THE EQUILIBRIUM ACIDITY OF CYCLIC AND LINEAR AMIDES AND ITS EFFECT ON THE ANIONIC POLYMERIZATION OF LACTAMS

Bohumír VALTER[a], M. I. TEREKHOVA[b], E. S. PETROV[b], Jaroslav STEHLÍČEK[a] and Jan ŠEBENDA[a]

[a] Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia and
[b] Karpov Institute of Physical Chemistry, 107 120 Moscow B-120, USSR

The equilibrium acidity of lactams with rings of various size and of linear N-substituted amides was measured in dimethyl sulfoxide by the spectrophotometric method. The pK values of these NH-acids thus determined varied in the range 22—27. The data are used to characterize the acidobasic equilibrium between the amide groups of the monomer, polymer and their N-anions during the anionic polymerization of lactams. The effect of acidity on the anionic copolymerization of lactams is also discussed.

One of the factors which determine decisively the rate of anionic polymerization of lactams is the concentration of lactam anions[1]. Similarly, the ratio of the rates of incorporation of various lactams in the copolymer depends on the relative content of anions of the copolymerizing lactams[2]. The concentration of lactam anions in the polymerization medium is connected with the dissociation of lactamates which depends, among other things, on the acidity of the lactam and of the forming polyamide.

Up to now, the relative acidities of lactams and polyamides have been estimated from the acidities of protonized compounds[1,3]. The only direct data on the acidities of lactams have been reported[4,5] for 4-butanelactam (pK 30·7), 5-pentanelactam (pK ~33), and 6-hexanelactam (pK 31·3). These values were determined potentiometrically in 1,2-dimethoxyethane. For acyclic amides, only acidity values of unsubstituted primary amides in dimethyl sulfoxide (DMSO) are known[6,7].

Thus, in order to investigate the kinetics of polymerization and copolymerization of lactams, we must know the acidities of lactams with rings of various size and of linear N-substituted amides, which would allow us to characterize the acidobasic equilibrium between amide groups of monomer and polymer and the effect of acidity of various lactams on their anionic copolymerization.

The acidity was determined using DMSO as a solvent, because in this solvent, in contrast to 1,2-dimethoxyethane, no complications arise due to the formation of ion pairs[8].

EXPERIMENTAL

Operations in a vacuum line were performed at <0.13 Pa (ref.[9]).

Materials

The measured lactams and amides were commercial products or compounds earlier synthesized in our laboratory and were purified before use by repeated distillation or crystallization. Dimethyl sulfoxide (DMSO, Lachema, pure) was let to crystallize by cooling to about 3/4 its volume, the liquid fraction was separated and the residue was redistilled in an inert atmosphere at 40 Pa. After that, DMSO was dried several days over an activated molecular sieve (4 Å). After subsequent two distillations with calcium hydride in the vacuum line, DMSO was kept in a sealed ampoule at $-25°C$. Potassium methylsulfinylmethanide ($CH_3SOCH_2^- K^+$): The stock solution ($\sim 0.25M$) was prepared[10] from potassium hydride and DMSO in the vacuum line and stored similarly to DMSO. Potassium triphenylmethanide: A solution in DMSO ($\sim 0.02M$) which was used in the determination of the equilibrium constant was prepared by a reaction of potassium methylsulfinylmethanide with triphenylmethane in the vacuum line and stored in ampoules similarly to DMSO.

Indicators

Fluorene (United Metallurgical and Chemical Works) was twice crystallized from ethanol, m.p. $114-115°C$. 1,1,3,3-Tetraphenylpropene: 1,3,3-Triphenyl-1-propanone, prepared from 1,3-diphenyl-2-propene-1-one[11], was transformed by the Grignard reaction with phenylmagnesium bromide into 1,1,3,3-tetraphenyl-1-propanol which was dehydrated according to Garbisch[12]. The product thus obtained was purified by column chromatography on silicagel with cyclohexane as eluent and crystallized from ethanol, m.p. $126.5-127.5°C$ (ref.[12] $126.5-127°C$).

Measurement of pK

The pK values were determined spectrophotometrically in DMSO (ref.[13]); the procedure is based on the determination of the equilibrium constant K of the transmetalation reaction between the compound to be determined (RH) and the potassium salt of a compound with a known pK, the so-called indicator (In). The pK value of the measured compound was calculated from the relation pK (RH) $=$ pK(In) $-$ log K. The equilibrium constant (K) was measured in an all-glass apparatus with a sealed-on quartz cell, layer thickness 0.05 cm (Fig. 1), using a Unicam 500 spectrophotometer at room temperature. First, glass balls containing a known quantity of the measured compound and indicator (~ 10 mg) and sealed in the vacuum line were placed in the apparatus, together with a breaking plug 3, and the neck was sealed in place 5. After being connected to the vacuum line with an ampoule containing the stock solution of potassium triphenylmethanide, the apparatus was evacuated and annealed with flame; on cooling, approx. 5 ml of the solution was transferred into a calibrated cell 2. After freezing with liquid nitrogen, the whole apparatus was sealed off the vacuum line in place 1. One part of the solution the volume of which had been measured in advance was poured from the calibrated vessel 2 into the mixing part 7 of the apparatus. DMSO was distilled from the remaining volume of the solution in the calibrated vessel into part 7; thus, the solution was diluted to the required concentration of c. 10^{-3} mol l^{-1}. After the calibrated vessel had been sealed off in place 8, the ball containing the indicator was broken, the solution was homogenized by rotating this part of the apparatus, transferred into the cell 6, and the absorbancy was determined. The ball containing the measured compound was broken, the change in absorbancy of the indicator was measured, and the equilibrium constant K was thus determined.

RESULTS AND DISCUSSION

The determined values of the equilibrium acidity of lactams and linear amides (Table I) confirmed the assumption that these compounds behave as very weak NH-acids. Since unsubstituted 3-propanelactam was not directly available for measurement, its acidity (pK ~22·7) was estimated from its dimethyl substituted derivative. The influence of the adjacent methyl group on NH-acidity was estimated from the acidity of 6-hexanelactam and 6-methyl-6-hexanelactam.

If the determined pK values of lactams are compared with those reported earlier[4,5], it can be seen that they greatly differ from each other. While the values for 5-pentanelactam and 6-hexanelactam are virtually the same, Sekiguchi and coworkers[4] report a difference of almost two pK units. The published data[4] seem to be too high, though they were determined in 1,2-dimethoxyethane, where lower values than in DMSO can be expected due to the formation of ion pairs and the consequent stabilization of the conjugated base (N-anion) by the cation of the alkali metal[13].

The measured values of equilibrium acidity of lactams also show that the change of the *trans* conformation of the amide group which appears in the nine- and higher--membered lactams to the less stable *cis* conformation of the amide group in lower lactams has no essential effect on NH-acidity. The assumption that the *trans* conformation of the amide group possesses higher acidity was based on the fact that the addition of N-alkylamide to a solution of sodium 6-hexanelactam in 6-hexanelactam considerably raised the concentration of free ions[1]. The independence of the acidity of lactams on the conformation of the amide group was confirmed by the determination of the acidity of linear N-substituted amides in which the energetically more advantageous *trans* conformation of the amide group is preferred. In spite of this, their acidity is virtually the same as that of the six- to eight-membered lactam with the *cis* conformation of the amide group.
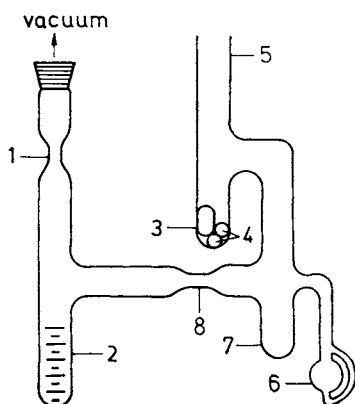

FIG. 1

Apparatus for determination of equilibrium acidity. 1, 8 places for sealing a part off, 2 calibrated vessel, 3 glass breaking plug, 4 balls with measured compounds, 5 sealing neck of the apparatus, 6 quartz cell, 7 mixing part

The acidity values in Table I also indicate that the acidobasic equilibrium between amide groups of six-membered and higher lactams and of their polymers, on the one hand, and their conjugated bases (N-anions), on the other, should not distinctly prefer one type of N-anions in the course of the anionic polymerization:

$$\overset{(-)}{N}-CO + \sim CO-NH\sim \rightleftharpoons HN-CO + \sim CO-\overset{(-)}{N}\sim \qquad (4)$$
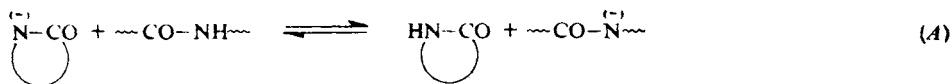
If the polymer precipitates from the polymerization mixture, this finding means that the corresponding part of N-anions is bound to the polymer in the solid state, where their further participation in polymerization equilibria and reactions may be limited.
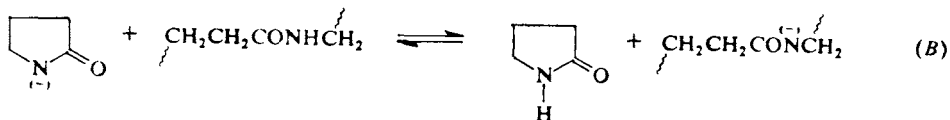
On the contrary, in the four- or five-membered lactam the acidity of the system should decrease during the polymerization, and N-anions should be present mainly as lactam anions up to high degrees of conversion.

TABLE I

Equilibrium acidities of lactams and linear amides in DMSO. The symbol K means the equilibrium constant of transmetalation reaction (mean value from 5—6 measurements)

Compound	K	pK
Indicator fluorene ($pK = 22 \cdot 9$) (ref.[8])		
3-Propanelactam	—	$22 \cdot 7^a$
3-Phenyl-3-propanelactam	$8 \cdot 01 \pm 0 \cdot 98$	$22 \cdot 0$
3-Methyl-3-phenyl-3-propanelactam	$6 \cdot 59 \pm 0 \cdot 71$	$22 \cdot 1$
3,3-Dimethyl-3-propanelactam	$0 \cdot 45 \pm 0 \cdot 017$	$23 \cdot 2$
4-Butanelactam	$0 \cdot 027 \pm 0 \cdot 004$	$24 \cdot 5$
Indicator 1,1,3,3-tetraphenylpropene ($pK = 26 \cdot 2$) (ref.[8])		
5-Pentanelactam	$0 \cdot 35 \pm 0 \cdot 05$	$26 \cdot 7$
6-Hexanelactam	$0 \cdot 107 \pm 0 \cdot 008$	$27 \cdot 2$
6-Methyl-6-hexanelactam	$0 \cdot 043 \pm 0 \cdot 006$	$27 \cdot 6$
7-Heptanelactam	$0 \cdot 11 \pm 0 \cdot 005$	$27 \cdot 2$
8-Octanelactam	$0 \cdot 076 \pm 0 \cdot 006$	$27 \cdot 3$
10-Decanelactam	$0 \cdot 18 \pm 0 \cdot 02$	$26 \cdot 9$
12-Dodecanelactam	$0 \cdot 097 \pm 0 \cdot 012$	$27 \cdot 2$
N-Octylbutyramide	$0 \cdot 14 \pm 0 \cdot 02$	$27 \cdot 1$
N-Propylpropionamide	$0 \cdot 35 \pm 0 \cdot 02$	$26 \cdot 7$

^{a} The value estimated from pK of 3,3-dimethyl-3-propanelactam.

$$\text{[structure]} + \text{CH}_2\text{CH}_2\text{CONHCH}_2 \rightleftharpoons \text{[structure]} + \text{CH}_2\text{CH}_2\text{CONCH}_2 \qquad (B)$$

The acidities of lactams also allow us to characterize the effect of water or lower alcohols (methanol, 2-methyl-2-propanol) on the anionic polymerization. These compounds may be present in the reaction mixture as a result of the preparation of alkali salts of lactams used as initiators from the respective hydroxide or alkoxide. By comparing the acidities of lactams with those of water (pK 31·4) and the alcohols just mentioned (methanol pK 29·0, 2-methyl-2-propanol pK 32·2), also determined in DMSO (ref.[14]), one can see that the acidities of all these compounds are lower than those of lactams

$$\text{HN-CO} + \text{RO}^{(-)} \rightleftharpoons {}^{(-)}\text{N-CO} + \text{ROH} \qquad (C)$$
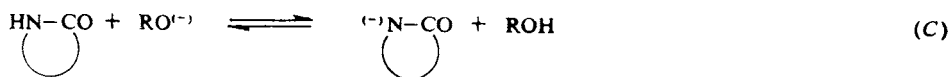
For this reason, the presence of water and alcohols in the anionic polymerization does not affect the concentration of lactam anions too much, but does decrease the concentration of N-acyllactam growth sites due to their hydrolysis or alcoholysis.

Data on the acidity of the lactams differing in their ring size or substituents may also be employed in the characterization of this influence on their anionic copolymerization. The concentrations of N-anions of copolymerizing lactams A and B which determine the ratio of their incorporation into the copolymer depend on the relative acidity of these lactams

$$\text{HN-CO} + {}^{(-)}\text{N-CO} \xrightarrow{K_{ac}} {}^{(-)}\text{N-CO} + \text{HN-CO} \qquad (D)$$
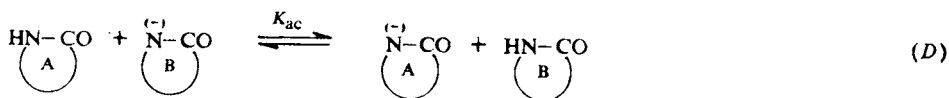
The acidity factor may therefore become operative only in the copolymerization of lactams with sufficiently different pK values; in other words, only in the copolymerization of 3-propanelactam or 4-butanelactam with higher lactams. For a greatly simplified reaction mechanism in which competitive condensation reactions of N-acyllactams were not considered, Bar–Zakay[3] derived a relation for the composition of a copolymer formed by the copolymerization of 4-butanelactam and 6-hexanelactam using the relative acidity of monomers K_{ac} which may be calculated from the difference of pK of both lactams ($\log K_{ac} = -\Delta pK$). However, he calculated $K_{ac} = 0·4$ from the basicity values of both lactams determined by Huisgen[15] and not from the pK values. The acidity values determined by us allow us to calculate the correct value, $K_{ac} = 0·002$. The reactivity of 4-butanelactam in the copolymerization

obtained by substituting this value into the Bar–Zakay relation is higher by three orders of magnitude than that of 6-hexanelactam. However, when evaluating these data, one should also consider the simplified copolymerization mechanism and conditions under which the equilibrium acidity was measured. This is why such ratio of reactivities cannot adequately describe the experimentally determined dependence of the copolymer composition on the copolymerization temperature[16,17].

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