Translated from *Uspekhi Khimii*, 48, 1856 - 1883 (1979) U.D.C. 547.922.2

Activators of the Anionic Polymerisation of Lactams

T.M.Frunze, V.V.Kurashev, V.A.Kotel'nikov, and T.V.Volkova

The influence of the structure of activators on the anionic polymerisation of lactams is examined and a classification of activators taking into account the chemical nature of the active centres formed and the side products is proposed. An approach to the specific selection of activating compounds for the regulation of the rate of polymerisation is described and the possibility, in principle, of employing activators with different functionalities for varying the structure and properties of the resulting polyamides is demonstrated. Data are presented on the modification of polyamides using macromolecular activators of the anionic polymerisation of lactams.
The bibliography includes 210 references.

CONTENTS

I. Introduction 991
II. The polymerisation mechanism 991
III. Classification of activators 992
IV. The influence of the chemical structure of activating compounds on their efficiency 995
V. The influence of the functionality of activators on the molecular structure of the polymers formed 998
VI. Macromolecular activators of the anionic polymerisation of lactams 1000

I. INTRODUCTION

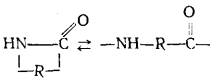
Among the industrial methods for the synthesis of polyamides, the polymerisation of lactams occupies a notable place. Thus, one of the most important and widely used examples of the class of polyamides, namely polycaproamide, is obtained on an industrial scale mainly by the hydrolytic polymerisation of ϵ-caprolactam.

When the activating influence of imides, the so-called activators, on the anionic polymerisation of lactams was established, the polymerisation of cyclic amides became even more important. The use of activators in the anionic polymerisation of lactams led to the development of a virtually new method for the synthesis of polyamides and articles made from them—by activated anionic polymerisation. By greatly reducing the energy expenditure, this method makes it possible to obtain articles by chemical moulding involving a "monomer–finished article" procedure. In view of the absence of the processing stage, a unique possibility is created for the formation of large articles of various configurations.

Numerous papers devoted to activating systems in the anionic polymerisation of lactams have been published. The aim of the present review is to give a systematic count of accumulated data, to examine the influence of the chemical structure of compounds of different types on their activating capacity in the anionic polymerisation of lactams, and to consider the possibility of using activators for the regulation of the molecular structure of the polyamides formed.

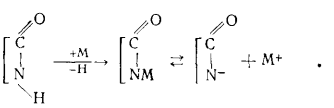
II. THE POLYMERISATION MECHANISM

The capacity of lactams of different structures for polymerisation is determined by thermodynamic and kinetic factors. It has now been established that the opening of the amide ring at the heterobond



is a thermodynamically favourable process for virtually all the known unsubstituted lactams, although the position of the thermodynamic equilibrium for each monomer depends on its chemical structure[1]. The possibility of obtaining a high-molecular-weight polymer is determined not only by the thermodynamic but also by the kinetic stability of the ring, i.e. its reactivity. The latter depends on a whole series of factors, among which the following may be mentioned: the resonance stabilisation of the amide linkage within the lactam ring, the conformation of the macromolecules (the presence of *cis*- and *trans*-isomers), the possibility of the formation of intermolecular hydrogen bonds, and the basicity of the monomer[1-5]. In addition, the kinetics of the overall polymerisation process depend to a large extent on the nature of the catalytic system used.

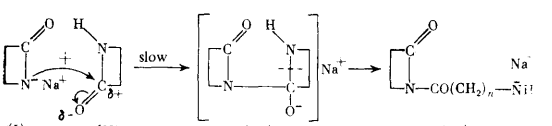
Being weak bases, lactams form salts when they interact with alkali metals, alkali metal and alkaline earth metal hydrides and amides, and organometallic compounds:



The anions formed on dissociation of salts catalyse the polymerisation of lactams.

The following mechanism of the anionic polymerisation of lactams can now be regarded as established[5-15]:

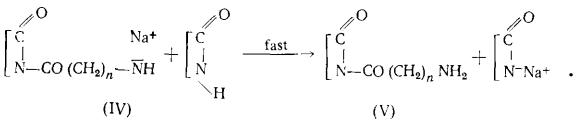
(a) The nucleophilic attack by the anion of lactam (I) on the carbonyl carbon atom of the monomer (II) results in the formation of the intermediate carbinolate anion (III), which is stabilised when the ring is opened with formation of the N-anion (IV)



(I) (II) (III) (IV)

(b) In contrast to the lactam anion, the anion of a primary amine is not stabilised. The N-anion (IV) is therefore highly reactive and rapidly reacts with the monomer, abstracting a proton from the latter. The driving force of this reaction is the appreciable difference

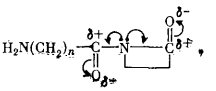
between the acidities of the amino- and amido-groups:



(IV) (V)

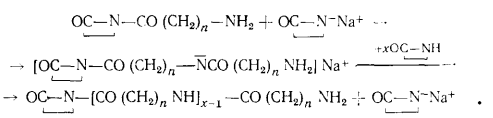
The imide dimer (V) (an *N*-substituted acyl-lactam) formed activates the propagation of the macromolecular chain.

The presence of two carbonyl groups linked to the nitrogen atom in the imide structure leads to a decrease of the resonance stabilisation of the amide linkage within the lactam ring (imide mesomerism):



which promotes an appreciable increase of the activity of the carbonyl group of the cyclic amide in relation to the nucleophilic lactam anion.

(c) Chain propagation is a reaction between the imide molecule and the lactam anion followed by a rapid proton exchange with the monomer, the anion and the terminal imide group of the growing polymer chain being regenerated in each addition step:



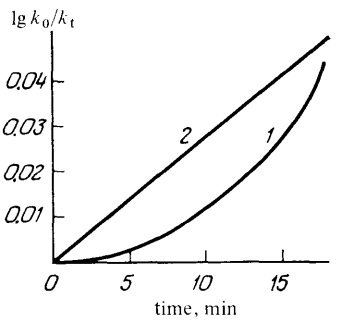
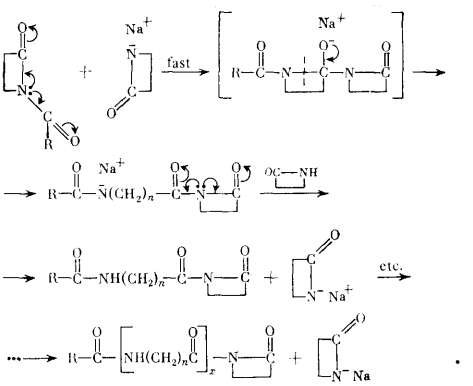


Figure 1. The rate of the anionic polymerisation of ϵ-caprolactam at 192.6°C in the presence of various additives: 1) 0.5 mole % of the sodium salt of ϵ-caprolactam; 2) 0.5 mole % of the sodium salt of ϵ-caprolactam and 0.5 mole % of tetra-acetylhexamethylenediamine [16].

The polymerisation of lactams in the presence of alkaline catalysts takes place with an appreciable induction period [16] (Fig. 1, curve *1*).

Presumably this is associated with the high activation energy for the formation of reactive compounds having the imide structure and the introduction of such compounds into the reaction system should activate the polymerisation process. This hypothesis has been confirmed by Ney and Grouther [17] and then by Šebenda and Kraličeк [16,18], who showed that the use as activators of acyl-lactams, acid chlorides, ethers, and esters, i.e. compounds containing the imide structure or capable of forming it on interaction with the lactam or its anion, eliminates the induction period and increases appreciably the rate of polymerisation of lactams (Fig. 1, curve *2*).

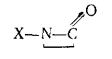
Thus, in the activated anionic polymerisation of lactams, the initial slow stage involving the nucleophilic addition of the lactam anion to the cyclic amide molecule is eliminated. In this case polymerisation begins immediately with rapid interaction of the activator molecules with the lactam anion, which is followed by the same intermediate reactions as in the non-activated polymerisation:



The scheme presented shows that the activated anionic polymerisation of lactams takes place as nucleophilic polyaddition of the lactam anion to the endocyclic carbonyl carbon atom of the imide, formed at the end of the growing macromolecule. One of the characteristic features of the anionic polymerisation of lactams is the absence of the elementary chain termination step. Theoretically, the stepwise addition of the lactam anion to the terminal imide group of the growing macromolecule can continue until the monomer is completely exhausted. However, as in polycondensation processes, this does not occur because of the influence of a number of physical and chemical factors, which include the following: the increase of the viscosity of the reaction medium, the attainment of equilibrium in the monomer–polymer system, and the decrease of catalytic activity. The change in the catalytic activity of the system during the anionic polymerisation of lactams is associated with numerous side reactions, which have been examined in detail in the excellent review by Šebenda [7].

III. CLASSIFICATION OF ACTIVATORS

It follows from the mechanism of the activated anionic polymerisation of cyclic amides examined above that the process activators are compounds having the general formula (I).



where X is an electron-accepting substituent. Evidently the activating capacity of compounds of this type will depend on the nature of the substituent at the nitrogen atom. Table 1 presents an estimate of the electrophilic properties of the substituents X capable of polarising the amide linkage within the ring. In analysing the data in Table 1, one should note that electron-accepting substituents function as a result of the presence of a positive charge on the key atom (Nos. 1 and 2) or in consequence of negative mesomeric and inductive effects (Nos. 3–9). When the

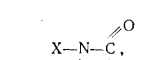
substituents are halogens (Nos. 10–13) or halogenoalkyl groups (No. 14), the strong $-I$ effect is partly compensated by a weak $+M$ effect. The combination of the two effects is reflected by the characteristic numerical Hammett (σ_n^*) and Taft (σ^*) constants.

Table 1. Estimated electrophilic properties of the substituents.

No.	Substituent R	Electronic formula	Conjugation effect	Dipole moment of C_6H_5R (Ref. 19)	σ_n^* substituent in aliphatic compound (Ref. 20)	σ_n (substituent in benzene ring) (Ref. 20)
1	$N(CH_3)_3$		$-I$; $-M$; $(+I_{CH_3})$	—	+0.859	1.90
2	NO_2		$-I$; $-M$	−4.03	+0.778	1.40
3	SO_2CH_3		$-I$; $-M$; $(+I_{CH_3})$	−4.44	+0.728	1.32
4	CN		$-I$; $-M$	−3.94	+0.628	1.30
5	$COCH_3$		$-I$; $-M$	−2.93	+0.516	0.60
6	$CO_2C_2H_5$		$-I$; $-M$; $(+I_{C_2H_5})$	−1.91	+0.522	0.71
7	COOH		$-I$; $-M$	—	+0.265	—
8	CHO		$-I$; $-M$	−2.75	+0.216	—
9	C_6H_5		$-I$; $-M$	—	+0.009	0.215
10	F		$-I$; $+M$	−1.57	+0.062	1.10
11	Cl		$-I$; $+M$	−1.57	+0.227	1.05
12	Br		$-I$; $+M$	−1.55	+0.232	1.00
13	I		$-I$; $+M$	−1.38	+0.276	0.85
14	CF_3		$-I$; $+M$	—	0.551	0.92

When the dipole moments are compared with the Hammett and Taft constants, one is bound to note a general tendency for all the electrophilic substituents listed in Table 1: an increase of the dipole moment corresponds to an increase of the constants σ_n^* and σ^*. The fact that, despite its large negative I effect, fluorine leads to a smaller value of σ_n^* than chlorine can be accounted for by its powerful $+M$ effect owing to conjugation with the benzene ring. The outer $2p$ orbitals of elements in the first Periods of the Periodic System are known[19] to be of approximately the same size as the π orbitals of double-bonded carbon. This leads to a more effective overlap of the orbitals than for heavier substituents (Cl, Br, and I).

It must be emphasised that the characteristics used to estimate the electrophilicity of substituents refer to substitution in aromatic and aliphatic series. However, the above tendency towards a change in the electrophilic properties of the substituents evidently persists also in the series of *N*-substituted lactams. Thus, it can be assumed

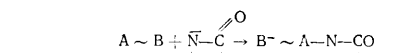
 (I)

that the whole series of compounds having the general formula (I) containing stronger electrophiles as *N*-substituents (Nos. 1–4 and 14) than the acyl group (No. 5), are effective, from the electronic standpoint, centres for the growth of macromolecules in the anionic polymerisation of lactams.

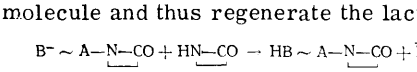
A wide series of both organic and inorganic compounds have been suggested as activators of the anionic polymerisation of lactams (see Table 2 below). Several attempts have been made at a classification of the activating compounds[6,21,22]. The influence of the geometrical and electronic structures of the above compounds on their activating capacity has been examined[8,22] and it has been suggested that activators be divided, on the basis of the nature of their action under the conditions of the anionic polymerisation of lactams, into "direct" activators, with an intrinsic activating capacity, and "indirect" activators, which interact with the lactam or its salt and form the activator.

According to Ikuzo et al.[22], activating compounds of the type A ~ B, where A and B are effective centres of the activator molecule, must meet the following requirements:

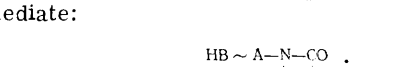
(1) A must be sufficiently electrophilic to combine with the lactam anion:



(2) The basicity of B must be sufficiently large to combine with a hydrogen atom linked to the nitrogen of the lactam molecule and thus regenerate the lactam anion:

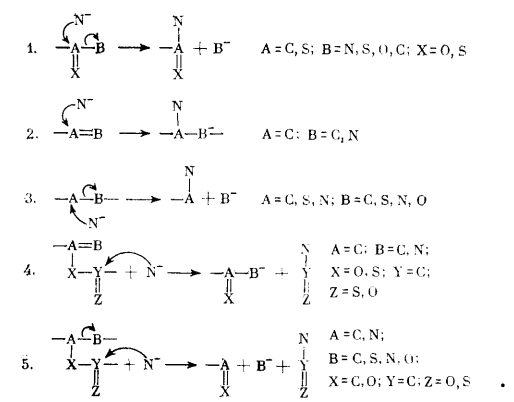


(3) A must assist in the cleavage of the C–N bond in the intermediate:



(4) The structure of A must be sterically favourable for attack by the lactam anion.

Compounds satisfying the above requirements have been divided into five types in accordance with their structure and the types of reactions leading to their formation[22]. The active centres of these compounds are shown schematically below:



The structures of many of the known types of activators (ethers and esters, *N*-alkylimides, lactaones, etc.) fit within the framework of the above requirements. In addition, Ikuzo et al.[22] tested the activating capacities of a number of other compounds, in particular a wide variety of triazine and pyridazine derivatives, azlactone derivatives, and other similar compounds. With some exceptions, the above compounds proved to be active under the conditions of the anionic polymerisation of lactams. On

Table 2. Classification of activating compounds.

No.	Class of compounds	Refs.	Suggested activation mechanism
1	(a) imides, carbamoyl-lactams, acyl-lactams	23—41	
	(b) isocyanates, isothiocyanates	42—49	$R-N=C=O+\bar{N}-CO \rightarrow R\bar{N}-CO-N-CO$
2	(a) carboxylic acid anhydrides and halides	50—58	$R-COX+\bar{N}-CO \rightarrow RCO-N-CO+\bar{X}$
	(b) halogenated linear and cyclic alkanones	59	$Cl-C-CO-C-Cl+\bar{N}-CO \rightarrow ClCCOC-N-CO+Cl^-$
	(c) organic peroxides	60	$Ar-COOOCO-Ar+\bar{N}-CO \rightarrow ArCOO-N-CO+\bar{O}CO-Ar$
3	(a) organic and inorganic acid esters	17, 60—80	$R-COO-R_1+\bar{N}-CO \rightarrow R-CO-N-CO+\bar{O}R_1$
	(b) lactones, thiolactones	81—90	$COO(CH_2)_n+\bar{N}-CO \rightarrow \bar{O}(CH_2)_n-CO-N-CO$
	(c) urethanes	91	$RNH-COOR_1+\bar{N}-CO \rightarrow RNHCO-N-CO+\bar{O}R_1$
4	(a) amides	92—99	$R-CONR_1R_2+\bar{N}-CO \rightarrow R-CO-N-CO+\bar{N}R_1R_2$
	(b) ureas, thioureas	100—103	$RNHCONHR+\bar{N}-CO \rightarrow RNHCO-N-CO+\bar{N}HR$
	(c) carbonylimidazoles	104, 105	$CH=CHN=CHNCOR+\bar{N}-CO \rightarrow RCO-N-CO+CH=CHN=CHN^-$
	(d) ketoamides	106—108	$RCORR_1R_2CONHR+\bar{N}-CO \rightarrow \begin{cases} RCOCR_1R_2CO-N-CO+\bar{N}HR \\ RNHCO-N-CO+R_1R_2C=C(\bar{O})R \end{cases}$
	(e) diketones	109—112	$RCOCH_2COR_1+\bar{N}-CO \rightarrow RCO-N-CO+CH_2=C(\bar{O})R_1$
5	(a) nitriles, CN-lactams	113, 114	$R-C\equiv N+\bar{N}-CO \rightarrow RC(=\bar{N})-N-CO$ (или $N\equiv C-N-CO+R^-$)
	(b) CN-halides	115	$R-C\equiv N+\bar{N}-CO \rightarrow \begin{cases} N\equiv C-N-CO+R^- \\ RC(=\bar{N})-N-CO \end{cases}$
	(c) dilactim ethers	116	$(CH_2)_xN=C-O-C=N(CH_2)_y+\bar{N}-CO \rightarrow (CH_2)_xN=C-N-CO+ O^-C=N(CH_2)_y \leftrightarrow OC-N^-(CH_2)_y$
	(d) cyanamides	104, 117	$NH_2-C\equiv N+\bar{N}-CO \rightarrow NH_2-C(=\bar{N})-N-CO$
	(e) carbodiimides, guanidines, imines, iminocarbonates	118—121	$ArN=C=NAr+\bar{N}-CO \rightarrow ArN=C(\bar{N}Ar)-N-CO$
	(f) azides	122	$R-N=N=N+\bar{N}-CO \rightarrow R-\bar{N}-N-CO+N_2$
	(g) triazines, pyridazines, pyrimidines, benzothiazoles	123—130	$N=CR-N=CR-N=CR+\bar{N}-CO \rightarrow N=CR-N=CR-\bar{N}=CR-N-CO$
6	(a) phosphonitrilic compounds $(PNX_2)_3$	131, 132	$N=PCl_2N=PCl_2N=PCl_2 \xrightarrow{+N-CO} N=PCl_2N=PCl_2N=PCl-N-CO+\bar{C}l$
	(b) alkylhalogenophosphines, alkyl halogenophosphites, phosphines, phosphates, phosphorus halides	133—138	$Ar-PX_2+\bar{N}-CO \rightarrow Ar-P(X)(N-CO)+X^-$; $ArPH_2+Na\bar{N}-CO \rightarrow ArP^+(H_2)(Na)\bar{N}-CO$
	(c) P_2O_5	139	$O=P-O-P=O+\bar{N}-CO \rightarrow O=P-N-CO+\bar{O}P=O$
7	oxides of Group VI elements, CO, CO_2, CS_2	140—149	$O=C=O+\bar{N}-CO \rightarrow O=C(\bar{O})-N-CO$

the basis of the results obtained, the authors concluded that there is a possibility of the specific synthesis of activators taking into account the above requirements.

However, one should note the difficulty of effecting the classification of activating compounds proposed by Ikuzo et al.[22]; by no means all activators can be described by

the proposed schematic equations (for example, cyanamides, CO, CO_2, sulphur and phosphorus halides and oxide halides, dilactim esters, diketones, etc.).

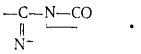
The classification of activating compounds proposed by Stehliček et al.[21] is based on their chemical structure:

(1) organic and inorganic acid esters and lactones;
(2) carboxylic acid anhydrides and halides;
(3) carboxylic acid amides, nitriles, and cyanamides;
(4) carbodiimides, isocyanates, isothiocyanates, ureas, urethanes, and guanides;
(5) derivatives of sulphonic and phosphoric acids;
(6) metal oxides and chlorides (Friedel–Crafts catalysts);
(7) other compounds such as fluoro-derivatives, organic peroxides, carbon disulphide, aromatic nitro-compounds, aliphatic polyhalides, etc.

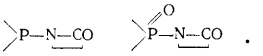
In this subdivision of indirect action activators compounds whose interaction with the lactam or its alkali metal salt leads to activating centres and side products (alcohols, acids, amines etc.) of different chemical types are included in a single class. For example, amides and nitriles, combined in a single class, interact with the lactam anion to form activating compounds having different chemical structures; the interaction of isocyanates with lactams does not lead to any side products, while urethanes, which belong to the same class according to Stehliček et al.[21], give rise to alcohols (Table 2).

We attempted to classify activators taking into account the chemical nature of the activating groups and side products formed. Table 2 includes activators of the anionic polymerisation of lactams taken from patent literature. All the compounds have been divided into seven classes, each class being further subdivided into subgroups in view of certain differences between the types of the active compounds formed within each class. Since it is impossible to specify unambiguously the mechanism of the formation of active centres, several versions of the proposed mechanism are quoted in many instances.

Compounds belonging to the first class are direct action activators, which form no side products poisoning the catalytic system and have therefore been considered separately. Compounds belonging to the second, third, and fourth classes form active centres with the same acyllactam structure. Despite this, these compounds have not been combined in a single class, since the side products formed differ in their chemical nature. Among compounds of the fifth class, the active species produced contains a group in which the nitrogen of the lactam ring is linked to an unsaturated system:



Characteristic side products are not formed for compounds of the fifth class. Phosphorus-containing compounds, forming active centres on interaction with the lactam or its anion, have been combined in the sixth class:



They give rise to acids as side products. The oxides of Group VI elements, CO, CO_2, and CS_2 have been assigned to the seventh class.

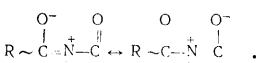
Thus, the classification which we propose for activators takes into account not only the nature of the active centre formed but also the nature of the side products, which have a significant influence on the rate of the anionic polymerisation of lactams. Thus alcohols, amines, acids, and other products arising on formation of the activating compounds lead to many side reactions, which poison the catalyst; among these, mention should be made of the decrease of the alkalinity of the system, the condensation of the aldehydes formed, the aminolysis of the reaction products, etc.

IV. THE INFLUENCE OF THE CHEMICAL STRUCTURE OF ACTIVATING COMPOUNDS ON THEIR EFFICIENCY

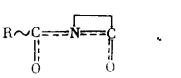
The influence of the chemical structure of activators on the rate of the anionic polymerisation of lactams has been considered in the literature mainly in relation to compounds of the acyl-lactam type. According to modern ideas[6,8–10], in the ground state of an *N*-substituted acyllactam the free electron pair of the nitrogen atom of the lactam ring can be involved in a resonance interaction with two neighbouring carbonyl double bonds (imide mesomerism),



which leads to the formation of two mesomeric forms:

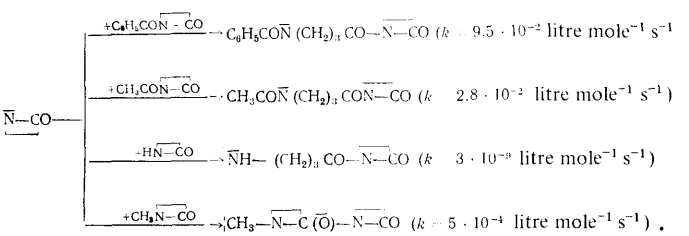


Such a resonance system can evidently be regarded as conjugated:



In the conjugated system the electron density in the endocyclic amide bond is reduced compared with a stabilised (also by resonance) lactam molecule. Evidently the electron-accepting properties of the group R tend to increase the polymerisation of the imide group in the direction of the electrophilic substituent, facilitating thereby the nucleophilic attack by the lactam anion on the increased positive charge of the endocyclic carbonyl group.

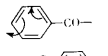
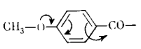
In order to elucidate the influence of the structure of a substituent at a nitrogen atom, measurements were made [150] of the rate of addition of pyrrolidinonatomagnesium bromide ($\dot{M}gBr^{-}\underline{N-CO}$) to *N*-substituted pyrrolidinones in tetrahydrofuran (THF) solution at 25 °C. The addition rate constants obtained are given below:



This method of estimating the activating capacity is in our view most correct, since it makes it possible to determine the differences in the influence of substituents in the very first stages of the interaction where the difference is most marked. Benzoylpyrrolidinone is more reactive than acetylpyrrolidinone, as can be seen from the addition rate

constants, which is probable due to the lower electronegativity of the acetyl group compared with the benzoyl group. For *N*-methylpyrrolidinone, one should expect a a lower value of k than that obtained, since the inductive effect of the CH_3 group acts in the opposite direction. However, the fact that in this instance the ring is not cleared constitutes, according to the authors[150], evidence demonstrating that compounds of this kind cannot be used as activators. The reaction of α-pyrrolidinone with its anion leads to polymerisation, despite the fact that the amine anion $H\overline{N}-(CH_2)_3CON-CO$ is not stabilised, as in the case of *N*-methylpyrrolidinone. The low addition rate constant explains the long induction periods in the non-activated polymerisation of lactams.

Table 3. Polymerisation of ϵ-caprolactam in the presence of *N*-acylcaprolactams as activators at 155°C.[151]*

Acyl group	Hardening time, s	Yield of polymer, %	Logarithmic viscosity, dl g^{-1}**
CH_3——→CO—	138	100	0.74
C_3H_7——→CO—	338	90.0	0.64
	625	81.6	0.65
	1520	18.3	0.52
$C_{16}H_{33}$—CO—	does not harden	4.5	0.25

*The percentage ratio of the activator and catalyst was 1.0:4.2.
**The viscosity was determined in a 0.5% H_2SO_4 solution at 25°C.

Scelis et al.[151] synthesised a number of *N*-acylcaprolactams, the acyl groups of which had different electronegativities (acetyl, butyryl, benzoyl, and *p*-methoxybenzoyl). The authors assumed that *N*-acyl-lactams having substituents with the most marked electron-accepting properties should exhibit the highest activity. However, the results (Table 3) showed that the size of the substituent has the dominant influence on the rate of the anionic polymerisation of lactams. The highest activity is manifested by *N*-acylcaprolactams with the smallest acyl groups. The effect associated with the electron-accepting properties of substituents is shown, according to authors[151], to a much smaller extent.

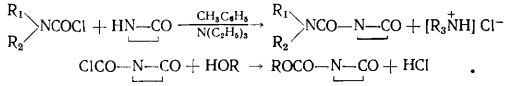
We believe that an estimate of the activating capacity on the basis of parameters such as the time of the onset of thickening, the degree of conversion, and the logarithmic viscosity of a dilute polymer solution is not altogether correct. It follows from the polymerisation mechanism that acyl groups exert the greatest influence on the reactivity of the carbonyl moiety of the imide group of the lactam in the first steps of the addition of the lactam anion.

Stehlíček et al.[152] investigated the influence of the structure of the acyl group on the rate of anionic polymerisation of ϵ-caprolactam by measuring the initial rate of polymerisation at a rigorously defined temperature (100° ± 0.2°C) and a concentration of the catalytic system of 0.2 mole %. The relative activating capacity was estimated from the time of the appearance of turbidity in the polymerising system and the following data were obtained for a number of *N*-acyl-lactams:

Group	CH_3	C_3H_7	C_4H_9	C_5H_{11}	C_6H_5	$CH_3OC_6H_4$
Time, min	13.8—14.5	14.3	17.2	14.7	14.1—16.3	16.5—17.2

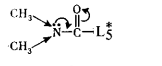
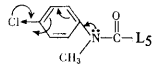
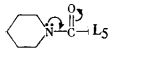
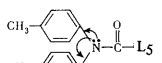
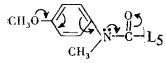
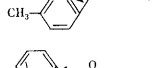
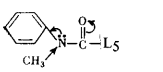
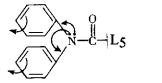
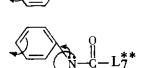
It was noted that anionic polymerisation activated by alkyl-imides obtained from aromatic carboxylic acids is much faster in the first seconds than in the presence of aliphatic acyl-lactams, but 30 s from the start of polymerisation the two rates become virtually equal.

Falkenstein and Dörfel[8] obtained disubstituted carbamoyl-lactams and esters of lactam-*N*-carboxylic acids via the mechanism



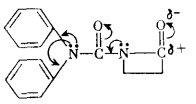
Examples of both classes of compounds proved to be effective activators of the anionic polymerisation of lactams at 120–150°C, and it was possible to vary the activating capacity of disubstituted carbamoyl-lactams and lactam-*N*-carboxylic acid esters within wide limits by the introduction of specific substituents. In order to estimate the efficiencies of the activators obtained, measurements were made of the time from the instant of mixing of the reagents to the onset of thickening and the results were compared with the basicity constants pK_b of the secondary amines used to obtain, *N*,*N*-disubstituted carbamoyl-lactams (Table 4).

Table 4. Dependence of the rate of polymerisation (thickening time) on the chemical structure of disubstituted carbamoyl-lactams[8].

Activator	Thickening time, min		pK_b for initial amine	Activator	Thickening time, min		pK_b for initial amine
	120°	150°			120°	150°	
	—	—	0.5		3.8	0.94	10.5
	—	—	0.9		1.85	0.5	13.4
	10	4.3	8.0		1.45	0.4	14.4
	7.8	2.5	9.1		1.1	0.2	14.4
	7.2	1.8	9.2		1.0	0.15	15

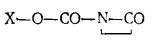
*L_5 = α-pyrrolidinone.
**L_7 = ϵ-caprolactam.

It follows from Table 4 that the activating effect of the compounds under consideration depends significantly on their chemical structure. Carbamoyl-lactams with aliphatic or alicyclic substituents at the exocyclic nitrogen atom (*N*,*N*-dimethyl, piperidinyl) do not activate the anionic polymerisation of lactams at all. The introduction of phenyl substituents leads to the appearance of an activating capacity in carbamoyl-lactams. This influence of the phenyl substituent is attributed [8] to the increase of the polarisation of the carbamoyl-lactam under the influence of the benzene ring in consequence of its negative inductive and mesomeric effects.

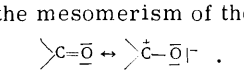


The rate of polymerisation depends both on the number of phenyl substituents and on the nature of the substituents in the benzene ring (if such are present).

In lactam-*N*-carboxylic acid ester



the activating effect diminishes with increase of the electronegativity of the substituent X (Table 5). It is believed [8] that the cause of this may be that the electronegative substituent X opposes the involvement of the polar structure in the mesomerism of the carbonyl group:



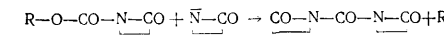
Thus the C...O bond order increases and the absorption band of the carbonyl group undergoes a bathochromic shift, as can be seen from Table 5. This corresponds to a decrease of the polymerisation of the amide bond in the lactam owing to the inductive effect, which leads to a weakening of the activating influence of the electronegative substituents.

Table 5. Dependence of the rate of polymerisation (thickening time) on the chemical structure of lactam-*N*-carboxylic acids [8].

Activator	Thickening time, min		ν_{CO}, cm^{-1}	Activator	Thickening time, min		ν_{CO}, cm^{-1}
	120°	150°			120°	150°	
ClC_6H_4—O—CO—L_5*	—	—	1726	$C_6H_5CH_2$—O—CO—L_5	1.25	0.25	1720
FC_6H_4—O—CO—L_5	—	—	1725	L_5CO—O—$(CH_2)_4$—O—COL_5	1.15	0.15	1710
$CH_3C_6H_4$—O—CO—L_5	—	—	1725	C_2H_5—O—CO—L_5	1.1	0.15	1717
C_3H_7—O—CO—L_5	1.5	0.5	1718	L_5CO—$O(CH_2)_6$—O—COL_5	1.1	0.1	1710
C_3H_7—O—CO—L_7**	1.4	0.3					
CH_2=CH—CH_2—O—COL_5	1.3	0.3	1720	L_7CO—$O(CH_2)_4$—O—CO—L_7	1.0	0.09	1708

*L_5 = ε-caprolactam.
**L_7 = η-caprinolactam.

Unfortunately Falkenstein and Dörfel [8] did not investigate the activating capacity of lactam-*N*-carboxylic acid esters as a function of the concentration of the catalyst; nor are data available about the isolation of any intermediates in the polymerisation process. The authors' explanation of the mechanism of the action of activators of this kind is therefore not sufficiently well founded. In all probability the activating effect of lactam-*N*-carboxylic acid esters should be sought in the possible interaction of the latter with the lactam or its anion (by analogy with carboxylic acid esters—see Table 2):



which leads to the exhaustion of the alkaline process catalyst. The acidity of the alcoholic residue will then play the main role in interaction with the process catalyst.

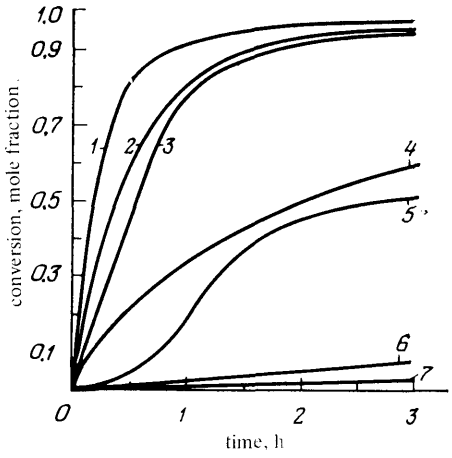
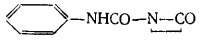


Figure 2. Time variation of the degree of conversion in the anionic polymerisation of ε-caprolactam at 130°C; [155] [NaH] = 0.0067 (mole fraction): 1) *N*-benzoyl-ε-caprolactam; 2) diisopropylcarbodiimide; 3) phenyl isocyanate; 4) *N*-acetyl-ε-caprolactam; 5) 1,3-diphenylurea; 6) 1,3-diethylurea; 7) n-butyl acetate.

Stehlíček et al. [21] showed in relation to a large class of compounds used as activators that, when the activating compounds interact with the lactam or its anion, the side products formed have an inhibiting influence on the rate of anionic polymerisation of lactams. Among the large number of compounds proposed as activators, only *N*-acyl-lactams and the products of the interaction of mono- and poly-functional isocyanates with lactams have therefore been widely used hitherto [153,154].

It is noteworthy that the conditions in the polymerisation of lactams have an appreciable influence on the nature of the action of activators of both direct and indirect types. A study [155] undertaken to estimate the relative activating capacities of various compounds used in the anionic polymerisation of lactams is of definite interest in this connection. Figs. 2 and 3 present kinetic curves for the variation of the degree of conversion with time in the presence of various activators of the anionic polymerisation of ε-caprolactam at 130° and 180°C. It is seen that the activating capacity of benzoylcaprolactam is higher than that of acetylcaprolactam, particularly at low polymerisation temperatures. The reaction of phenyl isocyanate with ε-caprolactam takes place with formation of phenyl-substituted carbamoyl-ε-caprolactam



by direct addition without the isolation of side products. Despite the intermediate stage, the initiation reaction is in this case (both at 130° and 180°C) appreciably faster than in the reaction involving acetylcaprolactam.

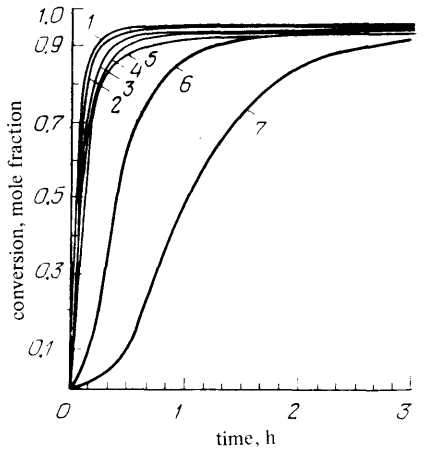


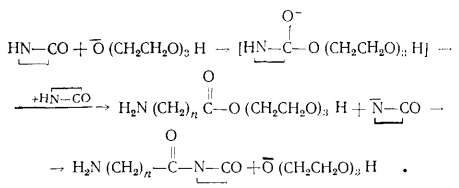
Figure 3. Time variation of the degree of conversion in the anionic polymerisation of ϵ-caprolactam at 180°C;[155] [NaH] = 0.0067 (mole fraction); mole fraction of activator 0.0067: 1) diisopropylcarbodiimide; 2) *N*-benzoyl-ϵ-caprolactam; 3) phenyl isocyanate; 4) *N*-acetyl-ϵ-caprolactam; 5) 1,3-diphenylurea; 6) 1,3-diethylurea; 7) n-butyl acetate.

sym-Ureas are known[21] to decompose at high temperatures to isocyanates and amines. The reduced effect of activators of this kind is determined by the basicity of the amined formed. In the case of aniline the free electron pair of the nitrogen atom is stabilised by the $-I$ and $-M$ effects of the benzene ring and the basicity of the amino-group is reduced. *sym*-Diphenylurea is therefore a more effective activator than 1,3-diethylurea, particularly at low polymerisation temperatures.

n-Butyl acetate gives rise to a longer induction period both at 130° and at 180°C. However, at the higher polymerisation temperature in the presence of n-butyl acetate it is possible to attain a high degree of conversion, comparable with the values obtained in the presence of *N*-acetyl-ϵ-caprolactam. When the n-butyl group is replaced by the t-butyl, phenyl, or isopropyl group, the activating capacity of the ester increases[21].

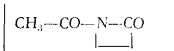
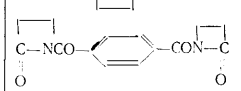
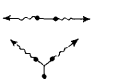
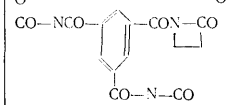
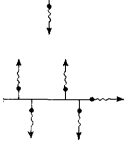
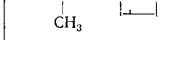
According to Stea and Gechell[155], diisopropylcarbodiimide has a high activating capacity over the entire temperature range. Its activating influence can be accounted for in two ways: by the interaction of the carbodiimide with an acid hydrogen atom (traces of water), leading to the formation of *sym*-dialkylureas[156], or by the addition to the carbodiimide of the lactam or its anion with formation of a polar substituent at the lactam nitrogen[21].

The fact that alcohols, which were usually regarded as inhibitors of the polymerisation of lactams, behave at the same time as its activators is of special interest. The use of alcohols as activators of the anionic polymerisation of lactams was first reported by Čefelin et al.[157] and then Mermoud[158] used triethylene glycol as the activator and obtained a product with a high degree of polymerisation. The problem of the use of alcohols for the activation of the polymerisation of lactams was investigated in detail by Sekiguchi[159]. His results show that activation under the influence of alcoholic hydroxyl is due to the imide groups formed as a result of the esterification (decyclisation) of the lactam molecules:



Sekiguchi[6] established experimentally that the activating capacity of alcohols depends to a large extent on the acidity of the alcoholic hydroxyl. Apart from triethylene glycol, an activating capacity is shown, according to his data, by diethylene glycol, 1-octanol, tetradecanol, s- and t-butyl alcohols, etc. We believe that, on the basis of Sekiguchi's mechanism of activation, alcohols should be regarded as catalysts of the anionic polymerisation of lactams, since the growing polyamide chain does not contain an alcoholic radical.

Table 6. The direction of the growth of macromolecular chains in the anionic polymerisation of ϵ-caprolactam in the presence of mono- and poly-functional activators[167].

Activator	Structural formula	Functionality	Schematic illustration of the direction of the macromolecular chain growth
N-Acetyl-ϵ-caprolactam		1	
N,N'-Isophthaloyl-bis-ϵ-caprolactam		2	
N,N',N''-Trimesoyl-ter-ϵ-caprolactam		3	
N-Methacryloyl-ϵ-caprolactam		>3	

V. THE INFLUENCE OF THE FUNCTIONALITY OF ACTIVATORS ON THE MOLECULAR STRUCTURE OF THE POLYMERS FORMED

The activators of the anionic polymerisation of lactams not only accelerate the polymerisation process but also constitute an effective means for the specific regulation of the molecular structure and hence of the properties of the polyamides formed[34,35,160–166].

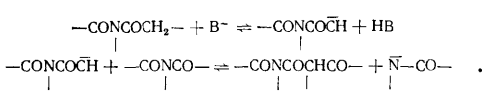
The majority of the activators considered above contain one functional group which ensures the activation and growth of the polymer chain in one direction and this leads to the formation of polymers having a predominantly linear structure. The use in the polymerisation of lactams of

polyfunctional activators, i.e. compounds containing several activating functional groups in their molecule, leads to the formation of polyamides of "star" or "comb" type[165,167]. Thus the direction of growth and the number of growing chains of the macromolecules are related to the disposition and number of the functional groups in the activator molecule. This is illustrated schematically in Table 6.

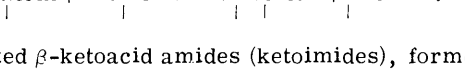
However, one should note that the polyamides obtained in the presence of monofunctional activators are not linear polymers in the strict sense of the term. It is known[165, 168-171] that the synthesis of polyamides is accompanied by side reactions leading to the formation of polymers with a low degree of branching. The degree of branching of these polyamides is determined in the study of their molecular weight distribution[165,168,169] and from end group analysis[170,171]. It was shown that the number of end groups in the polyamide macromolecules formed in the presence of a monofunctional activator is greater than two[170,171] and that the molecular weight distribution in such polyamides is broad owing to branching reactions occurring at late stages of the process[165,168,169].

The molecular structure of the polyamides obtained in the presence of polyfunctional activators is more complex. In this case the branching of the polyamides is caused, on the one hand, by the functionality of the activator (Table 6) and, on the other, it is due to the same side reactions which occur also in the formation of polyamides in the presence of monofunctional activators. In the presence of polyfunctional activators the products are polyamides containing, apart from soluble macromolecules, also insoluble macromolecules[34,35,161-166], which is associated with the three-dimensional structure of the latter[165,166,172]. In a study of the molecular structure of soluble specimens of polycaproamide in the initial stages of the polymerisation (up to the instant of gel formation) Pavlova showed[165] that the test specimens contain two groups of fractions—with higher and lower degrees of branching. The molecular weight distribution obtained by Pavlova et al.[165] from fractionation data revealed the presence of two maxima corresponding to narrow and broad distributions. The narrow distribution was explained by the presence in the polyamide chain of macromolecules with non-random branching due to the polyfunctionality of the activator, while the broad distribution was attributed to the presence of macromolecules with random branching[165]. The presence of the above two molecular structures in the polyamides formed—with random and nonrandom branching—can probably be explained by the occurrence of side reactions during the formation of the polyamides.

The reactions which can lead to branching under the conditions of the activated polymerisation of lactams can probably also lead to the formation of cross-linked macromolecules. Wichterle[173] and Šebenda[174] showed in model reactions that in an alkaline medium the imide groups of the compounds undergo the Claisen condensation when the α-carbon atom in the molecule is linked to at least one hydrogen atom:

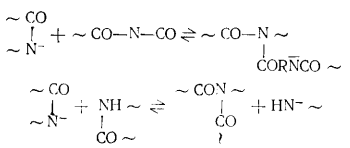


The *N*-acylated β-ketoacid amides (ketoimides), formed as a result of the above reaction, can react with the growing acyl-lactam centres and can lead to the formation of ketoimides of various structures[175,176]. When cyclic ketoimides interact with the lactam anion, they can be converted into ketoamides[176]:



Both ketoamides and ketoimides, containing reactive groups ($>C=O$, $-CH_2-$, $-\underset{|}{CH}-$) can lead to a large number of different compounds under the conditions of the anionic polymerisation of lactams, particularly to hydroxypyridine and uracil derivatives[173], which can serve in their turn as centres for branching and cross-linking in the polymers produced.

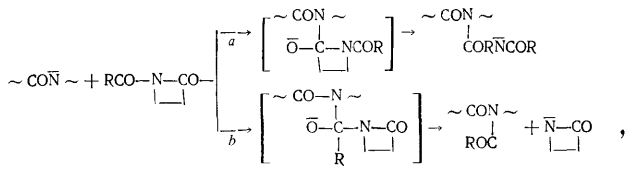
Wichterle and coworkers[177,178] and Šebenda[7] suggested that the branching of macromolecules in the anionic polymerisation of lactams can be caused by reactions of the type



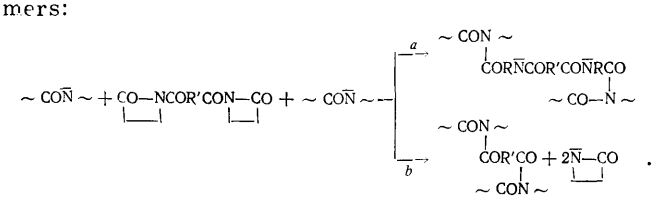
in addition to the side reactions mentioned above.

The above results indicate the possibility of branching and cross-linking in polyamides when the anionic polymerisation of lactams is carried out in the presence of monofunctional and polyfunctional activators. However, when the polymerisation of ϵ-caprolactam was performed in the presence of monofunctional activators (with different proportions of the components of the catalytic systems and at different concentrations) the formation of insoluble polyamides was not observed. Thus the above literature data do not fully explain the cause of the formation of cross-linked polyamides in the presence of polyfunctional activators.

Frunze et al.[172] relate the cause of the formation of cross-linked polyamides to the presence in the growing polyamide macromolecules of terminal acyl-lactam groups capable of reacting with the amide groups of other macromolecules. They showed, for the model reaction of a polyamide (G-669) with mono- and poly-functional activators, simulating the reactive end-groups of the growing polyamide chains, that the reactions of the polyamide with monofunctional activators lead to the formation of *N*-substituted polyamides only:



while the reactions of the polyamide with bifunctional activators result in the formation of cross-linked polymers:



It was shown later[175] that pathways *a* and *b* of the above reactions depend to a large extent on temperature.

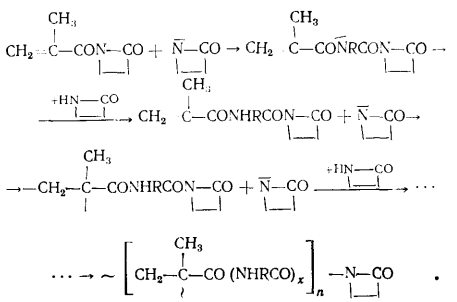
The literature data concerning the study of the molecular structures of polyamides, which were examined above, permit the conclusion that in the presence of monofunctional activators the products are linear polyamides with a low degree of branching, while in the presence of polyfunctional activators partially cross-linked polyamides with random branching are formed, the degree of branching increasing with increasing functionality of the activators [165].

N,*N*'-Acylbislactam (*N*,*N*'-isophthaloyl-, *N*,*N*'-terephthaloyl-, *N*,*N*'-adipoyl-, and *N*,*N*'-sebacoyl-biscaprolactams) were first used as bifunctional activators by Korshal et al. [160] in the anionic polymerisation of ε-caprolactam. They established that, depending on the concentration of the catalytic system, soluble or insoluble polyamides are formed and that, when a mixture of the above acylbislactams with a monofunctional activator in different proportions is used, it is possible to regulate fairly readily the molecular weight of the polymers produced [60]. *N*,*N*'-Diacylbislactams have now found extensive applications in the activation of the anionic polymerisation of lactams [32, 100, 114]. Diisocyanates [35-47, 164, 180], in the presence of which soluble polyamides with a high strength are formed, are widely used as bifunctional activators.

N,*N*',*N*''-Trimesoylter-ε-caprolactam, in the presence of which polyamides with randomly branched and partly cross-linked structures are formed, was used for the first time as a trifunctional activator for the polymerisation of ε-caprolactam [35, 161]. It was shown [161] that the polyamides obtained in the presence of the trifunctional activator are more elastic and have a higher impact strength than the polyamides obtained in the presence of a monofunctional activator.

Muller [181] suggested that cyanuric chloride be used as an activator of the anionic polymerisation of α-pyrrolidinone. According to the author, three chlorine atoms in cyanuric chloride are substituted by α-pyrrolidinone and the resulting triazine derivative of α-pyrrolidinone act as an effective trifunctional activator of the anionic polymerisation of the lactam.

The use of acyl-lactams containing unsaturated groups as activators of the anionic polymerisation of lactams is of great interest. Such activators include *N*-methacryloyl-ε-caprolactam [34, 162, 163]. Formally, *N*-methacryloyl-ε-caprolactam can be classified as a monofunctional activator, since its molecule contains only one imide functional group. However, the polyfunctional nature of this activator is manifested in the course of the polymerisation of lactams, as can be seen from the polymerisation mechanism [162, 163]:



It is noteworthy that *N*-methacryloyl-ε-caprolactam does not polymerise in the process involving the double bonds via either a radical or an ionic mechanism [182]. The adduct *N*-methacryloyl-(ε-aminocapryloyl)-ε-caprolactam, formed as a result of the first step in the polymerisation of ε-caprolactam, polymerises via the double bonds, which leads to the formation of a polyfunctional activator [162, 163, 183].

As in the presence of the trifunctional activator *N*,*N*',*N*''-trimesoylter-ε-caprolactam, in the presence of *N*-methacryloyl-ε-caprolactam the products are insoluble polyamides which are randomly branched and partly cross-linked polymers with high strength. Table 7 shows that the physicomechanical properties of the polyamides depend on the functionality of the activator used. The impact strength of the polyamides synthesised using polyfunctional activators is much higher than that of the polymers obtained with *N*-acetyl-ε-caprolactam.

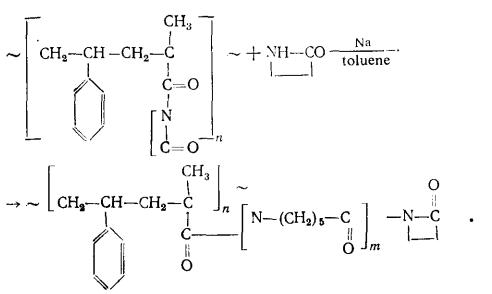
Table 7. Certain physicomechanical characteristics of polycaproamide obtained in the presence of activators with different functionalities relative to lithium Kapron B [162, 163, 184]

Activator	Content of fraction insoluble in HCOOH, wt.%	Ultimate strength, kgf cm^{-2}		Specific impact strength, kgf cm^{-2}
		on static bending	on compression	
N-Acetyl-ε-caprolactam	0	1300—1500	1100	100—150
N,*N*'-Isophthaloylbis-ε-caprolactam	0	1200—1400	1100	250—350
N,*N*',*N*''-Trimesinoylter-ε-caprolactam	60—70	1200—1400	1000	does not break
	40—50	1400—1500	—	does not break
N-Methacryloyl-ε-caprolactam	0	900	—	150—170
Kapron B				

Thus the data examined above permit the conclusion that the functionality of the activators has a significant influence on the molecular structure and properties of the polymers formed.

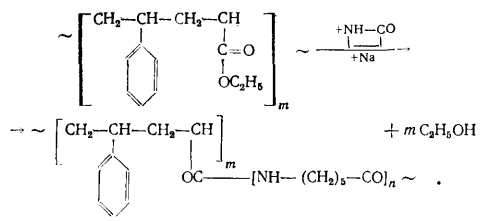
VI. MACROMOLECULAR ACTIVATORS OF THE ANIONIC POLYMERISATION OF LACTAMS

The use of polymeric molecules of different chemical types, containing acyl-lactam, isocyanato-, acid chloride, cyano-, and certain other functional groups, as activators of the anionic polymerisation of lactams leads to the formation of graft and block copolymers. This leads to the possibility of a specific regulation of the properties of the polymeric materials formed. Depending on the positions of the activating groups in the macromolecular chain of the activator, graft or block copolymers are produced. Thus Wichterle and Gregor [182] grafted ε-caprolactam to a copolymer of styrene and *N*-methacryloyl-ε-caprolactam containing acyl-lactam groups:



Korshak and coworkers[185-188] developed a method for the copolymerisation of styrene with ε-caprolactam in bulk to aid the chemical moulding of large articles. According to this method, in the first stage styrene undergoes radical copolymerisation with catalytic amounts of *N*-methacryloyl-ε-caprolactam in solution in ε-caprolactam. In the second stage ε-caprolactam is grafted to the macromolecular activator formed in the reaction mixture. The authors showed that an increase of the content of polystyrene units in the copolymer greatly increases the water resistance of the material but its strength (particularly the specific impact strength) decreases.

Graft copolymers have been obtained[189] by the anionic polymerisation of ε-caprolactam in the presence of a copolymer of styrene with ethyl acrylate, the ester group of which activates the polymerisation of the cyclic amide:



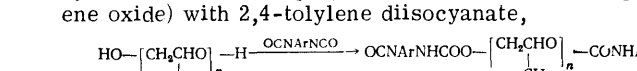
If the styrene–ethyl acrylate copolymer contains more than 1 wt.% of ethyl acrylate, a cross-linked insoluble product is formed, which the authors[190] explain by the presence of a tertiary carbon atom in the α-position relative to the ester group.

The grafting of α-pyrrolidinone[191] and ε-caprolactam[192] to poly(acryloylchloride) has been described:

It was noted that fibres and films with a high strength can be obtained from the graft copolymers of acrylic acid with ε-caprolactam and α-pyrrolidinone thus synthesised.

The use of acyl-lactam, acid chloride, isocyanato-, and other groups at the ends of macromolecules of different chemical type for the activation of the polymerisation of lactams in order to obtain block copolymers is known. In this case block copolymers with the structure A–B–A, in which the two outer segments A are polyamide units and the inner segment B is some other polymer, are as a rule obtained. The molecular weight of the inner segments and the ratio of the macromolecular activator and the lactam giving rise to the polyamide units of the outer segments vary within wide limits, which makes it possible to vary also the properties of the block copolymers. The use of polyethers and polyesters[193-196], polythioethers[196], polycarbonates[196], polybutadienes[197-199], polystyrene[197], [200-202], polysulphone[203], and polyamides of other chemical types[204-207] as the inner segments of block copolymers has been reported.

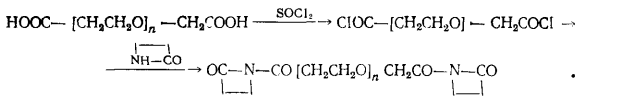
For example, a method has been described for the synthesis of block copolymers[196] by treating poly(propylene oxide) with 2,4-tolylene diisocyanate,



and subsequent polymerisation of ε-caprolactam in the presence of the resulting polymeric activator. It has been pointed out[196] that, apart from polyesters and polyethers, polythioethers, polyamides, and polycarbonates containing the following terminal functional groups can be used as the internal polymeric segment in the synthesis of block copolymers:

ε-caprolactam, ξ-oenantholactam, η-caprinolactam, ω-dodecylactam, and their *C*-substituted derivatives have been used as the lactam components.

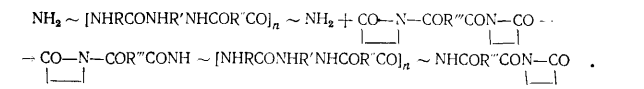
According to another procedure[193], the terminal carboxy-groups of poly(ethylene glycol) are initially converted into acyl chloride groups by reaction with thionyl chloride in solution in xylene and then into acyl-lactam groups as a result of reaction with ε-caprolactam in the presence of pyridine:



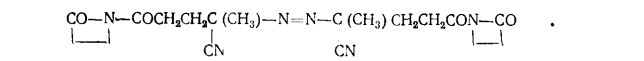
The compound obtained is used as a macromolecular activator of the anionic polymerisation of ε-caprolactam. The block copolymer formed has antistatic properties which are improved compared with those of polycaproamide.

Jamashita et al.[194] used poly(tetramethylene glycol) with terminal chloroformate groups, obtained by treating the terminal hydroxy-groups with phosgene, as the polymeric activator of the anionic polymerisation of α-pyrrolidinone and ε-caprolactam. As polymerisation proceeds in the presence of the above polymeric activator, the authors observed an increase in the degree of conversion of the lactam and an increase of the intrinsic viscosity of the block copolymer formed. A linear relation was observed between the logarithm of the intrinsic viscosity and the logarithm of the degree of conversion of the lactam, which indicates, according to the authors[194], the absence of a chain termination reaction. The comparatively low concentration of the polymeric activator (2–4%) indicates a fairly high efficiency of poly(tetramethylene glycol) bischloroformate as an activator of the polymerisation of lactams.

Lincoln[204] used the reaction of the terminal amino-groups of the mixed polyamide 6/66 with *N*,*N*′-acylbislactam in order to obtain a polymeric activator for the synthesis of a block polyamide:



Polystyrene with terminal *N*-acylpyrrolidinone groups[201], synthesised by the radical polymerisation of styrene using 4,4′-azobis(pyrrolidinono-4-cyanovalerate) as the initiator, proved to be an effective activator of the polymerisation of α-pyrrolidinone:



The linear increase of molecular weight with increasing degree of polymerisation of α-pyrrolidinone as well as the increase in the degree of conversion and of the intrinsic viscosity with time confirmed, according to the authors[201], the stepwise chain propagation and the absence of chain termination during polymerisation. The authors do not quote any information about the activation of the anionic polymerisation of the lactam involving the inner –C≡N groups of the macromolecular activator.

Korshak and coworkers [205,206] described the synthesis of block copolymers involving the interaction of an N,N'-acylbislactam with a diamine in an ϵ-caprolactam melt,

$$(n+1)\ \underset{\llcorner__\lrcorner}{\mathrm{CO{-}NCOC_6H_4CON{-}CO}} + n\ \mathrm{NH_2R'NH_2} \rightarrow$$

$$\rightarrow \underset{\llcorner__\lrcorner}{\mathrm{CO{-}NCOC_6H_4CO{-}}}\ [\mathrm{NHR'NHCOC_6H_4CO}]_n\ \underset{\llcorner_\lrcorner}{\mathrm{{-}N{-}CO}} + 2n\ \underset{\llcorner__\lrcorner}{\mathrm{NH{-}CO}},$$

with subsequent sodium-catalysed polymerisation of ϵ-caprolactam via the terminal acyl-lactam groups of the resulting polymeric activator. It was established that, with increase of the content of the polymeric activator in the reaction mixture, the degree of conversion of ϵ-caprolactam increases and the thickening time diminishes, which indicates an increase of the rate of polymerisation. When the ratio of the initial polymers is altered, block copolymers of the type A–B–A with different lengths of the segments are formed; this is also indicated by a change in the intrinsic viscosity and melting point of the resulting copolymers.

Very interesting and very promising studies have been made on the synthesis by anionic polymerisation of block copolymers of polybutadiene, containing terminal isocyanato-groups, with a lactam [197-199]. The presence of unsaturated double bonds in the butadiene segment,

$$\sim [\mathrm{CO(CH_2)_5\ NH}]_m\ \mathrm{{-}CONH{-}}\ [\mathrm{CH_2CH{=}CH{-}CH_2}]_n\ \mathrm{{-}NHCO{-}}\ [\mathrm{NH(CH_2)_5CO}]_m \sim$$

leads to further possibilities for the modification of the products. The authors [197] note the exceptionally high elasticity of the butadiene block copolymers even when the content of the ϵ-caprolactam units is up to 70–80%. It was shown that the plasticity of this polymer depends on the molecular weight of the polycaproamide segments. The high degree of conversion (~98% with respect to ϵ-caprolactam) shows that the macromolecular butadiene activator is highly effective. The impact strength, determined for hardened block copolymers with the above structure, increases with increasing content of the lactam units and increases sharply when the latter is more than 50%, which the authors [198] attribute to the higher impact strength of polycaproamide compared with the hardened polybutadiene. At the same time, the bending strength changes insignificantly with increasing fraction of polycaproamide in the block copolymer.

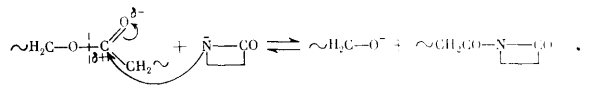
Thus the data presented concerning the use of macromolecular activators in the anionic polymerisation of lactams permit the following conclusions.

1. Prepolymers containing the $-O-$, $-COO-$, $-COCl$, $-CSCl$, $-SO_2Cl$, $-OCOCl$, $>C{=}C{=}O$, $-N{=}C{=}O$, $-\underset{\llcorner_\lrcorner}{\mathrm{CON{-}CO}}$, etc. functional groups are effective activators of the anionic polymerisation of lactams.

2. The activating capacity of compounds of this kind is determined mainly by the nature of the functional group and not the length and nature of the macromolecular chain.

3. The properties of graft and block copolymers depend both on the activator : lactam ratio and on the nature of the macromolecular chain of the polymeric activator.

The anionic polymerisation of lactams can be activated not only by the functional groups at the ends of the macromolecules but also by the functional groups which are fragments of the main polymer chain. Thus it has been reported [207,208] that polyesters and polyethers can be used as activators of the anionic polymerisation of lactams. As a result of nucleophilic attack by the anion of the ester group, the heterobond is dissociated with chain transfer to the lactam molecule:



This case constitutes an example of chain transfer reactions with dissociation, which are common in the polymerisation of heterochain monomers [209]. As the interchain exchange reactions proceed, the block copolymers formed at the beginning of the process can be converted into a statistical polymer. For example, Korshak and Frunze [210] established that, when a mixture of homopolyamides is heated, a block copolymer is formed initially; the interchain exchange reactions gradually reduce the size of the blocks and the system attains a state of equilibrium characterised by the most probable distribution of the monomeric units in the copolymer.

It has been noted [206] that, when the anionic polymerisation of ϵ-caprolactam is carried out in the presence of polyhexamethyleneisophthalamide with terminal N-acyllactam groups at 140° and 180°C, the products are block copolymers whose intrinsic viscosities differ appreciably [η_{int} (140°) > η_{int} (180°)]. The authors explain the difference between the viscosity characteristics [206] by the fact that at 140°C the exchange reactions leading to interchain exchange and ultimately to the formation of block copolymers with a less regular structure proceed much more slowly than in the polymerisation at 180°C.

Taking into account the set of the possible exchange reactions in the anionic polymerisation of lactams in the presence of macromolecular activators, one must bear in mind that in practice one cannot obtain a "pure" block copolymer of the type A–B–A. In reality, under the influence of the interchain exchange, the system may contain, together with the block copolymer formed, also a graft copolymer and a mixture of homopolymers. The chemical structure of the products will be determined in each specific instance by the process conditions, i.e. by the nature of the macromolecular activators and the lactam, their proportions, temperature, reaction time, etc.

REFERENCES

1. V.V. Korshak, V.A. Kotel'nikov, V.V. Kurashev, and T.M. Frunze, Uspekhi Khim., **45**, 1673 (1976) [Russ. Chem. Rev., No. 9 (1976)].
2. R. Huisgen, H. Brade, H. Walz, and I. Grogger, Chem. Ber., **90**, 1437 (1957).
3. H.C. Brown, J.H. Brenster, and H. Schechter, J. Amer. Chem. Soc., **76**, 467 (1954).
4. N.V. Mikhailov, M.V. Shablygin, and D.N. Shigorin, Dokl. Akad. Nauk SSSR, **170**, 1364 (1966).
5. R.C.P. Cubbon, Makromol. Chem., **80**, 44 (1964).
6. H. Sekiguchi, Nippon Kagaku Zasshi, **88**, 577 (1967); Uspekhi Khim., **38**, 2075 (1969) [Russ. Chem. Rev., No. 12 (1969)].
7. J. Šebenda, J. Macromol. Sci. Chem., **A6**, 1145 (1972).
8. G. Falkenstein and H. Dörfel, Makromol. Chem., **127**, 34 (1969).
9. N. Ogata, J. Polymer Sci., **A1**, 3151 (1963).
10. N. Ogata, Bull. Chem. Soc. Japan, **34**, 245 (1961).
11. N. Ogata, K. Sanui, and K. Konishi, Kobunshi Kagaku, **30**, 202 (1973).
12. G. Reinisch, Faserforsch. u. Textiltechn., **13**, 95 (1962).

13. G. Reinisch, Faserforsch. u. Textiltechn., **14**, 468 (1963).
14. K. Gehrke, Faserforsch. u. Textiltechn., **13**, 556 (1962).
15. M. Rothe, Angew. Chem., 77, 512 (1965).
16. J. Šebenda and J. Kraličeк, Coll. Czech. Chem. Comm., 26, 3028 (1961).
17. W. O. Ney and M. Grouther, US P. 2 739 959 (1953); Chem. Abs., 50, 13 504 (1956).
18. J. Šebenda and J. Kraličeк, "International Symposium on Macromolecular Chemistry, Section III, Wiesbaden, 1959", p. 6.
19. C. K. Ingold, "Theoretical Principles of Organic Chemistry [Structure and Mechanism in Organic Chemistry?] (Translated into Russian), Izd. Mir, Moscow, 1973, p. 111.
20. M. S. Newman (Editor), "Steric Effects in Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1960, pp. 573, 595.
21. J. Stehliček, J. Šebenda, and O. Wichterle, Coll. Czech. Chem. Comm., 29, 1236 (1964).
22. T. Ikuzo, S. Atuo, and G. Tochitaka, "International Symposium of Macromolecular Chemistry, Preprints of Scientific Papers, Tokyo, 1966", pp. 1–255.
23. Japanese P. 20 526 (1964); Ref. Zhur. Khim., 11S251 (1967).
24. Czech P. 113 917 (1965); Ref. Zhur. Khim., 24S314 (1966).
25. DDR P. 31 761 (1964).
26. Japanese P. 8760 (1973); Ref. Zhur. Khim., 5S338 (1974).
27. Australian P. 259 535 (1965).
28. BRD P. 1 175 434 (1965).
29. Japanese P. 8516 (1969); Ref. Zhur. Khim., 12S598 (1970).
30. B. P. 1 136 392 (1968).
31. B. P. 903 261 (1962); Chem. Abs., 57, 16 890 (1962).
32. B. P. 1 063 292 (1967).
33. USSR P. 160 312 (1964); Ref. Zhur. Khim., 16S285 (1966); Byul. Izobret, No. 3, 53 (1964).
34. USSR P. 255 558 (1969); Byul. Izobret., No. 33, 94 (1969).
35. USSR P. 168 017 (1964); Byul. Izobret., No. 3, 63 (1965).
36. Czech P. 142 159 (1971); Ref. Zhur. Khim., 20S352 (1972).
37. US P. 3 138 576 (1964).
38. US P. 2 326 817 (1966).
39. BRD P. 1 163 541 (1965).
40. BRD P. 3 671 500 (1972).
41. BRD P. 1 067 591 (1956); Chem. Abs., 55, 5028 (1961).
42. B. P. 863 859 (1961); Chem. Abs., 55, 16 005 (1961).
43. US P. 3 440 227 (1969).
44. Japanese P. 20 525 (1964); Ref. Zhur. Khim., 9S267 (1967).
45. US P. 3 427 289 (1969).
46. US P. 3 451 963 (1969).
47. Czech P. 139 640 (1971); Ref. Zhur. Khim., 18S344 (1972).
48. USSR P. 367 119 (1973); Byul. Izobret., No. 8, 67 (1973).
49. US P. 3 763 077 (1973).
50. US P. 2 806 841 (1953); Chem. Abs., 52, 3405g (1958).
51. BRD P. 1 067 587 (1959); Chem. Abs., 55, 10 968 (1961).
52. US P. 3 671 499 (1972).
53. Japanese P. 28 315 (1969); Ref. Zhur. Khim., 18S323 (1970).
54. US P. 3 060 153 (1962).
55. US P. 3 138 574 (1964).
56. Australian P. 286 173 (1968).
57. US P. 3 455 885 (1969).
58. Dutch P. 130 324 (1970).
59. US P. 3 154 525 (1964).
60. Czech P. 93 016 (1957); Chem. Abs., 55, 17 084 (1961).
61. US P. 2 809 958 (1953); Chem. Abs., 52, 19 252 (1958).
62. B. P. 755 944 (1954); Chem. Abs., 51, 6226 (1957).
63. Japanese P. 13 223 (1968); Ref. Zhur. Khim., 12S328 (1969).
64. Swiss P. 38 095 (1964).
65. US P. 3 037 003 (1962); Chem. Abs., 58, 14 147 (1963).
66. US P. 3 216 977 (1965).
67. Swiss P. 411 349 (1966).
68. Japanese P. 29 836 (1970); Ref. Zhur. Khim., 17S469 (1971).
69. Swiss P. 417 959 (1967).
70. Japanese P. 3994 (1971); Ref. Zhur. Khim., 1S246 (1972).
71. Japanese P. 27 830 (1968); Ref. Zhur. Khim., 18S320 (1970).
72. Japanese P. 26 676 (1972); Ref. Zhur. Khim., 13S376 (1974).
73. B. P. 931 913 (1963).
74. Japanese P. 29 835 (1970); Ref. Zhur. Khim., 17S468 (1971).
75. Japanese P. 20 991 (1963); Ref. Zhur. Khim., 22S1211 (1965).
76. French P. 1 326 246 (1963).
77. B. P. 923 450 (1963).
78. B. P. 931 394 (1963).
79. French P. 1 448 966 (1966).
80. US P. 3 069 392 (1962).
81. US P. 3 592 873 (1971).
82. US P. 3 214 415 (1965).
83. Japanese P. 34 156 (1970); Ref. Zhur. Khim., 16S380 (1971).
84. US P. 3 597 401 (1971).
85. B. P. 1 098 093 (1968).
86. Japanese P. 30 510 (1969); Ref. Zhur. Khim., 20S474 (1970).
87. Japanese P. 16 716 (1970); Chem. Abs., 73, 67 307 (1970).
88. US P. 3 631 223 (1971).
89. Belg. P. 635 215 (1964); Chem. Abs., 61, 121 112 (1964).
90. BRD P. 1 239 474 (1970).
91. US P. 3 936 046 (1962).
92. Czech P. 131 648 (1969); Ref. Zhur. Khim., 23S275 (1970).
93. BRD P. 2 230 732 (1974).
94. US P. 3 755 266 (1973).
95. Japanese P. 29 833 (1970); Ref. Zhur. Khim., 17S466 (1971).
96. US P. 3 575 938 (1971).
97. Czech P. 140 534 (1971); Ref. Zhur. Khim., 8S422 (1973).
98. US P. 3 755 267 (1973).
99. US P. 3 759 876 (1973).
100. US P. 3 138 574 (1964).
101. US P. 3 148 174 (1964).
102. US P. 3 086 962 (1963).

103. French P. 2 119 199 (1972).
104. Japanese P. 16 966 (1970); Ref. Zhur. Khim., 15S376 (1971).
105. French P. 1 379 540 (1964); Chem. Abs., 63, 1895 (1965).
106. Czech P. 171 754 (1969); Ref. Zhur. Khim., 22S444 (1970).
107. Japanese P. 32 787 (1973); Ref. Zhur. Khim., 15S389 (1974).
108. Czech P. 142 084 (1971); Ref. Zhur. Khim., 23S391 (1973).
109. Japanese P. 42 759 (1972); Ref. Zhur. Khim., 17S345 (1973).
110. US P. 3 403 135 (1968).
111. US P. 3 207 729 (1965).
112. US P. 3 216 977 (1965).
113. Czech P. 93 016 (1957); Chem. Abs., 55, 17 084 (1961).
114. BRD P. 1 203 465 (1966).
115. US P. 3 228 916 (1966).
116. US P. 3 141 006 (1964).
117. BRD P. 1 071 946 (1959); Chem. Abs., 55, 13 912 (1961).
118. B. P. 924 453 (1963).
119. Japanese P. 12 829 (1968); Ref. Zhur. Khim., 13S366 (1969).
120. US P. 3 454 537 (1969).
121. Japanese P. 19 032 (1968); Ref. Zhur. Khim., 16S315 (1969).
122. Japanese P. 32 434 (1970); Ref. Zhur. Khim., 16S370 (1971).
123. Japanese P. 7575 (1974); Ref. Zhur. Khim., 19S496 (1974).
124. US P. 3 444 142 (1969).
125. US P. 3 250 750 (1966).
126. US P. 3 249 590 (1966).
127. US P. 3 485 822 (1969).
128. US P. 3 448 085 (1969).
129. US P. 3 478 025 (1969).
130. US P. 3 488 425 (1970).
131. US P. 3 448 086 (1969).
132. Japanese P. 47–29 796 (1972); Ref. Zhur. Khim., 1S499 (1974).
133. Japanese P. 547 (1965); Ref. Zhur. Khim., 1S305 (1967).
134. Japanese P. 1235 (1969); Ref. Zhur. Khim., 6S506 (1970).
135. Japanese P. 11 238 (1868); Ref. Zhur. Khim., 16S306 (1969).
136. US P. 3 210 324 (1965).
137. Japanese P. 16 957 (1979); Ref. Zhur. Khim., 15S377 (1971).
138. US P. 3 158 589 (1964).
139. US P. 3 135 719 (1964).
140. BRD P. 1 062 929 (1956); Chem. Abs., 54, 26 018 (1961).
141. US P. 2 912 115 (1958); Chem. Abs., 54, 2810 (1961).
142. Japanese P. 11 541 (1961); Chem. Abs., 55, 11 942 (1961).
143. US P. 3 682 869 (1972).
144. US P. 3 681 295 (1972).
145. BRD P. 1 183 680.
146. US P. 3 174 951 (1965).
147. French P. 2 036 300 (1970).
148. US P. 3 683 046 (1973).
149. US P. 36 811 294 (1972).
150. S. Bar-Zakay, M. Levy, and D. Vofhi, J. Polymer Sci., A1, 4, 221 (1966).
151. R. P. Scelia, S. E. Schönfeld, and L. D. Donaruma, J. Appl. Polymer Sci., 8, 1363 (1964).
152. J. Stehliček, J. Labsky, and J. Šebenda, Coll. Czech. Chem. Comm., 32, 545 (1967).
153. M. A. El-Azmirli, V. V. Korshak, V. A. Sergeev, and E. F. Saikina, Vysokomol. Soed., A9, 946 (1967).
154. M. A. El-Azmirli, V. V. Korshak, and V. A. Sergeev, Trudy Moskov. Khim.-Tekhnol. Inst. im. Mendeleeva, 52, 153 (1967).
155. G. Stea and G. B. Gechell, Europ. Polymer J., 6, 233 (1970).
156. J. C. Stechan and G. P. Hess, J. Amer. Chem. Soc., 77, 1067 (1955).
157. P. Čefelin, E. Sittler, and O. Wichterle, Coll. Czech. Chem. Comm., 24, 3287 (1959).
158. C. Mermoud, "Symposium International de la Chimie Macromoliculaire, 1963", Paris, Phodiaceta, B 1, 1963, p. 326.
159. H. Sekiguchi, Nippon Kagaku Zasshi, 88, 577 (1967).
160. V. V. Korshak, A. M. Kogan, V. A. Sergeev, R. B. Shleifman, L. B. Gurevich, and G. B. Andion, Symposium, "Geterotsepnye Vysokomolekulyarnye Soedineniya" (Heterochain High-Molecular-Weight Compounds), Izd. Nauka, Moscow, 1964, p. 24.
161. V. V. Korshak, T. M. Frunze, V. V. Kurashev, R. B. Shleifman, and L. B. Danilevskaya, Vysokomol. Soed., 8, 519 (1966).
162. V. V. Korshak, T M. Frunze, V. V. Kurashev, V. I. Zaitsev, and T. M. Babchinitser, Vysokomol. Soed., 12, 416 (1970).
163. T. M. Frunze, V. V. Kurashev, and V. J. Saitzev, Makromol. Chem., 137, 87 (1970).
164. J. Čzerny, Plast. modern et elast., 21, No. 5, 107 (1969).
165. S. A. Pavlova, T. M. Funze, L. V. Dubrovina, V. V. Kurashev, V. V. Korshak, and V. I. Zaitsev, Vysokomol. Soed., 16A, 22 (1974).
166. G. L. Slonimskii, A. A. Askadskii, K. A. Bychko, V. V. Korshak, T. M. Frlov, V. V. Kurashev, and V. I. Zaitsev, Vysokomol. Soed., 15A, 2656 (1973).
167. V. V. Korshak, T. M. Frunze, V. V. Kurashev, and V. I. Zaitsev, Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 6197, 1973); Ref. Zhur. Khim., 20S189 (1975).
168. E. H. Mattus, R. M. Hedrick, and J. H. Buttler, Amer. Chem. Soc. Polym. Prepr., 9(1), 390 (1968).
169. G. Stea and G. B. Gechell, Europ. Polymer J., 1, 213 (1965).
170. J. Šebenda and J. Kouril, Europ. Polymer J., 7, 1637 (1971).
171. C. V. Goebel, P. Čefelin, J. Stehleček, and J. Šebenda, J. Polymer Sci., A1, 9, 1411 (1972).
172. T. M. Frunze, V. V. Kurashev, V. I. Zaitsev, R. B. Shleifman, and V. V. Korshak, Vysokomol. Soed., 16A, 1257 (1974).
173. O. Wichterle, Makromol. Chem., 35, 174 (1960).
174. J. Šebenda, Coll. Czech. Chem. Comm., 31, 1501 (1966).
175. J. Šebenda, B. Masař, and Z. Bukač, J. Polymer Sci., C16, 339 (1967).
176. J. Šebenda and J. Kouril, Europ. Polymer J., 7, 1637 (1971).
177. O. Wichterle, J. Šebenda, and J. Kraličeк, Khim. i Tekhnol. Polimerov, 7, 39 (1961).
178. O. Wichterle, P. Sittler, and P. Čefelin, J. Polymer Sci., 53, 249 (1961).

179. V.V.Korshak, T.M.Frunze, V.V.Kurashev, L.B.Danilevskaya, and T.V.Volkova, Vysokomol. Soed., 17A, 1409 (1975).
180. L.G.Bakhtimirova, L.D.Romanova, and Yu.N.Ugol'nikov, USSR P.367119 (1973); Ref. Zhur.Khim., 16S344 (1974).
181. US P.3 022 274 (1962).
182. O.Wichterle and V.Gregor, J.Polymer Sci., 34, 309 (1958).
183. V.V.Korshak, M.M.Gudimov, T.M.Frunze, V.A.Sergeev, N.M.Abakumova, V.V.Kurashev, A.S.Kogan, and A.S.Tkachenko, Plast.Massy, No.9, 47 (1976).
184. T.M.Frunze, R.B.Shleifman, T.M.Babchinitser, V.V.Kurashev, and V.I.Zaitsev, Vysokomol.Soed., 13, 1103 (1971).
185. USSR P.169 782 (1965); Byul.Izobret., No.7, 102 (1965).
186. V.V.Korshak, T.M.Frunze, V.V.Kurashev, and E.L.Baranov, Dokl.Akad.Nauk SSSR, 160, 349 (1965).
187. V.V.Korshak, T.M.Frunze, V.V.Kurashev, and E.L.Baranov, Plast.Massy, No.12, 3 (1965).
188. T.M.Frunze, V.V.Kurashev, and E.L.Baranov, Izv.Akad.Nauk SSSR, Otd.Khim., Nauk, 1860 (1965).
189. M.Matzner, D.L.Schober, and J.E.McGrath, Europ.Polymer.J., 9, 469 (1973).
190. M.Matzner, D.L.Schober, and J.E.McGrath, Amer.Chem.Soc.Polym.Prepr., 13, 754 (1972).
191. US P.3 243 476 (1966).
192. US P.3 243 477 (1966).
193. Japanese P.16 027 (1966); Ref.Zhur.Khim., 15S1352 (1970).
194. J.Jamashita, H.Motsui, and K.Ito, J.Polymer Sci., A1, 10, 3577 (1972).
195. US P.3 758 631 (1973).
196. B.P.1 067 153 (1967).
197. W.Z.Hergenrother and R.J.Ambrose, J.Polymer Sci., A1, 12, 2613 (1974).
198. W.Z.Hergenrother and R.J.Ambrose, J.Appl. Polymer Sci., 19, 3225 (1975).
199. US P.3 940 372 (1976); Chem.Abs., 84, 165 392 (1976).
200. US P.3 887 643 (1975); Chem.Abs., 83, 133 043 (1975).
201. Y.Yamashita, Y.Murase, and K.Ito, J.Polymer Sci., A1, 11, 435 (1973).
202. US P.3 770 849 (1973).
203. US P.3 657 385 (1972).
204. B.P.1 150 725 (1969); Chem.Abs., 71, 3910 (1969).
205. USSR P.416 367 (1974); Byul.Izobret., No.7, 78 (1974).
206. V.V.Korshak, T.M.Frunze, V.V.Kurashev, and L.B.Danilevskaya, Vysokomol.Soed., 18A, 848 (1976).
207. Japanese P.12 871 (1970); Ref.Zhur.Khim., 13S293 (1972).
208. V.V.Korshak, T.M.Frunze, L.B.Danilevskaya, and V.V.Kurashev, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 637 (1968).
209. B.A.Rozenberg, V.I.Irzhak, and N.S.Enikolopyan, in "Mezhtsepnoi Obmen v Polimerakh" (Interchain Exchange in Polymers), Izd.Khimiya, Moscow, 1975, p.203.
210. V.V.Korshak and T.M.Frunze, Dokl.Akad.Nauk SSSR, 97, 678 (1954).

Institute of Organoelemental Compounds,
USSR Academy of Sciences,
Moscow