# THE EQUILIBRIUM ACIDITY OF SUBSTITUTED N-(PHENYLCARBAMOYL)-6-HEXANELACTAMS AND DISUBSTITUTED UREAS AND THEIR EFFECT ON THE ANIONIC POLYMERIZATION OF LACTAMS

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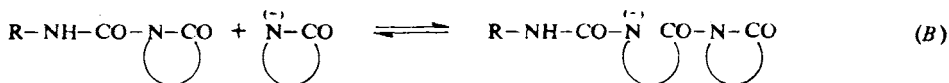[b] *Karpov Institute of Physical Chemistry, 107 120 Moscow B-120, USSR*

The equilibrium acidity of substituted N-(phenylcarbamoyl)-6-hexanelactams, N-butyl-N'-
-phenylurea and N,N'-diethylurea was determined spectrophotometrically in dimethyl sulfoxide.
Using the determined p$K$ values, the effect of activator acidity of the N-(phenylcarbamoyl)-
lactam type on the anionic polymerization of lactams was estimated, and the possible effect
of the individual types of urea on the concentration of lactam anions was predicted.

One of the activator types used in the anionic polymerization of lactams are N-(carba-moyl)lactams which can be added to the reaction mixture at the beginning of poly-merization or can be formed *in situ* by fast reactions, *e.g.*

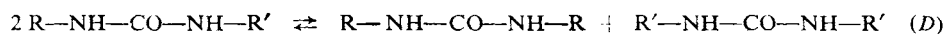$$R-N=C=O \ + HN-CO \longrightarrow R-NH-CO-N-CO \qquad (A)$$
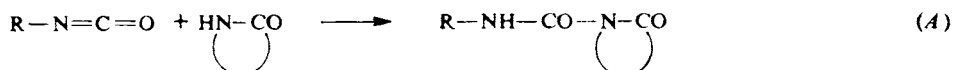
The effect of the activator consists in the increased polarization of the amide group of the lactam ring in the direction of the electrophilic substituent, which facilitates the nucleophilic attack of the lactam anion. In the first propagation step, N-carba-moyllactam is deacylated with formation of an N,N'-disubstituted urea structure, incorporated in the polymer chain. Hence, the acidity of N-carbamoyllactam affects

$$R-NH-CO-N-CO \ + \ \overset{(-)}{N}-CO \ \rightleftharpoons \ R-NH-CO-\overset{(-)}{N} \ CO-N-CO \qquad (B)$$

$$R-NH-CO-\overset{(-)}{N} \ CO-N-CO \ + \ HN-CO \ \rightleftharpoons \ R-NH-CO-NH \ CO-N-CO \ + \ \overset{(-)}{N}-CO \qquad (C)$$

the concentration of lactam anions only at the very onset of polymerization, while the acidity of some N,N'-disubstituted urea structures affects the whole process of polymerization. It has been found[1] that the anionic polymerization activated with N-(phenylcarbamoyl)lactam is considerably slowed down by the addition of N-methyl-N'-phenylurea. This effect has been explained by the fact that the acidity of this urea is much higher than that of lactams[1]. This assumption has been confirmed by the finding that the equilibrium acidities of lactams containing seven members and more $(pK \sim 27)$ (ref.[2]) determined in dimethyl sulfoxide (DMSO) are much lower than those of N,N'-diphenylurea $(pK\ 20.6)$ (ref.[3]) and N-methyl-N,N'-diphenylurea $(pK\ 19.9)$ (ref.[3]) determined in the same solvent.

However, the activation effect of N-(phenylcarbamoyl)lactams may be weakened not only by the presence of the relatively acid hydrogen atom in the carbamoyl group, but also by weakening the transfer of polar effect of the phenyl group through the free electron pair on nitrogen of the carbamoyl group. It was found[1,4] that the presence of electron-acceptor substituents in position 4 on the benzene ring in the case of N-(phenylcarbamoyl)-6-hexanelactams is reflected in a decrease in the rate of anionic polymerization.

For a detailed investigation of the anionic polymerization activated with N-(phenylcarbamoyl)lactams one should determine both the acidities of variously substituted N-(phenylcarbamoyl)lactams and those of N-alkyl-N'-arylurea. It is also necessary to determine the acidity of N,N'-dialkylurea which may arise by rearrangement of the primarily formed N-alkyl-N'-arylurea[5]

$$2\ R\text{—}NH\text{—}CO\text{—}NH\text{—}R' \rightleftarrows R\text{—}NH\text{—}CO\text{—}NH\text{—}R + R'\text{—}NH\text{—}CO\text{—}NH\text{—}R' \quad (D)$$
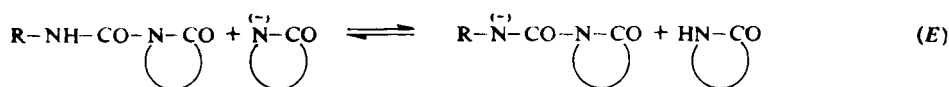
## EXPERIMENTAL

Handling of the solutions, purification of DMSO, preparation of potassium methylsulfinylmethanide ($CH_3SOCH_2^- K^+$) and 1,1,3,3-tetraphenylpropene have been described earlier[2]. 9-Phenylfluorene was prepared by the reduction of 9-phenyl-9-fluorenol obtained from phenylmagnesium bromide and fluorenone[6] and crystallized from ethanol, m.p. $146.5 - 147.5°C$ (ref.[6] $145°C$). 9-Benzylfluorene was prepared by a reaction between fluorenyllithium and benzyl chloride[7], purified by column chromatography on silicagel (cyclohexane as eluent) and crystallized from ethanol, m.p. $134 - 135°C$ (ref.[7] $131 - 134°C$). N-(Phenylcarbamoyl)lactams were prepared earlier[1] by a reaction of the respective isocyanate with lactam, disubstituted ureas were obtained by reacting amine with isocyanate: N,N'-diethylurea, m.p. $110 - 111°C$; N-butyl-N'-phenylurea, m.p. $127.5 - 128.5°C$.

The pK values were determined using spectrophotometrically determined equilibrium constants K according to a procedure described earlier[2,8].

## RESULTS AND DISCUSSION

The equilibrium constants of the transmetalation reaction of N-(phenylcarbamoyl)-6-hexanelactams given in Table I confirm the assumed higher acidity values of these

compounds compared with the acidity of 6-hexanelactam[2] (pK 27·2). The difference in the acidity value is seven or more pK units; in other words, the difference is already so great that one must assume a considerable influence of the activator of such type on the anionic polymerization of lactams due to the acid character of the carbamoyl group. If we assume that the difference in the pK values of compounds under investigation, of the monomer and of the polymer chain, remains unchanged during the transition from DMSO to the real polymerization system (i.e. lactam and polyamide at elevated temperature), the concentration of lactam anions may decrease due to such a great difference in the NH-acidities, because the reaction

$$\text{R-NH-CO-}\underset{\bigcup}{\text{N-CO}} + \underset{\bigcup}{\overset{(-)}{\text{N-CO}}} \rightleftharpoons \text{R-}\overset{(-)}{\text{N-}}\text{CO-}\underset{\bigcup}{\text{N-CO}} + \text{HN-}\underset{\bigcup}{\text{CO}} \qquad (E)$$

is considerably shifted to the right, despite the initial lactam concentration in the polymerization being higher by two or three orders of magnitude than that of the activator.

TABLE I

Equilibrium acidities of N-(phenylcarbamoyl)-6-hexanelactams and disubstituted ureas in DMSO. The symbol $K$ means the equilibrium constant of transmetalation reaction (mean value from 5—6 measurements) with the indicator 9-benzylfluorene (I), 9-phenylfluorene (II), 4-bromopyrazole (III) or 1,1,3,3-tetraphenylpropene (IV)

| Compound | Indicator[a] | K | pK |
|---|---|---|---|
| 6-Hexanelactams | | | |
| N-(Phenylcarbamoyl)- | I | 31·7 ± 3 | 20·3 |
| N-(p-Methoxyphenylcarbamoyl)- | I | 8·3 ± 0·9 | 20·9 |
| N-(p-Cyanophenylcarbamoyl)- | II | 8·3 ± 0·8 | 17·6 |
| N-(p-Nitrophenylcarbamoyl)-[b] | III | 1·5 ± 0·2 | 16·8 |
| Ureas | | | |
| N,N'-Diethyl- | IV | 1·45 ± 0·17 | 26·0 |
| N,N'-Diphenyl- | I | 31 ± 4 | 20·6[c] |
| N-Butyl-N'-phenyl- | I | 0·26 ± 0·06 | 22·4 |

[a] pK values: I 21·8 (ref.[9]), II 18·5 (ref.[9]), III 17·0 (ref.[10]), IV 26·2 (ref.[9]). [b] Anion: $\lambda_{max} = 450$ nm, $\varepsilon_{450} = 30·9 . 10^3$ l mol$^{-1}$ cm$^{-1}$. [c] Taken from the literature[3].

The effect of substituents on the NH-acidity of N-(phenylcarbamoyl)-6-hexane-lactams was expressed quantitatively by means of the Hammett equation. The determined values of equilibrium acidity $pK$ are correlated with the Hammett constants of the substituents, $\sigma$,

$$pK = 20\cdot2 - 2\cdot69\sigma \, ,$$

the value of the reaction constant $\varrho$ does not virtually differ from the reaction constant of benzanilides[11] $(\varrho\ 2\cdot96)$.

The equilibrium acidity values of disubstituted ureas show that an addition of N,N'-diethylurea or of some other N,N'-dialkylurea may have only a minimal influence on the concentration of lactam anions, because the difference in the acidity values between this type of urea and the lactam is small. On the contrary, an addition of N,N'-diphenylurea or N-alkyl-N'-arylurea may lead to an essential decrease in the rate of polymerization, as in this case the difference in the acidity values between the urea and lactam again amounts to almost seven or five $pK$ units, respectively.

Under the assumption mentioned above, the known $pK$ values of disubstituted ureas allowed us to decide how the concentration of lactam anions might be affected by the formation of a polymer chain, one end of which contains the rest of the activator used and has the structure of N,N'-disubstituted urea:

$$R-NH-CO-NH\sim\sim\sim N-CO$$
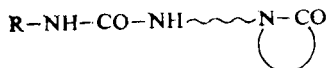
Such endgroup of the chain may arise not only with N-carbamoyllactams used as activators, but also with N-acyllactams. In the latter case side reactions occurring in the process of anionic polymerization may give rise to isocyanate[12], and thus indirectly also to N-carbamoyllactam.

By comparing the $pK$ values of disubstituted ureas, one can see that the effect of endgroups of the polymer chain of the type of disubstituted ureas is pronounced in the case of formation of N-arylureido endgroups which due to the presence of an aromatic substituent contain a hydrogen atom of such acidity that this end-group may interact with the lactam anion, thus decreasing the concentration of lactam anions. On the contrary, with activators of the N-(alkylcarbamoyl)lactam type, the interaction of the endgroup of the polymer chain with the lactam anion is negligible, because the arising endgroup corresponds to dialkylsubstituted urea whose acidity is much weaker and comparable to that of the lactam.

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Translated by L. Kopecká.