membered lactams were found[38] by the linear extrapolation of the values for (5–8)-membered lactams (Fig. 2) in view of the fact that the ΔS obtained for the polymerisation of (5–8)-membered lactams fit satisfactorily on a straight line. These results are naturally extremely approximate.

It is noteworthy that the ΔS for the hypothétical polymerisation of cycloalkanes containing between 3 and 8 units in the ring (except cyclohexane) also vary linearly with the number of such units (Fig. 2, curve *2*).

3. Estimation of ΔG for the Polymerisation of Lactams (under Standard Conditions)

The free energies of polymerisation ΔG of lactams containing between 5 and 13 ring units are presented in Table 5. Evidently ΔG for the polymerisation reaction varies from a positive value (for the five-membered ring) and a value close to zero (for a six-membered lactam) to negative values, which reach a maximum for (9–10)-membered lactams, and then falls somewhat. The polymerisation of α-pyrrolidinone and α-piperidinone is exothermic (negative ΔH) and exoentropic (negative ΔS). The negative ΔS for the polymerisation of five- and six-membered lactams is probably due to the fact that the number of degrees of freedom diminishes on passing from the monomer to the polymer. Consequently the polymerisation of five- and six-membered lactams is favourable from the standpoint of the enthalpy factor but not on entropy grounds. For seven- and eight-membered lactams, the main contribution to ΔG for the polymerisation reaction comes from the enthalpy term, for nine-, ten-, and eleven-membered lactams the contributions of ΔH and ΔS are approximately the same, while for twelve- and thirteen-membered cyclic amides ΔH for the polymerisation reaction is negligible and the polymerisation proceeds mainly as a result of the entropy change.

Table 5. Free energies of polymerisation ΔG of lactams with different numbers of ring units.

No. of ring units n	ΔH*, kcal mole^{-1}	ΔS*	$T\cdot\Delta S_{298.16}$, kcal mole^{-1}	ΔG, kcal mole^{-1}
5	−1.1	−7.3	−2.2	1.1
6	−1.7	−6.0	−1.8	0.1
7	−3.3	1.1	0.3	−3.6
8	−5.4	4.0	1.2	−6.6
9	−8.4	10.0	3.0	−11.4
10	−5.6	15.0	4.5	−10.1
11	−2.8	20.0	6.0	−8.8
12	0.5	25.0	7.5	−7.0
13	−0.7	30.0	9.0	−9.7

*The average values of ΔH obtained from the results of different workers are quoted (see Table 2).

Fig. 3 presents the values of ΔG for the polymerisation of lactams and cycloalkanes[25] as a function of the number of ring units. It is seen that the variation of ΔG for the polymerisation of lactams and cycloalkanes is very similar. The values of ΔG for five- and six-membered rings are close to zero, becoming negative for larger rings. Using the equation

$$\ln[M]_c = \frac{\Delta H^0}{R\,T_{lim}} - \frac{\Delta S^0}{R},$$

expressing the dependence of the equilibrium (critical) concentration of the monomer $[M]_c$ on the limiting polymerisation temperature[27], we calculated the critical monomer concentrations at 25°C (Table 6); the limiting temperatures for six- and seven-membered lactams are also quoted.

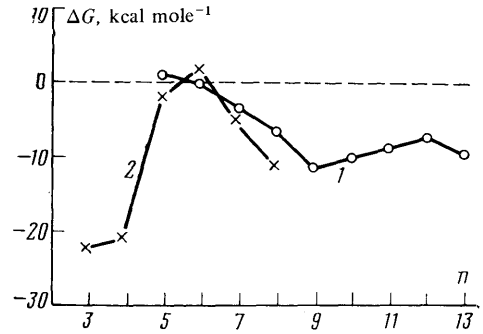


Figure 3. Variation of ΔG for the polymerisation of lactams (curve *1*) and cycloalkanes (curve *2*) as a function of the number of units in the ring (n).

Table 6. The "polymerisation ⇌ depolymerisation" equilibrium.

Lactam	$[M]_c$ at 25°C, M	T_{lim} for pure monomer, °C
α-Pyrrolidinone	6.3	—
α-Piperidinone	1.2	60[53]
ε-Caprolactam	$2.1\cdot10^{-3}$	254[54]
ξ-Oenantholactam	$1.4\cdot10^{-5}$	—
η-Caprylolactam	$4.3\cdot10^{-9}$	—
Pelargolactam	$4.0\cdot10^{-8}$	—
Decanolactam	$3.6\cdot10^{-7}$	—
Undecanolactam	$7.8\cdot10^{-6}$	—
Laurolactam	$8.2\cdot10^{-8}$	

Since ΔH° is negative, the concentration of the monomer in equilibrium with the polymer increases with temperature and the relation between $\ln[M]_c$ and $1/T$ is represented by a straight line with a negative slope (slope = $\Delta H^\circ/R$) making an intercept on the ordinate axis equal to $\Delta S^\circ/R$ (Fig. 4). The data presented in Table 6 and in Fig. 4 indicate high critical concentrations in the "polymerisation ⇌ depolymerisation" equilibrium for five- and six-membered lactams, which ultimately determines the comparatively low equilibrium degree of polymerisation of the lactams.

Thus one may conclude that the polymerisation of (7–13)-membered lactams is thermodynamically feasible (ΔG is negative). The small positive values of ΔG for the polymerisation of α-pyrrolidinone and α-piperidinone and

the extremely large errors of the determination of the thermodynamic characteristics preclude a conclusion concerning the thermodynamic feasibility of the polymerisation of five- and six-membered cyclic amides.

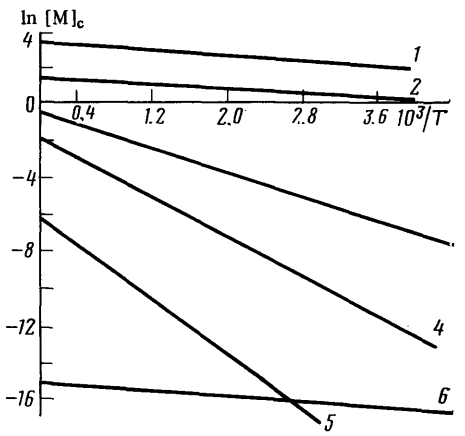


Figure 4. Variation of $\ln [M]_c$ with $1/T$ in the polymerisation of lactams with different numbers of units in the ring: 1) α-pyrrolidinone; 2) α-piperidinone; 3) ϵ-caprolactam; 4) ζ-oenantholactam; 5) η-caprylolactam; 6) laurolactam.

Taking into account the thermodynamic factors only, it is possible to set up a series based on the reactivities of the lactams as a function of ring size:

$$9 > 10 > 13 > 11 > 12 > 8 > 7 \geqslant 6,5.$$

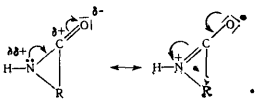
III. KINETIC APPROACH

The negative value of ΔG does not, however, imply that polymerisation is possible under any conditions. The probability of achieving thermodynamically allowed polymerisation depends on its being allowed by kinetic factors, i.e. on whether or not the given process occurs at an appreciable rate under the chosen reaction conditions. The kinetic capacity of monomers for polymerisation is determined by the mobility of the corresponding bonds under the reaction conditions, since thermodynamically unstable compounds can be kinetically quite stable and may not polymerise if they do not contain a labile bond.

One may quote as an example cycloalkanes for which it has been as yet impossible to find polymerisation conditions despite their considerable thermodynamic instability [25,55].

1. The Chemical Structure of the Monomer

Heterocyclic compounds to which lactams belong are capable of selective ring opening at the site of the heterobond. However, this fact is not related to the lower energetic stability of the heterobond compared with the C–C bond (the energy of the C–C bond is 63 kcal mole^{-1}, that of the C–N bond 66 kcal mole^{-1}, and that of the C–O bond 79 kcal mole^{-1}), but is associated with its susceptibility to polarisation under the influence of various chemical agents. The polarisability of the lactam ring can be represented schematically as follows:



The electron-accepting carbonyl group causes a shift of electron density (the $-M$ effect; the inductive effect of the N–H bond may be neglected), as a result of which the amide group is polarised. The possibility of the hyperconjugation effect in the lactam molecule was discussed above.

The presence of the resonance effect in the amide group has been demonstrated by Pauling and Corey [56], who carried out a very thorough investigation of the NH–CO group by X-ray diffraction. The bond angles and interatomic distances in amides are presented in Fig. 5.

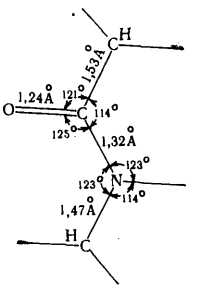
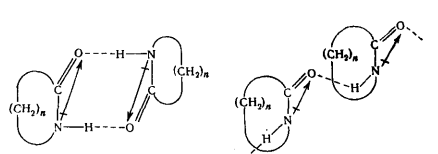


Figure 5. Amide linkages [56].

It is evident from Fig. 5 that the C–N bond length in the amide group is shorter than the normal length of the isolated C–N bond, which is 1.5 Å. This result demonstrates a certain amount of double bond character of this linkage. In this case the NH–CO group is planar and all its valence bonds, illustrated in Fig. 5, lie in the plane of the figure; this in fact permits the existence of the *cis*- and *trans*-forms (see above).

The existence of the *cis*- and *trans*-configurations of lactams can be observed by measuring the dielectric constants of their benzene solutions at variable concentrations. Like the acyclic amides, the *cis*-lactam forms a hydrogen-bonded dimer, in which the two electric moments (arrows in the formula) mutually cancel out.



With increase of concentration, the degree of association of the molecules rises and, in the case of the *cis*-lactam, the dielectric constant falls. On the other hand, the *trans*-lactam can form only a linear associated species in

which the electric moments are additively combined and the dielectric constant of the benzene solution therefore increases with concentration.

The dipole moments of lactams presented in Table 7 show that they depend little on the number of units in the lactam ring, although the dipole moment of the five-membered lactam is somewhat reduced.

Table 7. The dipole moments of lactams[57] (measured in benzene).

No. of ring units n	5	6	7	8	9	10	11	13
Dipole moment, D	3.55	3.83	3.88	3.86	3.85	3.79	3.78	3.78

Here it is appropriate to examine the studies by Ogata[48-50], devoted to the influence of the resonance effect of the amide group on the ability of lactams to polymerise. He investigated the addition of hydrogen chloride to certain cyclic and linear amides by infrared spectroscopy. The constant for the equilibrium between the amide group and HCl was calculated from the equation

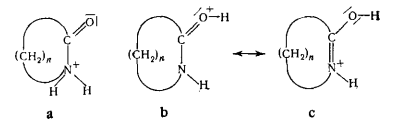
$$K = \frac{[-\overset{+}{N}H_2CO-]}{[-NHCO-]\cdot[H^+]}.$$

Table 8. The equilibrium constants and heats of addition of hydrogen chloride to the amide group[50].

Amide derivative	K			$-\Delta H$, kcal mole^{-1}
	20° C	40° C	55° C	
α-Pyrrolidinone	159	68	—	7.64
α-Piperidinone	164	79	—	6.58
ε-Caprolactam	177	124	91	3.15
ξ-Oenantholactam	107	82	82	1.63
Decanolactam	83	45	45	3.70
N-Methyl-α-piperidinone	49	38	—	2.34
N-Methyl-ε-caprolactam	35	20	12	5.12
NN'-Dibutylacetamide	35	22	—	4.14
N-Hexylacetamide	58	48	—	2.16

The heats of addition of HCl to the amide were calculated from the slope of the curve describing the linear relation between $\ln K$ and the equilibrium values of the absolute temperature. Table 8 lists the average equilibrium constants for the above addition reaction involving several amide compounds. On the basis of the results, the author reaches a conclusion concerning the relative basicities of lactams. He believes[50] that seven- and eight-membered lactams are the most basic. With increase in the size of the lactam ring, its basicity falls, as can be seen from Table 8. The capacity of the five- and six-membered rings for protonation is also lower than that of the seven-membered lactam. In view of the disappearance of the characteristic $\diagdown$N–H absorption frequency and the appearance of a new frequency characteristic of the $\diagdown$NH$_2$ absorption, Ogata concludes that the proton adds to the nitrogen atom of the amide group.

We may note that the protonation of nitrogen (structure a) leads to the disappearance of resonance stabilisation, while the protonation of oxygen does not (structures b and c):



a b c

The system with protonated oxygen should therefore be more stable. Nevertheless many investigators[58,59] share Ogata's view concerning the protonation of nitrogen in the amide group of the lactam.

It was stated above that, according to Ogata[49,50], the eight-membered lactam contains equivalent amounts of the *cis*- and *trans*-forms. On this basis, the author concludes that, if the amounts of the two conformations of the amide group become equal, the resonance effect in this group diminishes with a consequent increase of the capacity of the lactams for polymerisation, which we believe to be unlikely. It was shown above that the resonance effect in the amide group of the lactam plays a certain role in the estimation of the reactivity of cyclic amides, but it is by no means decisive.

Thus the kinetic probability of the polymerisation of lactams is to a large extent determined by the chemical structure of the monomer, namely:

(1) by the conformation of the molecules (the presence of *cis*- and *trans*-isomers);

(2) by the stabilisation of the amide group due to the mesomeric, inductive and hyperconjugation effects;

(3) by the polarity of the molecules (the presence of hydrogen bonds or the occurrence of dipole–dipole interactions);

(4) by the basicity of the monomer.

2. The Capacity of Lactams for Polymerisation as a Function of the Type of Initiation

The type of initiator—a radical, cation, or anion—most suitable in a particular instance depends on the chemical structure of the monomer.

There is no information in the literature about the radical polymerisation of lactams. It has proved possible to polymerise via the cationic mechanism virtually all unsubstituted lactams with the exception of the six-membered compound. The method of ionic high-speed polymerisation of lactams made it possible to extend the range of monomers suitable for the synthesis of polyamides. Thus, α-piperidinone and α-pyrrolidinone, which were previously believed to be incapable of polymerisation[28,60,61], were in fact polymerised in the presence of anionic catalysts[62]. Ney and coworkers[63-65] achieved the anionic polymerisation of these lactams in the presence of *N*-acyl compounds and the sodium salts of the lactams on heating the reaction mixture to a temperature exceeding somewhat the melting point of the monomer, but not higher than 60°C. The introduction of an *N*-acyl compound (activator) in the polymerisation reaction made it possible to increase sharply the yield of the polymer compared with the same conditions but in the absence of the activator. Somewhat later, the polymerisation of α-pyrrolidinone were achieved by Ney in the presence of quaternary ammonium bases[66].

Barnes et al.[63] demonstrated the possibility of the polymerisation of a six-membered lactam (α-piperidinone) using the same reaction conditions as in the polymerisation

of α-pyrrolidinone[65]. However, the polymerisation of α-piperidinone proceeds with much greater difficulty than that of the five-membered lactam. The above studies by Ney and coworkers are of great theoretical importance, since they established that five- and six-membered lactams, previously believed to be stable and incapable of polymerisation, are quite reactive monomers, forming polyamides under relatively mild conditions. Somewhat later, a number of other patent reports were published on the anionic polymerisation of α-pyrrolidinone[67-78] and α-piperidinone[74-78], confirming the ability of these compounds to form high-molecular-weight products.

The method of the anionic polymerisation of five- and six-lactams in the presence of activating *N*-acylamide compounds has been used successfully to polymerise various lactams containing more than six units in the ring: ε-caprolactam, ζ-oenantholactam, η-caprylolactam, and others. The dependence of the capacity of the monomers of polymerisation on the type of initiator is illustrated by the data in Table 9, from which it is clear that, in the presence of such initiators, polymers with a high molecular weight are formed. Although the polymerisation of five- and six-membered lactams is thermodynamically allowed, under these conditions the polymerisation of α-piperidinone is kinetically feasible only in the presence of initiators of a specific type.

Table 9. Examples of the polymerisation of lactams as a function of the type of initiation.

No. of ring units *n*	Monomer	Type of initiation			
		cationic	references	anionic	references
5	α-Pyrrolidinone	+	50	+	85—93
6	α-Piperidinone	—	50	+	85—94
7	ε-Caprolactam	+	50,79—81	+	85—100
8	ζ-Oenantholactam	+	81,82	+	87—102
9	η-Caprylolactam	+	79,81	+	87—102
10	Pelargolactam		—	+	87—102
11	Decanolactam	+	50	+	87—102
12	Undecanolactam		—	+	87—89,91—102
13	Laurolactam	+	83—84	+	87,88,91—102

Table 10. The capacity of lactams for polymerisation as a function of ring size.

Type of initiation	Activity series for rings of different size	References
Acetylating agent	8,7>13≫5.6	53,103
Water	8>7>11≫5.6	50
HCl	7>8≃9≫5.6	85

When the capacities of lactams for polymerisation were compared as a function of ring size, it was shown that eight- and nine-membered lactams exhibit the greatest tendency towards polymerisation, that of seven-membered lactams being somewhat inferior; the capacity of five- and six-membered lactams for polymerisation is much smaller, particularly that of the six-membered lactams (the available data are presented in Table 10).

The lactam reactivity series is close to the series expected on the basis of the measured free energies, although there are differences. Thus, according to Ogata's data[50], the thermodynamically less stable eleven-membered lactam is less reactive in cationic polymerisation than the thermodynamically more stable seven-membered lactam. We believe that the reason for this apparent anomaly may be that at 257° C ε-caprolactam is more reactive than the lactam of capric acid and because of the failure to attain thermodynamic equilibrium for the eleven-membered lactam under the chosen conditions, so that Ogata's data[50] correspond to the polymerisation kinetics under the chosen process conditions only. With increase of reaction temperature, the relative rates of polymerisation of the lactams would probably become equalised and it should be possible to select polymerisation conditions such that the thermodynamically less stable lactam becomes more reactive than the thermodynamically more stable lactam also from the kinetic standpoint.

It is interesting to note that five- and six-membered lactams are much more reactive under the conditions of anionic polymerisation than under the conditions of the polymerisation initiated by hydrochloric acid or water. This can be explained from the standpoint of the different mechanisms under these conditions (Fig. 6). In anionic polymerisation, the lactam ring is activated by the nucleophile. In polymerisation under the influence of water or acids, there is electrophilic attack on the lactam ring. Owing to the low electron density in the amide group, this reaction does not proceed as readily as in the presence of a nucleophile. As a result, anionic polymerisation is faster and less selective than the other two reactions.

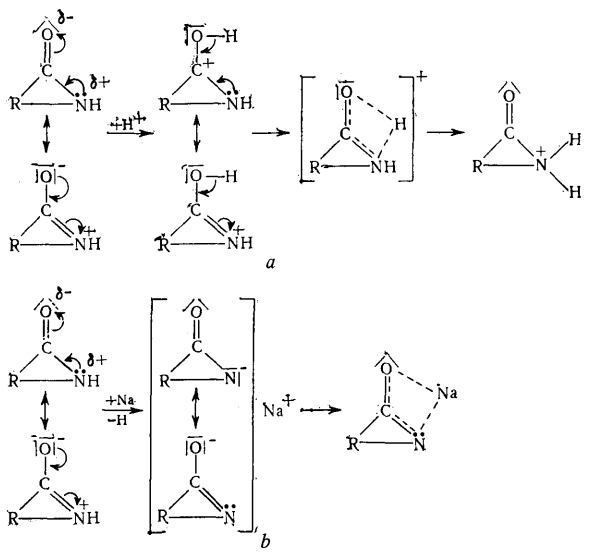


Figure 6. The mechanism of the initiation of the cationic (*a*) and anionic (*b*) polymerisation of lactams.

Lactams incapable of polymerisation in the presence of water or acids, are readily polymerised via the anionic mechanism. These differences in reactivities are also manifested when the temperatures required for polymerisation are compared. Thus polymerisation initiated by

water or acid usually requires temperatures of the order of 250°C, as in other instances of cationic polymerisation. Anionic polymerisation takes place at much lower temperatures.

IV. THE INFLUENCE OF SUBSTITUENTS ON THE REACTIVITY OF LACTAMS

There are many data concerning the influence of substituents on the reactivity of lactams, which has proved to be lower than that of unsubstituted cyclic amides[104-111]. Dainton and coworkers[25,28] demonstrated by semi-empirical calculations of the free energies of the hypothetical polymerisation reactions of cycloalkanes that substitution always decreases the reactivity (Fig. 7).

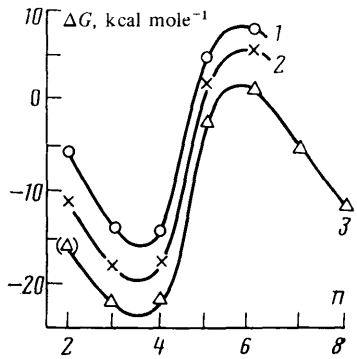


Figure 7. Variation of the free energy of polymerisation of cycloalkanes under standard conditions with ring size (n): 1) 1,1-dimethyl derivatives of cycloalkanes; 2) methyl derivatives of cycloalkanes; 3) unsubstituted cycloalkanes.

The calculations showed that the substituent in the cycloalkane ring influences the enthalpy and entropy of polymerisation of the compound with the given ring size[25,28]. The authors assumed that the results of the calculations will be valid, at least qualitatively, for the polymerisation of heterocyclic compounds, which was subsequently confirmed on the basis of extensive experimental data (Table 11).

It is seen from the Table that the influence of substituents on the capacity of lactams for polymerisation is extremely varied and depends both on the size of the substituent, its position in the ring, and the number of substituents, on the one hand, and on the size of the lactam ring, on the other.

1. C-Substituted Lactams

Five- and six-membered rings. Substituents are known[119] to facilitate ring closure, thereby displacing the monomer ⇌ polymer reaction equilibrium towards the monomer. Five- and six-membered lactams lose their capacity for polymerisation even in the presence of only one alkyl substituent at the carbon atom (Table 11).

The study of the cyclisation of 4-bromobutylamines has shown that substituents can greatly increase the rate of formation of the five-membered ring[120]. The estimation of the influence of the thermodynamic characteristics on the capacity of substituted lactams for polymerisation is at present difficult, since the entropies of polymerisation of these lactams are not available. According to Cubbon[52], a substituent in the lactam ring causes only a slight alteration of the entropy compared with the unsubstituted lactam, but greatly increases the entropy of cyclisation of the lactam and to a greater extent the more bulky the substituent.

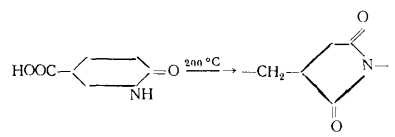
Table 11. Heats of polymerisation and the capacities for polymerisation of substituted lactams.

No. of ring units n	Lactam*	$-\Delta H$, kcal mole^{-1}	References	Capacity for polymerisation	Initiator	References
5	α-pyrrolidinone	1.3	32	+	water, alkali	50,103,113
	1-methyl	0.8	112	—	alkali	113
	5-methyl-	—	—	—	water, alkali	113
	4-carboxy-	—	—	+	–	114
	N-methyl-	0 8	33,112	—	water, acid, alkali	33,52
6	α-Piperidinone	1.1	32	+	alkali	52,53,103
	1-methyl-	—	—	—	alkali	113
	N-methyl-	—0.5	33,112	—	alkali	113
7	ε-Caprolactam	3.3	38	+	water, acid, alkali	50,79,103
	1-methyl-	2.3	112	+	water, alkali	112,113
	5-methyl-	3.8	33	+	6,6 salt**	52
	7-methyl-	3.8	33	+	6,6 salt**	52
	7-ethyl-	4.5	115	+	water, acid	115
	7-propyl-	3.4	115	+	water, acid	115
	5-n-heptyl-	—	—	—	6,6 salt**, water	116
	5-phenyl-	—	—	—	water	113
	1,1-dimethyl-	4.8	117	+	water, alkali	117
	N-methyl-	2.3	33,112	—	water, alkali	48,123
8	ξ-Oenantholactam	5.4	38	+	water, alkali	52,85
	1-methyl-	3.9	33,112	+	water, alkali	52,113
	8-ethyl-	6.8	115	+	water, acid	115
	8-propyl-	4.9	115	+	water, acid	115
	N-methyl-	3 9	33,112	+	water	52,123
9	η-Caprylolactam	7.8	34	+	water, acid, alkali	34,79,118
	N-methyl-	—	—	+	water, alkali	118
	N-n-butyl-	—	—	+	water, alkali	118
13	Laurolactam	1.5	41,42	+	water, acid, alkali	42,118
	N-methyl-	—	—	+	water, alkali	118
	N-n-butyl-	—	—	+	water, alkali	118

* The authors begin the numbering of the ring positions from the heteroatom.
** The 6,6 salt is hexamethylenediammonium adipate.

Thus one may conclude that the entropy and enthalpy effects of the substituent make the free energy of cyclisation of the lactam more negative compared with the unsubstituted analogue, as a result of which the equilibrium is displaced towards the cyclic compound.

The ready conversion of 4-carboxy-α-pyrrolidinone into a polyamide on heating above the melting point of the monomer, described by Klein and Reimschuessel[114], constitutes an appreciable deviation from the usual behaviour of substituted cyclic carbonyl monomers:



Such capacity for polymerisation can in all probability be accounted for by the reactivity of the substituent in the lactam, the latter isomerising to a cyclic imide on heating.

Seven- and eight-membered rings. While the heats of polymerisation of *C*-substituted five- and six-membered lactams are lower than those of the corresponding unsubstituted analogues, ΔH for substituted seven- and eight-membered lactams may be both greater and smaller than the enthalpies for the corresponding unsubstituted cyclic amides. Since the entropies of polymerisation of the above compounds are not available, one can only suppose that in this instance the thermodynamic characteristics of the substituent promote the cyclisation reaction, displacing the polymer $\rightleftharpoons$ monomer equilibrium towards the monomer. This is confirmed by the concentrations found in the polymerisation of substituted lactams with seven- and eight-membered rings (Table 12).

Table 12. The equilibrium concentrations of the monomer in the polymerisation of seven- and eight-membered lactams[52].

Lactam*	Content of lactam at equilibrium, wt.%	*T*, °C	Initiator, %
ϵ-Caprolactam	7	260	6,6 salt, 5
5-methyl-	8.8	254	6,6 salt, 10
7-methyl-	9.5	254	6,6 salt, 7
4-methyl + 6-methyl isomers	12.2	254	6,6 salt, 5
5-ethyl-	30.2	254	6,6 salt, 10
5-n-propyl-	41	254	6,6 salt, 10
5-isopropyl-	37	254	6,6 salt, 20
5-t-butyl-	74	254	6,6 salt, 20
5-cyclohexyl-	50	254	6,6 salt, 20
ζ-Oenantholactam	0	260	water, 4
8-ethyl-	3	260	water, 2
8-n-propyl-	6	260	water, 2
N-methyl-	20	260	water, 2

* The authors begin the numbering of the ring positions from the heteroatom.

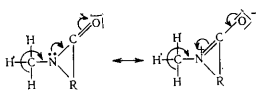
The data in Table 12 show that the introduction of a substituent into the lactam ring leads to an increase of the equilibrium concentration of the monomer in the monomer–polymer system, the influence of the substituent on the lactam polymerisation process being greater the greater the bulk of the substituent.

(9–13)-Membered Rings. There are contradictory data concerning the influence of the substituent on the formation of nine-membered lactam rings[121,122]. However, according to the available results for the polymerisation of various lactams, the influence of substituents on the capacity of lactams for polymerisation is smaller the larger the ring.

2. *N*-Substituted Lactams

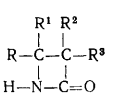
It is seen from Table 11 that the strain in the rings of *N*-substituted lactams is much smaller than in the rings of the unsubstituted lactams and their capacity for polymerisation is correspondingly smaller[112]. Data are available for the capacities for polymerisation of *N*-methyl-ζ-oenantholactam[111] and the *N*-methyl derivative of the lactam of lauric acid[118]. The polymerisation of *N*-methyl-ϵ-caprolactam has been investigated by many workers[48,53,106,168] under the conditions of both hydrolytic and anionic polymerisation. The possibility of the polymerisation of *N*-methyl-ϵ-caprolactam, suggested in one of the investigations[124], has been the subject of much doubt[48,53,110,111]. The capacity of *N*-acetoacetyl-ϵ-caprolactam for anionic polymerisation has also been studied[125] and it has been found that the *N*-acetoacetyl-substituted lactam not only does not undergo polymerisation but actually inhibits the polymerisation of ϵ-caprolactam.

Prochaska[108] suggested that a necessary condition for the polymerisation of lactams is the presence of a hydrogen atom in the amide group. This view is supported by Jumoto[107] and Hall[113]. On the basis of infrared spectroscopic data for five-, six-, and seven-membered lactams, Ogata[49] concluded that the absence of capacity for polymerisation is a common property of all *N*-substituted lactams. He believes[49] that this is caused by the high stability of such cyclic compounds due to the increase of the resonance effect in the amide group as a result of *N*-substitution and not due to the absence of a hydrogen atom:



The increase of the resonance stabilisation of *N*-substituted lactams owing to the inductive effect of the alkyl groups should lead to an increase of the dipole moment of the molecule. In fact, according to Ogata[110], the dipole moment of *N*-methyl-ϵ-caprolactam is 4.23 (cf. $\mu = 3.89$ for ϵ-caprolactam, Table 7). The capacity for polymerisation of *N*-substituted (8–13)-membered lactams indicates a decrease of the influence of the substituent with increase of ring size.[52]

It has been found that even the most reactive four-membered substituted cyclic β-lactams having the general formula



where R=H, alkyl, aryl, alkylaryl, or arylalkyl and R^1, R^2, and R^3 = H, CH_3, or C_2H_5, show a decrease of the tendency towards polymerisation with increase of the degree of substitution[126].

Thus examination of the influence of substituents on the reactivity of lactams shows that the following postulates may be regarded as proved.

1. The substituent reduces the reactivity of lactams.
2. The influence of the substituent is greater the smaller the size of the lactam ring.
3. An increase in the size of the substituent in the lactam ring also results in a decrease of the reactivity of the cyclic amide.
4. The reactivity of lactams depends on the position of the substituent in the ring.

It is apparently possible to arrange systematically data for the polymerisation of substituted lactams in terms of the ease of formation of the cyclic monomer. Two factors operate in cyclisation. The first is the enthalpy effect, the magnitude of which is a function of ring size and the presence of substituents. The second is the ease with which groups at the end of the chain can approach one another to a distance necessary for cyclisation, namely the entropy effect. The probability of cyclisation diminishes with increase in chain length, which evidently leads to a decrease of the entropy of cyclisation.

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