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Anionic Polymerization of ε-Caprolactam in the Presence of Piperidine *N*-carboxamides

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Abstract—Piperidine *N*-carboxamides were shown to activate the anionic polymerization of ε-caprolactam. The activator structure affects properties of the resulting polycaproamide.

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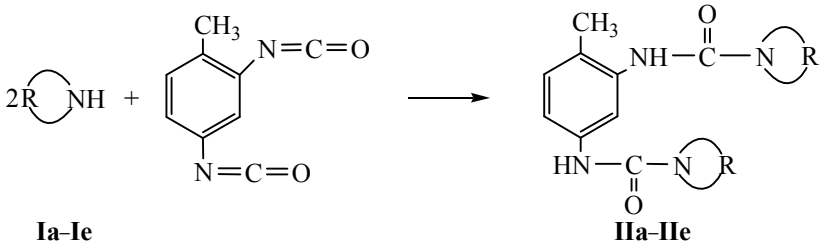
Most methods of producing polycaproamides by anionic polymerization require the use of an activator. Therefore the interest grows to the study of various activators in the anionic polymerization of lactams. This is due not only to the fact that they accelerate the polymerization, but also being the center of growth of polyamide chains they allow a direct control of the molecular structure and, consequently, the properties of the resulting polyamide [1].

A class of activators of anionic polymerization of ε-caprolactam widely used in industry includes the various *N*-acyllactams as well as other compounds of similar structure [2]. The presence in the molecule of such compound of two carbonyl groups attached to the nitrogen atom decreases the resonance stabilization of the amide bond of lactam ring and leads to a marked increase in activity of the endocyclic carbonyl group involved in the polymerization with respect to the lactam nucleophilic anion. This increases the activity of the exocyclic carbonyl group.

At the same time by means of quantum-chemical calculations a possibility was shown in [3] of the opening of the *N*-acyllactam heterocycle at the NH–CH_2 bond. The ability of cyclic imine *N*-carboxamides to oligomerization suggests a possibility of their use as activators in the ε-caprolactam anionic polymerization [4].

As piperidine *N*-carboxamides for the study we have chosen dipiperidincarboxamide **IIa**, *N,N*'-(4-methyl-1,3-phenylene)-bis-(3-methylpiperidine-1-carboxamide) **IIb**, *N,N*'-(4-methyl-1,3-phenylene)-bis-(4-methylpiperidine-1-carboxamide **IIc,** *N,N*'-(4-methyl-1,3-phenylene)-bis-(2-ethylpiperidine-1-carboxamide) **IId,** and *N,N*'-(4-methyl-1,3-phenylene)-bis-(2,4-dimethylpiperidine-1-carboxamide) **IIe,** obtained in the reaction of 2,4-tolylene diisocyanate with various piperidines at both isocyanate groups.



Ia–Ie **IIa–IIe**

R = —CH_2—$(CH_2)_3$—CH_2— (**a**); —CH_2—CH(CH_3)—$(CH_2)_2$—CH_2— (**b**); —CH_2—CH_2—CH(CH_3)—CH_2—CH_2— (**c**);
—CH_2—CH(C_2H_5)—$(CH_2)_2$—CH_2— (**d**); —CH(CH_3)—$(CH_2)_3$—CH(CH_3)— (**e**).

Table 1. Melting point and elemental analysis data of piperidine *N*-carboxamides **IIa–IIe**

Comp. no.	mp, °C	Found, %			Formula	Calculated, %		
		N	C	H		N	C	H
IIa	119	16.39	63.86	8.54	$C_{19}H_{28}N_4O_2$	16.27	66.25	8.19
IIb	185	15.25	65.31	9.13	$C_{21}H_{32}N_4O_2$	15.05	67.74	8.60
IIc	189	15.27	65.22	9.08	$C_{21}H_{32}N_4O_2$	15.05	67.74	8.60
IId	162	14.13	67.59	9.35	$C_{23}H_{36}N_4O_2$	13.99	68.96	9.06
IIe	121	14.15	65.84	10.22	$C_{23}H_{36}N_4O_2$	13.99	68.96	9.06

The structures of obtained *N*-carboxamides were confirmed by ^{1}H NMR and IR spectroscopy. During the reaction, in the IR spectrum appeared an absorption band at 1620 cm^{-1} [stretching vibrations of the carbonyl group in the amide-type structures C(O)NH], and the absorption band at 2262 cm^{-1} corresponding to the antisymmetric stretching vibrations of the isocyanate group disappeared.

Melting point of the piperidine *N*-carboxamides and the elemental analysis data are shown in Table 1.

The polymers obtained with the piperidine *N*-carboxamides as activators of anionic polymerization of ε-caprolactam were of a light beige color.

Activating ability of the studied compounds was evaluated from the yields of the polymers. The data in Table 1 show that the presence of substituents and their position in the ring fragment of the activator affects the polyamide yield. The presence of substituents at 2 and 6 positions of the ring fragment of compounds **IId, IIe** leads to the formation of the polymers with a high yield, in contrast to **IIa** containing no substituents. The change in the substituent position, in particular, the separation from the imide group, can also result in a decrease in the activating ability (compounds **IIb, IIc**). It is possible to obtain with compounds **IId, IIe** polymers with the softening temperature close to that of the polyamide obtained on the basis of tolylene diisocyanate. The presence of unreacted ε-caprolactam in polycaprylamide when compounds **IIa**, **IIb** and **IIc** are used as activators leads to a decrease in the softening temperature.

A study of the dependence of the polymer yield on time showed that with our activators the induction period is short and the kinetics curves are of S-shape (Fig. 1), which is manifested in non-activated polymerization of ε-caprolactam and evidences a slow formation of growth centers in the system.

Figure 1 shows that with the studied activators the induction period of polymerization of ε-caprolactam is longer compared with an induction period of polymerization in the presence tolylene diisocyanate. This is due, firstly, to the lower reactivity of acylimine group compared with acyllactam. Secondly, the partial positive charge on the electrophilic carbon atom is neutralized by the electron-donor properties of the heterocycle. Therefore, nucleophilic addition of anionic catalyst proceeds slower.

Study of physico-mechanical characteristics (Tables 2, 3) shows that the sample obtained with **IIe** as an activator is not inferior in the properties to the analog obtained on the basis of industrial activator (tolylene diisocyanate), and the sample based on **IId** is twice better by the tensile strength. As a rule, increase in the polymer strength leads to a decrease in its elastic properties that can be seen from Table 3.

A significant drawback of polycaprylamide is high water absorption leading to a deterioration of strength and stability of products during their use in an environment with high humidity. It was presumable that the activation with piperidine *N*-carboxamides would enhance the water resistance of polycaprylamide due to the presence of hydrophobic

Table 2. Yield and softening point of polycaproamide produced at the action of various activators

Activator	Polymer yield, % (after extraction)	Softening point, °C
TDI[a]	93	228
IIa	68	206
IIb	56	195
IIc	75	205
IId	95	218
IIe	96	225

[a] TDI is 2,4-toluene diisocyanate.

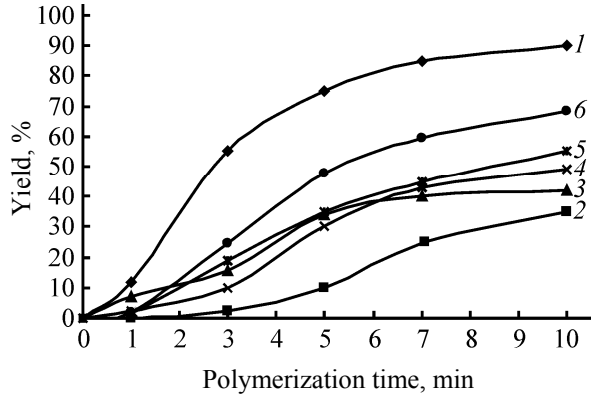


Fig. 1. Dependence of the yield of polycaproamide on the polymerization time at the use of various activators: (*1*) 2,4-tolylene diisocyanate, (*2*) **IIa**, (*3*) **IIb**, (*4*) **IIc**, (*5*) **IId**, and (*6*) **IIe**.

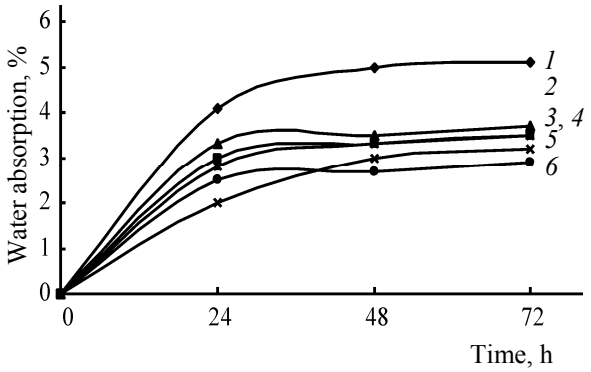


Fig. 2. Water absorption by polycaproamide obtained using various activators: (*1*) 2,4- tolylene diisocyanate, (*2*) **IIa**, (*3*) **IIb**, (*4*) **IIc**, (*5*) **IId**, and (*6*) **IIe**.

groups $(CH_2)_n$ and benzene ring. Figure 2 shows that the introduction of the studied activators reduces the water absorption of polycaprylamide almost twofold.

Thus, in this work the influence of the structure of activators obtained by reacting tolylene diisocyanate with various piperidines on the synthesis, physico-mechanical properties, and water absorption of the polycaprylamide formed was assessed. The investtigations revealed that the activators *N,N'*-(4-methyl-1,3-phenylene)-bis-(2-ethylpiperidine-1-carboxamide) and *N,N'*-(4-methyl-1,3-phenylene)-bis-(2,4-dimethyl-piperidine-1-carboxamide) among the considered series of piperidine *N*-carboxyamides are the most effective for producing polycaprylamide.

EXPERIMENTAL

The IR spectra in the medium spectral region were registered on a Perkin Elmer PC 16 spectrophotometer from the tablets prepared by mixing 3 mg of sample with 200 mg of KBr and pressed at a pressure of 10 t; the tablet diameter was 0.012 m.

^{1}H NMR spectra were obtained on a Bruker 400 instrument with an operating frequency 400 MHz, solvent DMSO-d_6. Elemental analysis was carried out on an elemental composition analyzer CHN-3. Thermo-mechanical curves of polymer samples were taken at a constant strength in the installation for the complex analysis.

Physico-mechanical properties (tensile strength σ, elongation ε) were determined in accordance with GOST 11262-80 on samples of type 1 at the test temperature 20±2°C. Samples were tested at least 24 h after their production and pre-conditioned at the test temperature for 4 h. The tensile testing machine rate was 100 mm min^{-1}.

The synthesis of piperidine *N*-carboxamides **IIa**–**IIe** was carried out by the method described in [3].

Compound IIa. ^{1}H NMR spectrum, δ, ppm: 1.50 s (12H, $CH_2CH_2CH_2$); 2.35 s (3H, CH_3); 3.34 d (8H, NCH_2); 6.0 s (2H, NH); 7.02–7.90 s (3H, arom. protons).

Compound IIb. ^{1}H NMR spectrum, δ, ppm: 1.06 d (6H, CH_3); 1.34–1.67 m (10H, $CHCH_2CH_2$); 2.35 s (3H, CH_3), 3.17–3.42 m (8H, NCH_2); 6.0 s (2H, NH); 7.02–7.90 s (3H, arom. protons).

Compound IIc. ^{1}H NMR spectrum, δ, ppm: 1.06 d (6H, CH_3); 1.34–1.67 m (10H, $CHCH_2CH_2$); 2.35 s (3H, CH_3), 3.29, 3.39 m (8H, NCH_2); 6.0 s (2H, NH); 7.02–7.90 s (3H, arom. protons).

Table 3. Physical and mechanical properties of polycaproamide[a]

Activator	σ, MPa	ε, %
TDI[b]	27	184
IIa	19	9
IIb	12	6
IIc	18	180
IId	52	15
IIe	24	185

[a] σ is tensile sungth, ε is elongation.
[b] TDI is 2,4-tolylene diisocyanate.

Compound IId. The ^{1}H NMR spectrum, δ, ppm: 0.96, 1.55 m (10H, CH_3CH_2); 1.34–1.59 m (12H, $CH_2CH_2CH_2$); 2.35 s (3H, CH_3) 3.33 m (2H, NCH); 3.29, 3.39 m (8H, NCH_2); 6.0 s (2H, NH); 7.02–7.90 s (3H, arom. protons).

Compound IIe. ^{1}H NMR spectrum, δ, ppm: 1.30 d (12H, CH_3); 1.34–1.59 m (12H, $CH_2CH_2CH_2$); 2.35 s (3H, CH_3); 3.51 m (4H, NCH); 6.0 s (2H, NH); 7.02–7.90 s (3H, arom. protons).

ε-Caprolactam sodium salt was obtained as a 75% solution in ε-caprolactam by reacting the latter with metallic sodium in toluene at 110–112ºC until complete consumption of sodium. The resulting product was precipitated, dried, and stored in a desiccator in a vacuum.

Synthesis of polyamide. In an argon flow, 1 mol % of Na-caprolactam was dissolved in ε-caprolactam at 180ºC and then at continuous stirring was added 3 mol % of piperidine *N*-carboxamide. When viscosity of the reaction mixture increased, the additional polymerization of the reaction mixture was performed for 150 min in order to reduce the amount of unreacted monomer. In the reaction course samples were taken to study the kinetics of the process.

Purification of the polymer products obtained from the unreacted monomers was carried out by extraction with boiling acetone in a Soxhlet apparatus for 8 h.

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