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Oligomerization of Cyclic Imines *N*-Carboxamides by the Action of Anion Type Catalyst

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Abstract—Using methods of nuclear magnetic resonance, gel-permeation chromatography, and differential-scanning calorimetry, we showed that *N*-carboxamides were capable of polymerization. The polymerization mechanism of *N*-carboxamides in the presence of ε-caprolactam sodium salt was suggested.

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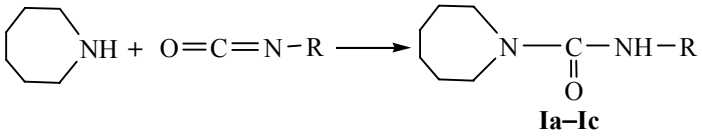
Recently the interest of scientists grew to the chemistry of cyclic imines. Consequently the spectrum of their application was extended. These compounds can be used in pharmacology as antibacterial drug components [1]. They can be used also as polyvinyl chloride plasticizers, catalysts in polyurethane synthesis, epoxy resin hardeners, antioxidants for rubber, etc. [2–5].

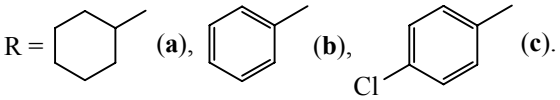
Cyclic saturated imines (pyrrolidine, piperidine, hexamethyleneimine and others) and their derivatives can be considered as potential monomers, whose polymerization may lead to new high-molecular compounds possessing unique properties inherent to this class. However, there are no data in the literature on their application as monomers for the synthesis of polymers.

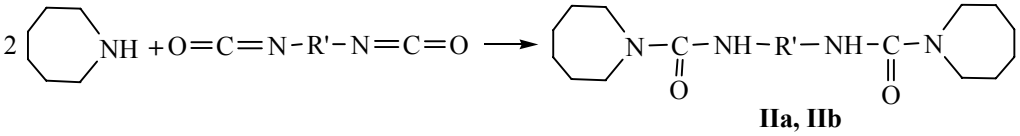
Our earlier studies showed that cyclic saturated imines are incapable of entering into the polymerization under the conditions of anionic initiation [6]. Therefore it is of interest to estimate the influence of different substituents at the nitrogen atom of the cyclic imine carboxamides on the ability to polymerization via ring opening.

N-(cyclohexylazepane)-1-carboxamide **Ia**, *N*-phenylazepane-1-carboxamide **Ib**, *N*-(4-chlorophenyl) azepane-1-carboxamide **Ic**, *N*,*N*'-(4-methyl-1,3-phenylene)-diazepane-1-carboxamide **IIa**, and also *N*,*N*'-hexane-1,6-diylazepane-1-carboxamide **IIb** obtained by the reaction of hexamethylene imine with different isocyanates were selected as cyclic imine *N*-carboxamides for the investigation.

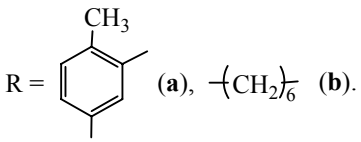


Ia–Ic



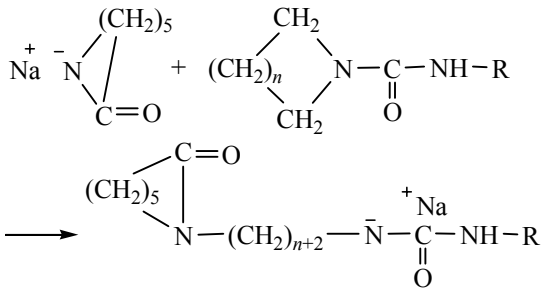


IIa, IIb

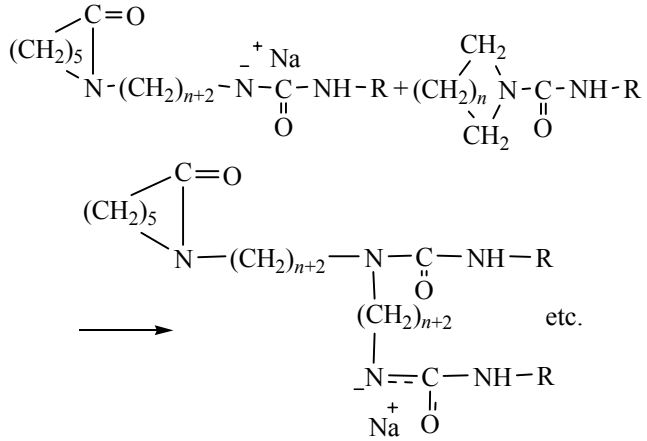


Probable mechanism of cyclic polymerization of the imine *N*-carboxamides under the action of ε-caprolactam sodium salt **III** can be represented as follows:

(1) Initiation reaction. At the nucleophilic attack of the lactam anion on the monomer amide carbon atom an anion is formed, which is stabilized through the cycle opening to give the N-anion, which plays the role of an active center:



(2) Chain growth reaction. The obtained N-anion attacks the monomer molecule at the amide carbon atom of the ring, opens the *N*-carboxamide ring, and adds to it to form in this case a trimer, which again carries an anion. The trimer anion again attacks *N*-carboxamide molecule and thus the chain growing continues through the repeated opening of the activated ring by the monomer anion.



Reactions with the participation of selected cyclic imine *N*-carboxamides in the presence of a catalytic amount of compound **III** at 180–190°C afford the products of light beige color, whose yield is given in Table 1. It follows from the data in Table 1 that in all cases when *N*-carboxamides were used the yields of the obtained compounds extracted into acetone were sufficiently high.

The study of molecular-mass characteristics by the gel-permeation chromatography method showed that at least four monomer molecules were added in the reaction. The reaction products of cyclic imines *N*-carboxamides **Ia** and **IIb**, which contain no aromatic rings in their chemical structure, are characterized by the largest values of M_w. To explain the observed results we carried out a comparative analysis of the first LUMOs of the studied compounds (Fig. 1). It was shown that the LUMO of *N*-carboxamides containing aromatic substituents in their structure have no occupancy on the carbon atoms of the heterocycle fragments CH_2–N (Figs. 1b, 1d). The occupancy on these atoms appears only in the third (in the case of **Ib**) and the second (**IIa**) LUMOs (Figs. 2, 3). This predetermines the greater probability of the nucleophilic attack on the heterocycle carbon atom, accompanied by the breaking of C–N bond, in the case of aliphatic *N*-carboxamides in comparison with aromatic analogs.

Study of the structure of the obtained compounds by means of ^{1}H NMR spectroscopy confirms the opening of the *N*-carboxamide imine ring and the addition of the next molecules. Thus, by the example of compound **IIa** (Fig. 4) it is possible to observe the appearance of new signals in the region of 0.6–1.2 ppm which belong to the protons of CH_2-groups of the opened imine cycles.

The broadening of signals in this spectrum indicates the presence the studied reaction product of the

Table 1. Yields and molecular-mass characteristics of *N*-carboxamides and of the reaction products[a]

Oligomerization substrate	Yield, %	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{carboxamide}$
Ia	51	1330	290	4.6	224
Ib	72	990	570	1.7	218
Ic	65	640	480	1.3	252
IIa	59	880	730	1.2	372
IIb	61	2400	1150	2.1	366

[a] M_w is weight-average molecular mass, M_n is number-average molecular mass, M_w/M_n is the polydispersity index, $\bar{M}_{carboxamide}$ is molecular mass of the corresponding *N*-carboxamide.

hydrogen atoms with different environment, characteristic of the high-molecular compounds with repeating units. At the same time the spectrum of the reaction product contains the signals of CH_2 group protons of cyclic structure. A similar observation, in spite of the symmetrical structure of compound **IIa** shows the unequal capability of imine cycles to opening, which is confirmed by the occupancy nature of the heterocycles MOs (Fig. 3).

The values of melting points obtained by the method of differential-scanning calorimetry also confirm the fact that the actions of high temperatures in the presence of compound **III** leads the formation of new reaction products. Thus, the melting points values of the reaction products are appreciably different from the same characteristics of the corresponding monomers (Table 2).

The melting diffusivity indicates the spread of the molecular mass values of the new compounds. The diffusivity of the samples **Ia** and **IIb** correlates with their polydispersity indices.

Thus, the oligomerization of cyclic imine *N*-carboxamides was carried out in the presence of anionic type catalyst. It was shown that the products obtained on the basis of aliphatic *N*-carboxamides has higher molecular weight in comparison with the aromatic substrates.

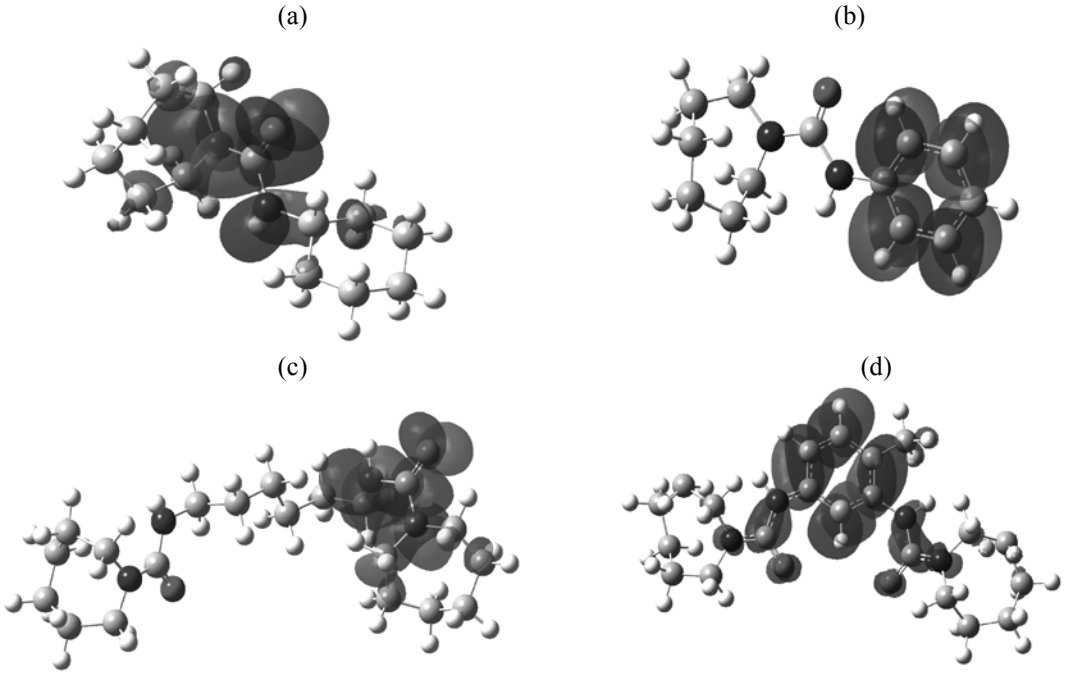


Fig. 1. Pictograph image of LUMOs of compounds: (a) **Ia**, (b) **Ib**, (c) **IIa**, and (d) **IIb**.

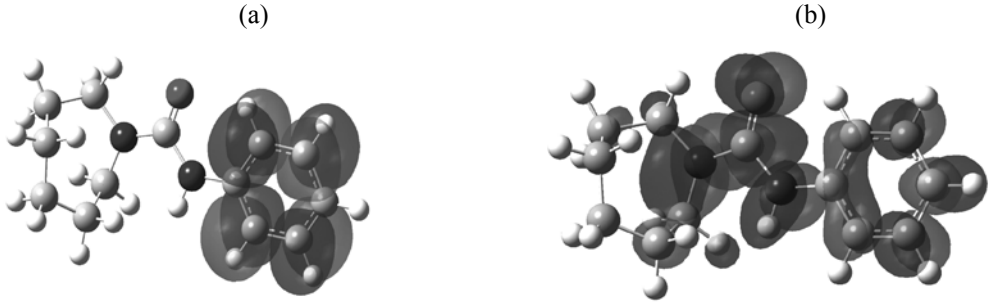


Fig. 2. Pictograph image of the (a) first and (b) third LUMOs of compound **Ib.**

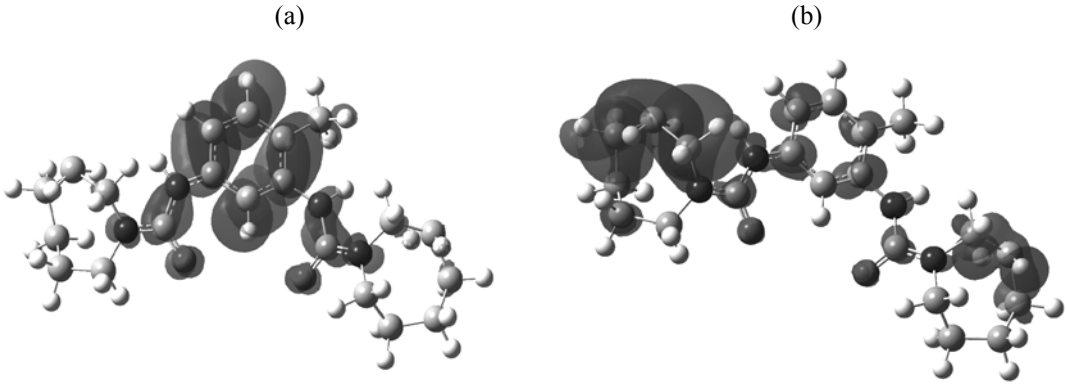


Fig. 3. Pictograph image of the (a) first and (b) third LUMO of compound **IIa.**

EXPERIMENTAL

The investigation objects are the adducts of isocyanates of various structure with hexamethylene imine.

Synthesis of *N*-carboxamide. To 40% DMF solution of hexamethylene imine was added dropwise equimolar amount of isocyanate over 30 min. The reaction mixture temperature was maintained in the range of 0–4°C by cooling with ice. Then the mixture was stirred at this temperature to the complete isocyanate conversion. The residual amount of isocyanate groups was determined by titration [7]. The obtained precipitate was filtered off, dried in air, and reprecipitated (chloroform–hexane) for purification. The obtained products were dried at 50–60°C in a vacuum to the constant weight.

The majority of the cyclic imine *N*-carboxamides are soluble in the strong polar solvents. Structure of the obtained *N*-carboxamides is confirmed by IR spectroscopy. During the reaction progress an absorption band appeared at 1620 cm^{-1} [stretching vibrations of C=O group in amide structures of C(O)–NH type].

Compound Ia. ^{1}H NMR spectrum, δ, ppm: 1.29 m (4H, CH_2CH_2), 1.49 m (6H, $CH_2CH_2CH_2$), 1.53 m (4H, CH_2), 1.55 m (4H, CH_2), 3.16 m (4H, CH_2N), 3.54 m (1H, CHN), 6.0 s (1H, NH).

Compound Ib. ^{1}H NMR spectrum, δ, ppm: 1.29 m (4H, CH_2CH_2), 1.55 m (4H, CH_2), 3.16 m (4H, CH_2N), 6.0 s (1H, NH), 7.0–7.64 m (5H, Ar).

Compound Ic. ^{1}H NMR spectrum, δ, ppm: 1.29 m (4H, CH_2CH_2), 1.55 m (4H, CH_2), 3.16 m (4H, CH_2N), 6.0 s (1H, NH), 7.25–7.58 m (4H, Ar).

Compound IIa. ^{1}H NMR spectrum, δ, ppm: 1.29 m (8H, CH_2CH_2), 1.55 m (8H, CH_2), 2.35 s (3H, CH_3), 3.16 m (8H, CH_2N), 6.0 m (2H, NH), 7.02 s, 7.26 s, 7.90 s (3H, Ar).

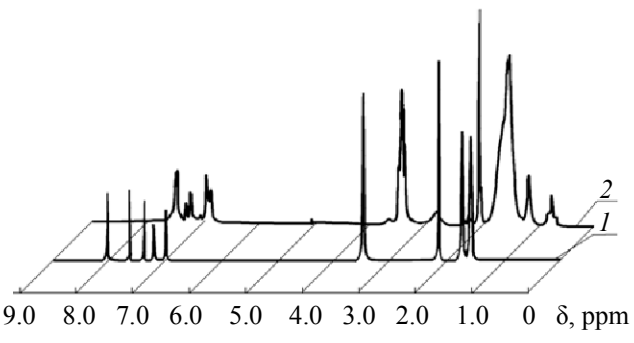


Fig. 4. ^{1}H NMR spectra (DMSO-d_6) of (*1*) compound **IIa** and (*2*) its oligomerization product.

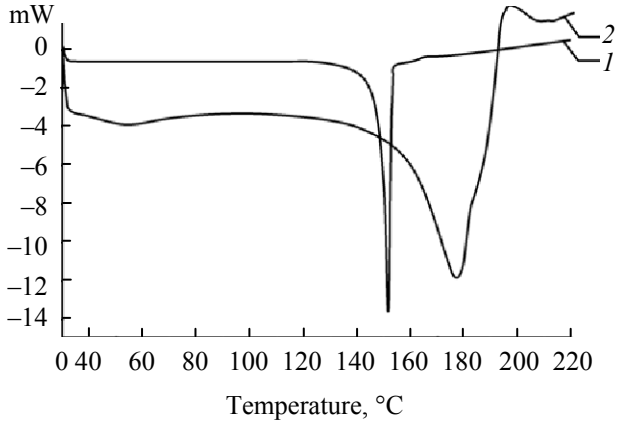


Fig. 5. DSC curves: (*1*) compound **IIb** and (*2*) oligomer on its base.

Table 2. Temperatures of the beginning and equilibrium melting of the reaction products (T_{beg} and T_{eq}, respectively) and melting points of *N*-carboxamides $T_{carboxamide}$

Oligomerization substrate	T_{beg}, ºC	T_{eq}, ºC	$T_{carboxamide}$, ºC	Diffusivity $D = T_{eq} - T_{beg}$
Ia	89	115	156	26
Ib	122	140	117	18
Ic	152	172	156	20
IIa	160	167	172	7
IIb	140	176	140	36

Compound IIb. ^{1}H NMR spectrum, δ, ppm: 1.29 m (12H, CH_2CH_2), 1.55 m (12H, CH_2), 3.16 m (12H, CH_2N), 6.0 m (2H, NH).

ε-Caprolactam sodium salt was obtained as 75% solution in ε-caprolactam by reaction of the latter with metal sodium in toluene at 110–112°C to complete sodium conversion. The obtained product was precipitated, dried, and stored in a desiccator in a vacuum.

The oligomers synthesis was performed in a three-neck flask equipped with reflux condenser, stirrer, and thermometer under argon atmosphere, as follows: 1 mol % of catalyst and ε-caprolactam sodium salt were dissolved in the cyclic imine *N*-carboxamide. The mixture was stirred at 180–190°C for 150 min.

The target oligomeric products were purified by extraction with boiling acetone in Soxhlet apparatus for 8 h.

The IR spectra were recorded on a Perkin-Elmer PC-16 spectrometer. The ^{1}H NMR spectra were registered on a Tesla-100 instrument (100 MHz) in DMSO-d_6. Molecular mass characteristics were taken on a Waters 150C chromatograph, solvent DMF. DSC investigations were performed on a Mettler Toledo DSC-1 instrument with the heating rate 5 deg min^{-1}. The quantum-chemical calculations of the monomers were made by B3LYP/6-31G(d) method by means of GAUSSIAN-2003 program [8].

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