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POLYMERIZABILITY OF LACTAMS

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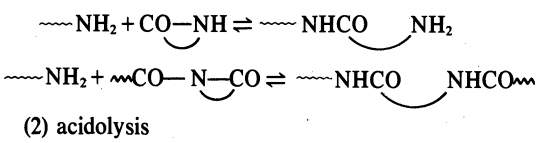
Abstract—The ability of lactams to undergo ring-opening polymerization largely depends on the ring size, substitution and presence of heteroatoms in the lactam ring. The heat of polymerization varies with ring size from practically zero up to 20 kcal/mol. Also the entropy of polymerization can vary in a much broader range than for, e.g. vinyl monomers. Changes in the amide group conformation affect both the thermodynamic values and the reactivity of the amide group. Hence, the lactam family represents a very versatile group of monomers from the point of view of polymerizability as well as properties of the resulting polymer.

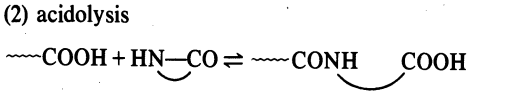
INTRODUCTION

The chemical and kinetic aspects of lactam polymerizations have been dealt with in numerous papers and it was proved that the reaction mechanism of polymerization is independent of the size of the lactam ring.[1–4] The monomer units are incorporated into the polymer molecules through the following catalyzed or uncatalyzed reactions:

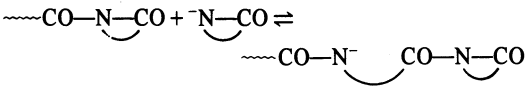
(1) aminolysis of lactam or *N*-acylated lactam:



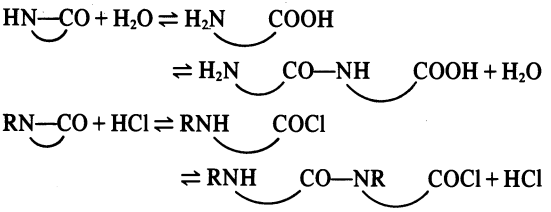
(2) acidolysis



(3) acylation of lactam anion by *N*-acylated lactam growth centers



(4) cleavage of lactam and subsequent condensation



Unless phase separation occurs, all these transacylation reactions are reversible. From the appearance of the first polymer amide groups, the same kind of reactions can proceed at the monomer as well as at the polymer amide groups. As a result, a set of thermodynamically controlled equilibria is established between monomer, cyclic oligomers and linear chains. These equilibria are a characteristic feature of lactam polymerizations and the equilibrium fraction of each component is determined by the size of the lactam ring, substitution, temperature, concentration of initiator and solvent.

The ring-opening polymerization of lactams at the amide group comprises the conversion of a cyclic lactam unit into a linear one without the formation of any new chemical bonds. When talking about the polymerizability we have in mind both the thermodynamic feasibility and a suitable reaction path to convert the cyclic monomer into a linear polymer. However, the term polymerizability is sometimes used as a synonym for both the rate of polymerization and the thermodynamic instability of the lactam.

It has to be stressed that the order of rates of polymerization of various lactams usually differs from their free energies and heats of polymerization. Thus the initial rate of hydrolytic polymerization is almost the same for capro-, enantho-, and caprylolactam,[5–7] whereas the corresponding heats of polymerization differ significantly[7] ($-\Delta H_p = 3.3$, 5.3 resp. 7.8 kcal mol^{-1}). Similarly, the sequence of free energies of polymerization for substituted caprolcatams is just opposite to the order of rates of anionic polymerization[8–10] (Fig. 1). In addition, the sequence of rates of polymerization may vary with the temperature and catalyst, e.g. in the copolymerization of capro-, and caprylolactam.[11] Therefore, the reactivity of the lactam amide group under the given reaction conditions should be always distinguished from the thermodynamic feasibility of polymerization. Generally, the reactivity of the polymerizing lactam ring depends on its conformation which may be different under different reaction conditions. For example, the conformation of the neutral lactam differs from that of the protonated lactam. Whereas in caprylolactam the amide group has a non-planar transoid conformation with a torsion angle of 148°, the protonated lactam has a nearly planar cis conformation.[12–22] Hence, the order of reactivities of different lactams can be influenced by the nature of catalyst. At usual concentrations the catalyst does not change the nature of the major fraction of monomer and polymer and the thermodynamic values should be independent of the reaction mechanism. Hence, only ΔH and ΔS values should be used for the comparison of the polymerizabilities of various lactams.

FREE ENERGY OF POLYMERIZATION

The change of free energy accompanying the conversion of one mole of lactam into one mole of linear monomer units in the polymer is given by the difference of the molar free energies of the monomer segment of an amorphous high molecular weight polymer and of the liquid monomer:

$$\Delta G_p = G_{p,a} - G_{m,l} = \Delta H_p - T\Delta S_p. \qquad (1)$$

However a negative value of ΔG_p only indicates whether polymerization is possible. Some highly strained lactams do not polymerize because of the lack of a suitable reaction path or undergo other, kinetically or thermodynamically more favoured reactions (e.g. *N*-substituted three-membered lactams).

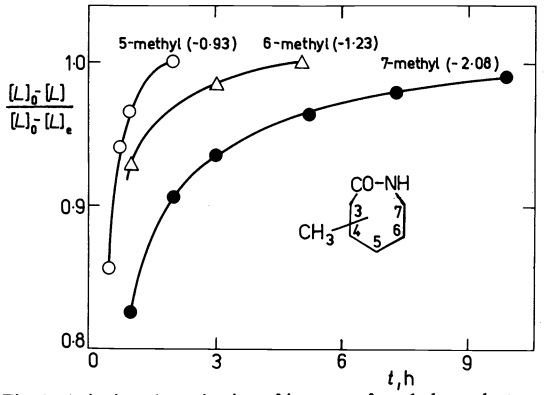


Fig. 1. Anionic polymerization of isomers of methylcaprolactam. Catalyst: 0.5 mol% sodium caprolactam and 0.5% of imide.[8–10] Temperature: 172°C (5 methyl and 7-methylhexanelactam) resp. 175°C (6-methylcaprolactam-isomer); the ΔG values are given parentheses.

At low initiator concentrations, the thermodynamic values are independent of the reaction mechanism, so that the polymerizability may be rationalized in terms of the ease of formation of the cyclic monomer or its opening into a linear chain unit. Under ideal conditions the equilibrium monomer concentration $[L]_e$, is related to temperature and standard heat and entropy of polymerization through equation

$$RT \ln [L]_e = \Delta H_p^0 - T\Delta S_p^0 = -RT \ln K. \quad (2)$$

When the interaction between monomer and polymer is taken into account, the free energy of polymerization is given by[23]

$$\Delta G_p = RT[\ln \phi_1 - (\ln \phi_2)/n + 1 - 1/n + \chi(\phi_2 - \phi_1)] \quad (3)$$

where ϕ_1 and ϕ_2 are the volume fractions of monomer and polymer and χ is the polymer–monomer interaction parameter. The simplified equation

$$\Delta G_p = RT[\ln \phi_1 + 1 + \chi(\phi_2 - \phi_1)] \quad (4)$$

can be used if the molecular weight of the polymer is high enough.

RING STRAIN AND HEAT OF POLYMERIZATION

In polymerizations at normal pressure, the $p\Delta V$ term in $\Delta H = \Delta E - p\Delta V$ is negligible and the enthalpy change is almost equivalent to the change in internal energy of the monomer. Thus, the heat of polymerization may be used as a measure of the strain energy in the cyclic compound.[24] In some cases, the enthalpy difference between the cyclic compound and its polymer does not reflect the actual ring strain, since the polymerization of a strained lactam into an open chain polyamide does not necessarily release all strain of the cyclic monomer. This occurs in polymers of highly substituted cyclic monomers, in which some strain can be imposed on the monomer unit inside the polymer chain as compared to the isolated open chain monomer unit. Interactions of this kind have to be taken into account in calculations of the heats of polymerization from the heats combustion of the monomer and low molecular weight open chain amides.[25]

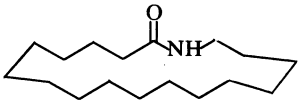
Reliable ΔH_p values can be obtained from measurements of the heat evolved during polymerization,[26–29] or from the difference between the heats of combustion of the amorphous polymer and liquid monomer. For partly crystalline polymers, the evaluation of calorimetric data is becoming more difficult, because both the crystallinity and the heat of crystallization must be known.[28] Equations (2–4) can be applied to such monomer–polymer equilibria for which the equilibrium monomer concentrations at different temperatures are available with sufficient precision.[8–10,30] This method is limited to completely amorphous polymers because the crystalline ordered areas do not take part in the monomer–polymer equilibrium.[31]

The sources of ring strain in lactams are

(1) inhibition or reduction of amide group resonance
(2) bond angle distortion (angle strain)
(3) bond stretching or compression
(4) repulsion between eclipsed hydrogen atoms or substituents on neighbouring ring atoms (conformational strain, bond torsion, bond opposition)
(5) nonbonded interaction between atoms or substituents attached to different parts of the ring (transannular strain, compression of van der Waals radii)

The magnitude of each type of strain depends on the ring size, substitution and nature of ring atoms.

Distortion of bond angles is the major source of the high strain in three- and four-membered lactams. In five-membered lactams the strain is due to bond opposition forces arising from eclipsed conformations. In medium rings, strain arises primarily from nonbonded interactions, bond opposition as well as prevention of resonance of the amide group. Any kind of strain including transannular interactions can be avoided completely in very large rings by arranging the ring atoms into two almost parallel chains[32]



and the strain of such lactams approaches zero.

With increasing size of the lactam ring, the heat of polymerization passes through a minimum for the six-membered lactam and after passing a maximum for the nine-membered lactam approaches zero for very large lactams (Fig. 2).

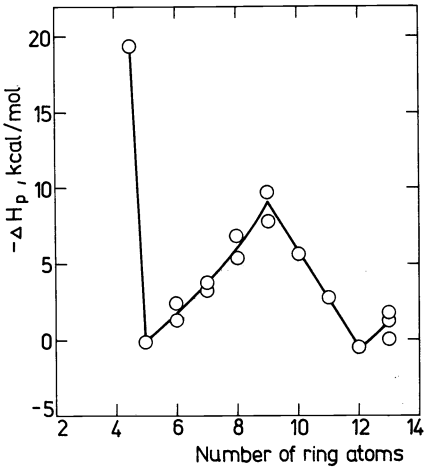


Fig. 2. Heat of polymerization of unsubstituted lactams (refs. 7, 25–29, 33–36).

The polymerization of lactams usually proceeds with a decrease of volume. At very high pressures the effect of volume contraction during polymerization on the monomer–polymer equilibrium cannot be neglected and the values of $\Delta H - p\Delta V$ must be used for calculations of the ring-strain. Polymerizations which are thermodynamically impossible at normal pressures can become possible at very high pressures. For example, the fairly stable six-membered lactam has a very unfavourable monomer–polymer equilibrium under normal pressure and can be polymerized only at low temperatures.[37] On the other hand, at 20,000 atm piperidone could be polymerized to a high yield even at 160°C.[38]

ENTROPY OF POLYMERIZATION

In the polymerization of a great number of small particles into one polymer chain this aggregation process results in a decrease of translational entropy of the system. In the ring-opening polymerization of cyclic monomers, the decrease of translational entropy is partly counter-balanced by the increase in rotational and vibrational entropy resulting from the conversion of a more or less rigid cyclic monomer into a flexible monomer unit inside a polymer chain. The net entropy of polymerization of lactams is more positive (e.g. −3 e.u. for seven-membered lactams) than the entropy of polymerization of vinyl monomers (−25 to −30 e.u.).

Besides four- and five-membered lactams, the highest rigidity of the monomer can be expected for medium rings with 8–11 ring atoms. Conversion of the latter lactams to a polymer results in a large increase in the rotational and vibrational entropy because of the enhanced flexibility of the open chain monomer unit. As a consequence the contribution of the entropy term to the free energy of polymerization is expected to increase very steeply for medium rings. Calculations of ΔS_p^0 values from specific heats indicates that the entropy of polymerization increases linearly from the five-membered to the eight-membered lactam.[29] Linear extrapolation to large rings[36] yielded $\Delta S_p^0 = 30$ e.u. for laurinolactam. This value appears too high with respect to $\Delta S_p^0 = -3.75$ e.u. calculated from monomer–polymer equilibria.[33] This large difference is due to the fact that in larger lactams the mobility of ring atoms increases with increasing ring size so that the polymerization entropy should not increase as steeply as for smaller rings in which the mobility of the ring atoms is very restricted. It may be rather assumed that for large rings the value of ΔS_p should follow a line similar to that derived from the content of cyclic oligomers (Fig. 3).

For large lactams the values of ΔH_p approach zero and entropy changes become increasingly important. Whereas the heat of polymerization makes the main contribution to the free energy of polymerization for strained lactams up to the eight-membered ring, the polymerization entropy makes the main contribution to ΔG_p for more than twelve-membered lactams. The entropy changes become more favourable in the copolymerization of two lactams. Therefore, pyrrolidine and piperidone may be copolymerized even at higher temperatures at which homopolymerization does not proceed.[39]

Skuratov *et al.*[29] calculated the polymerization entropy from specific heat measurements of the monomer and polymer. The estimated value of ΔS_{298}^0 e.g. for caprolactam (+1.1 e.u.) is however too positive because the authors disregarded the fact that the polymer was not completely crystalline. Making allowance for the partial crystallinity, the value of ΔS_p^0 becomes more negative and approaches the value −3.2 e.u. calculated from monomer–polymer equilibria.[40]

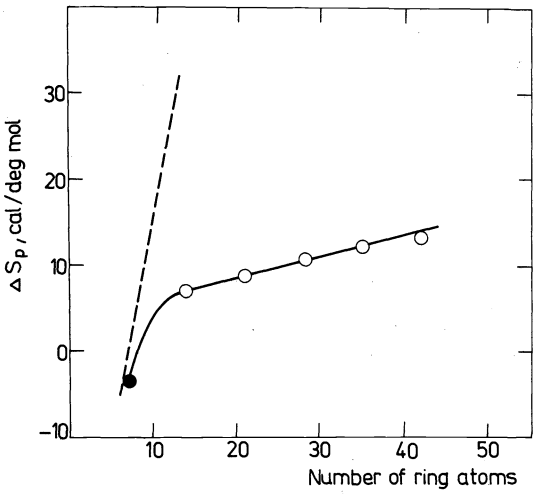
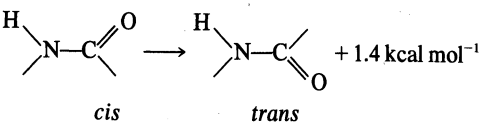


Fig. 3. Ring size and entropy of polymerization. Calculated values for lactams[36] (dashed line) compared with values obtained from the equilibrium content of caprolactam and its oligomers (full line).

CONFORMATION OF THE AMIDE GROUP

The more stable *trans* conformation predominantes in straight chain amides[41] and in more than nine-membered lactams.[42] Up to the eight-membered lactam the amide group is forced to adopt the *cis* conformation[42] which is by 1.4 kcal mol^{-1} less stable than the *trans* form.[43] Irrespective of the actual ring strain, this energy is released in the conversion of the *cis*-amide group (in lactams up to enantholactam) into the *trans* form of the polymer



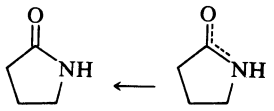
cis *trans*

From this point of view, the planar *cis* amide group significantly contributes to the heat of polymerization of five- and six-membered lactams. This enthalpic factor is the main driving force in the polymerization of the almost unstrained six-membered lactam and the experimental[29] and calculated[36] values of the heat of polymerization ($\Delta H_p = -1.1$ resp. 1.7 kcal mol^{-1}) are very close to the enthalpy difference between the *cis* and *trans* amide group.

The highest resonance stabilisation of the amide group may be achieved only if the latter is planar. Any deviation from planarity of the lactam amide group lowers its resonance stabilization, increases ring strain and results in a higher polymerizability. The non-planar transoid conformation of the amide group in capryllactam increases the ring strain by additional 1.5 kcal/mol.[13] The maximum resonance energy is released in the polymerization of bicyclic lactams with the amide nitrogen at the bridgehead in which the amide group cannot be planar.[44]

In more detailed investigations[12–22,45] it was shown that there exist slight differences of the amide group conformation among the lactams of each group. In pyrrolidone the amide group cannot adopt a fully planar conformation without introducing some strain into the ring due to the

repulsion of eclipsed hydrogens. An additional heat effect arises from the tendency of retaining an exocyclic double bond in the five-membered ring[46] which decreases the resonance stabilization of the amide group in pyrrolidone.



Therefore pyrrolidone should polymerize easier than piperidone. The amide group of the six-membered lactam may easily attain a planar conformation. Also the tendency of formation of an endocyclic double bond in six-membered rings[46] increases the resonance stabilization of the amide group.

The nine-membered lactam was assumed to be sufficiently flexible to allow the more stable *trans* amide group to co-exist with the strainless *cis* form.[42] However, a strainless planar *trans* form is not possible and the actual conformation is rather a cisoid and transoid structure which reduces the $p-\pi$ overlap and decreases resonance stabilization of the amide group.[12] Therefore, an increased amount of delocalization energy is released in the conversion of the non planar conformation of the lactam in the fully resonance stabilized *trans* form of the polymer amide group. Thus, the large ring strain in the nine-membered lactam arises both from strong transannular interaction and from inhibition of resonance stabilization.

The planar *trans* conformation can be strainless in ten-membered and larger lactams so that the contribution of conformational changes of the amide group to the free energy of polymerization will be minimum. Only the ten-membered lactam contains about 5% of a cisoid conformation and a corresponding amount of energy will be released during polymerization.

Independent of the ring size, the resonance stabilization of a planar amide group in *N*-substituted lactams is the same as in the open chain *N*-substituted lactam unit inside a polymer chain. For this reason, the heat of polymerization of *N*-substituted lactams (up to the nine-membered lactam) should be by about 1.4 kcal mol.$^{-1}$ lower than the heat of polymerization of unsubstituted *cis* lactams. Calorimetric data revealed[47] that *N*-methylation reduces the exothermicity of polymerization of enantholactam by about 1.4 kcal mol^{-1}. Also for the six- and seven-membered lactams[47] similar differences between the heats of polymerization of *N*-substituted and unsubstituted lactams were estimated (1.7 and 1.5 kcal mol^{-1}). On the other hand *N*-substitution of large lactam rings should not alter the value of the heat of polymerization as much as in the case of small rings, except that the substituent at the nitrogen increases transannual strain.

EFFECT OF HETEROATOMS

Replacement of a methylene group by a heteroatom changes the thermodynamic parameters of the cyclic as well as linear monomer unit. Carbon-heteroatom bonds differ from C–C bonds with respect to bond length and bond angle as well as ionic character of the bond.[48] Ogata[49–51] showed that introduction of –O– resp. –S– groups in seven-membered lactams increases their polymerizability. For example, the monomer–polymer equilibrium of substituted seven-membered lactam ethers and thioethers is shifted to higher polymer yields than for the corresponding caprolactam derivatives. Contrary to 4,6-dimethylcaprolactam which failed to polymerize,[52] the corresponding dimethyl-lactam ether or thioether could be polymerized.[49,51] Increased polymerizability of the latter lactams most probably arises from increased ring strain.

The introduction of an additional amide group into the lactam ring also increases its polymerizability. 2,5-Dioxopiperazine was found to polymerize and copolymerize easier than piperidone.[53–55] Accordingly, the heat of polymerization of cyclo-di-β-alanyl was higher[56] (ΔH_p = −7.4 kcal mol^{-1}) than that of enantholactam (ΔH_p = −5.3 kcal mol^{-1}). It may be concluded that an additional amide group inside the cycle increases the ring strain because of the larger bond angles at two rings atoms, and stiffness of the amide group.

In calculations of the equilibrium concentration of macrocycles in caprolactam polymers, the heat of polymerization of cyclic oligomers was assumed to be zero.[57] Due to the aforementioned effects of additional amide groups inside the ring, the actual polymerizability is certainly higher and, therefore, the estimated content of the individual cyclic oligomers is lower than the calculated one (Fig. 4).

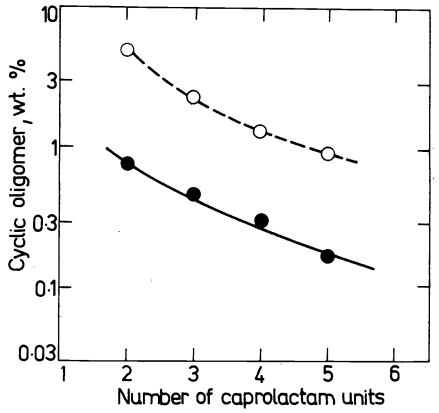


Fig. 4. Content of cyclic oligomers in caprolactam polymers. Calculated[57] (○); found[58] (●).

EFFECT OF SUBSTITUENTS

The rate and equilibrium of lactam polymerization are significantly affected by the number, size and location of substituents. It is worth mentioning that substituents may affect the kinetic and thermodynamic factors differently. Whereas the rate determining step of polymerization is very sensitive to sterical effects in the vicinity of the amide group,[59] the free energy of polymerization is affected more by substitution at tetragonal atoms favouring ring closure. In the polymerization of methylcaprolactam isomers the equilibrium is attained with 5-methylhexanelactam earlier than with the 7-methyl derivative (Fig. 1); on the other hand the equilibrium polymer content is the lowest for the 5-isomer and the highest for the 3- and 7-isomers (Fig. 5).

Substituents affect both the heat and entropy of polymerization of cyclic monomers mainly through conformational effects.[61–64] Except in some large lactams, steric repulsions between substituents usually do not increase the enthalpy of the cyclic lactam (Fig. 6). However, new interactions arising from substituents increase the enthalpy of the linear monomer unit relative to the cyclic one[32] and thus decrease the heat of polymerization (Fig. 6).

Similarly, substitution decreases considerably the entropy of the linear monomer unit inside a polymer chain

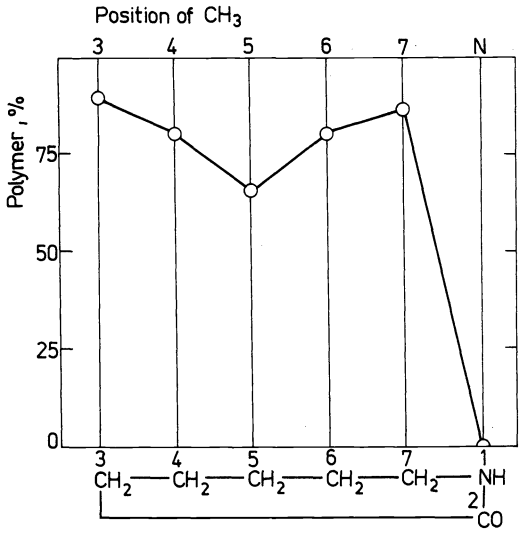


Fig. 5. Equilibrium polymer content for methylcaprolactam isomers at 250° (refs. 8–10, 60).

by restricting its rotation whereas the entropy of the lactam is affected only very little. Therefore, substitution shifts the enthalpy and entropy of polymerization in favour of the cyclic structure and decreased polymerizability.

Repulsion of substituents may occur even for monosubstituted lactams with a substituent in the vicinity of the nitrogen atom (Fig. 6) since the preferred *trans* conformation of the amide group imposes some rigidity on the amide bond. Among all bonds of the linear monomer unit, the CH_2–N bond has the highest mobility so that a substituent next to the nitrogen reduces the entropy of the open chain unit more than a substituent in the other positions.

The polymerizability of substituted lactams was discussed[64] in terms of the change of the number of gauche interactions and the configuration of the amide bond. It was assumed that each additional gauche interaction increases ring strain by 0.8 kcal/mol, the changes in gauche interactions being related to the planar zig-zag form of the linear monomer unit. The zig-zag conformation is not always the conformation with the lowest energy. In some polyamides from substituted lactams the substituted monomer unit is shorter than the unsubstituted one[65] so that the substituted unit is not present in a planar zig-zag conformation. The conformation of the polymer chain is influenced not only by the number but also by the position of the substituent and this fact will be reflected both in the enthalpy and entropy of the polymer chain. The actual effect of methylation on the heat of polymerization of the seven-membered lactam suggests that the contribution of one additional gauche conformation is rather 0.3–0.5 kcal/mol^{-1} than the estimated value 0.8 kcal/mol and depends on the position of the methyl group.

The length of a linear hydrocarbon substituent next to the nitrogen affects the equilibrium yield of polymer in a complicated manner. The polymerization equilibrium passes through a minimum at C_3–C_4 (Fig. 7) and a maximum around C_6.

The effect of substitution on the heat of polymerization depends not only on the size and position of the substituent but also on the size of the lactam ring.

We may conclude that from the point of view of

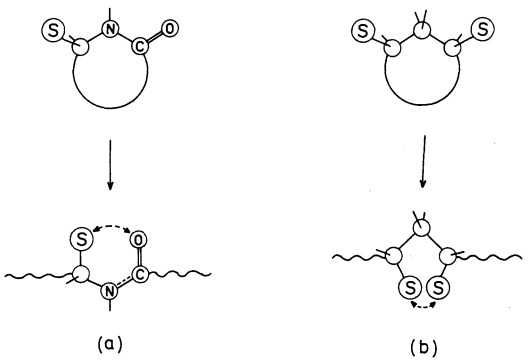


Fig. 6. Repulsion of substituents in linear monomer units.

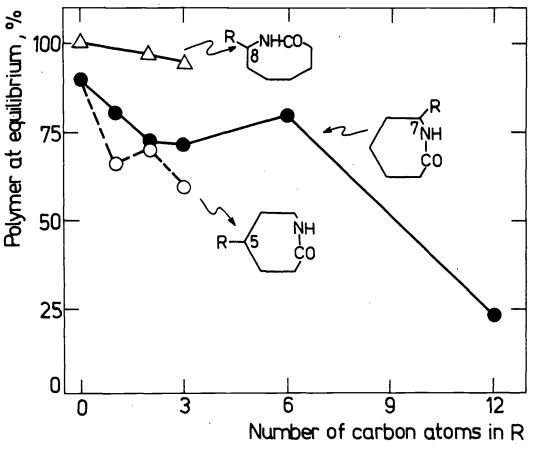


Fig. 7. Effect of chain length of a linear alkyl substituent on the monomer–polymer equilibrium of seven- and eight-membered lactams. Alkyl groups in position 7 (●) and 8 (△) at 260° and in position 5 (○) at 254° (refs. 8, 9, 66–71).

polymerizability the series of lactams synthesized and polymerized so far already represents a very versatile group of monomers. The possibility of varying the ring size and substitution in an almost unlimited range together with the unique properties of the amide group are certain to arouse increasing interest.

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