ANIONIC COPOLYMERIZATION OF BISLACTAMS WITH 6-CAPROLACTAM*

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Anionic copolymerization of 6-caprolactam with bislactams derived both from 2,2'-alkylene-
-bis(cyclohexanones) (type *I*) and from 4,4'-alkylene-bis(cyclohexanones) (type *II*) was studied.
The rate of polymerization under adiabatic conditions depends on the type of bislactam used.
The differences can be explained by comparison with copolymerization of 6-caprolactam with
model derivatives of substituted 6-caprolactam.

Polymers, prepared by activated anionic polymerization of 6-caprolactam under adiabatic condi-
tions[1] at low initial temperature, differ in certain properties from those prepared or manufactured
at the temperatures above their melting point. These differences consist mainly in an increased
content of crystallinic phase (50—60%) and in a lower content of low-molecular weight part, which,
on one side, increases the hardness and the tensile strength but, on the other side lead to an impaired
impact strength notched and impact strength. These defects form the main difficulty in wider
applications of polycaprolactam prepared by anionic polymerization as a construction material.
However, certain properties can be improved, either by anionic copolymerization of 6-caprolactam
with other lactams[2,3], which is, of course, to the detriment of a lowered melting temperature and
the strength, or by formation of three-dimensional structure. In both cases the crystallinic part
of the polymer simultaneously falls down.

From the point of view of the anionic polymerization, the choice of crosslinking procedures
is considerably limited, because of its sensitivity towards, *e.g.* compounds with acid hydrogen.
Three-dimensional structure is formed at anionic polymerization when certain multifunctional
activators are used, *e.g.* di-, tri-isocyanates[4], N,N'-terephthaloyl-bis- and N,N',N''-trimesinoyl-
-tris(caprolactam)[5] or even polyfunctional activators, such as copolymers of N-methacryloyl-
caprolactam with unsaturated monomers[6]. In all these cases the propagation reaction itself
allows the formation either of star-like polymers or at most the comb-like polymers. Multidimen-
sional structure is formed by side reacylation reactions leading to unstable hydrolysable crosslink-
points with imide structure, or by side condensation reactions prodeeding simultaneously at the
anionic polymerization of 6-caprolactam. Side reactions are also the cause of the formation of
three-dimensional polymers when other activators are used[4].

Three-dimensional structure of 6-caprolactam polymerizates can by unambiguously formed
by copolymerization of 6-caprolactam with certain bislactams. In this case the three-dimensional
polymer is formed independently of the side condensation reactions. In contrast to hydrolytic

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polymerization[7-9], the use of bislactams for anionic copolymerization with 6-caprolactam is quoted exclusively only in patent literature[10,11].

The present work is devoted to the study of anionic copolymerization of 6-caprolactam with certain bislactams of the type *I* or *II*; syntheses, some properties, hydrolytic polymerization and copolymerization with 6-caprolactam in the presence of 6-aminocaproic acid, were described in our preceding papers[8,9,12]:
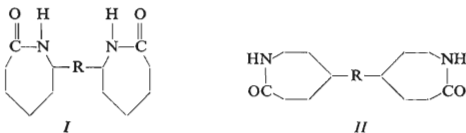
Ia—IIa, R single covalent bond
Ib, R = —CH₂—
Ic, R = —(CH₂)₄—
IIb, R = >C(CH₃)₂

The study of the anionic copolymerization of the quoted bislactams with 6-caprolactam was performed under adiabatic regime under the conditions which secured the exclusion of an internal stress of the specimens[13] which were ment to use for the study of mechanical properties[14]. The low initial (135°C) and the final temperatures favourably effect the equilibrium cycle-chain to the side of the polymer and also the side condensation and splitting reactions, which normally accompany the anionic polymerization, can be expected to proceed to a lower extent. However, the low initial temperature limits the choice of concentrations of the used bislactams because of their low solubility in the melt of 6-caprolactam.

The course of the anionic copolymerization of bislactams differs to some extent from that of the hydrolytic copolymerization. While the presence of bislactams has, in the concentration range used, practically no effect on the rate of hydrolytic copolymerization of 6-caprolactam, the rate of the anionic copolymerization, followed indirectly by measuring the changes of the temperature with time, depends on the type of bislactam. As it is evident from Table I and Fig. 1a, the rate of copolymerization of 6-caprolactam with bislactams of the type *II*, *i.e.* with the bridge in the position 5, practically does not depend on their concentrations. In the presence of bislactams type *I*, where the caprolactam cycles are bridged in the direct neighbourhood of amide groups, the reaction rate falls with increasing concentration. The drop of reaction rate could be attributed either to the presence of side products of bislactams, or to a different sensitivity of 6-caprolactam and of bislactams towards side reactions, also a different acidity of amide group and steric effects at the polymerization could account for the described phenomenon.

At the preparation of bislactam *Ia,* it was possible to isolate as a side product 7-(2-oxocyclohexyl)-1-aza-2-cycloheptanone (*IIIc*), which has an inhibition effect on anionic copolymerization with 6-caprolactam. The fall of reaction rate in its presence is evidently caused by condensation

reactions of this keto-compound in alkaline medium; a similar effect can be observed with cyclo-hexanone and 2,2′-bis(cyclohexanone) (Table I). Bislactams, used for the copolymerization, were of adequate purity (the purity was checked by thin-layer chromatography.)

If we neglect as well the assumed small difference in the acidity of 6-caprolactam and of bislactams and also the different possibilities of side reactions proceeding at
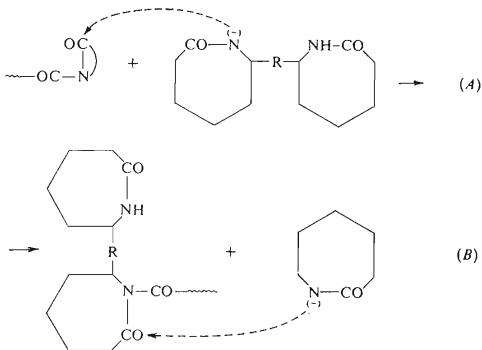
TABLE I

Anionic Copolymerization of 6-Caprolactam with Bislactams Type *I*, *II* and *IV*, and Polymerization of 6-Caprolactam in the Presence of Model Compounds

Initial temperature 135°C, concentrations of N-acetyl-6-caprolactam and of 6-caprolactam sodium salt were $0.25 \cdot 10^{-2}$ mol/mol of 6-caprolactam, c initial concentration of bislactam or of model compound (mol %), t_{26} time of polymerization corresponding to the temperature change of 26°C (min), ΔT_p temperature change due to polymerization (°C), ΔT_c temperature change due to crystallisation (°C), p polymer content (%).

| c	t_{26}	ΔT_p	ΔT_c	p	c	t_{26}	ΔT_p	ΔT_c	p
		Ia					*IIb*		
0	12·0	53·0	18·0	97·0	0·125	13·5	53·0	16·0	96·7
0·031	14·0	53·5	10·0	96·4	0·250	14·0	53·0	15·5	96·5
0·062	15·0	53·0	9·5	95·8	0·500	15·0	53·5	11·0	95·7
0·125	21·0	52·5	9·0	95·4	0·700	15·5	52·5	12·0	95·1
0·250	29·0	53·0	—	93·3	1·000	15·0	53·0	12·5	94·9
0·500	49·5	—	—	58·0	1·250	18·0	53·5	6·0	94·3
		Ib[a]					*IV*		
0·125	15·0	52·0	16·0	96·8	0·500	18·5	52·5	15·2	97·2
0·250	18·0	53·0	15·0	96·3			*IIIa*		
0·500	21·5	52·0	13·5	96·1	0·500	16·5	52·0	15·0	96·8
	23·5[b]	52·0[b]	12·5[b]	95·5[b]			*IIIb*		
1·000	25·5	52·0	11·5	95·9	0·250	16·0	52·0	14·5	94·1
		Ic			1·000	28·0	52·0	10·0	95·2
0·250	13·5	53·0	14·5	97·0			*IIIc*		
		IIa			0·250	19·0	—	—	93·8
					1·000	28·0	—	—	19·0
0·125	15·5	53·3	14·0	96·0			Cyclohexanone		
0·250	15·5	53·5	14·0	97·2	0·250	19·0	53·0	10·0	94·0
0·500	17·0	53·5	9·0	96·8			2,2′-Bis(cyclohexanone)		
0·700	17·5	52·5	7·0	96·2	0·500	28·0	—	—	59·8
1·250	18·5	52·0	4·0	94·0					

[a],[b] Diastereoisomers: [a] m.p. 236°C, [b] m.p. 195—197°C.

the anionic polymerization of lactams[15-18], it is possible to attribute the fall of the reaction rate in the presence of bislactams type I, to steric effects. The study of atom-models revealed, that steric hindrance can become important at the propagation addition reaction of voluminous bislactam anion on a relatively difficult accessible endocyclic carbonyle of the end N-acyllactam group (A), or in the next step, at the addition of 6-caprolactam anion on the voluminous imide group with bislactam built in the chain end (B):


$$(A)$$

$$(B)$$

In accord with the last mentioned opinion, the rate of copolymerization of 6-caprolactam with bislactams type I falls in the following series: $Ic > Ib > Ia$, i.e. with decreasing distance between lactam cycles. Similar results were obtained when studying copolymerization effect of alkylcaprolactams (Table I) used as model compounds of some bislactams, e.g. isobutyl derivative $(IIIa)$ served as a model of bislactam Ib, and similarly, cyclohexyl derivative $(IIIb)$ was used as a model of bislactam Ia:

III

$$a, \text{ R} = -CH_2-CH(CH_3)_2 \qquad b, \text{ R} = - \bighexagon \qquad c, \text{ R} = - \bighexagon_{O}$$
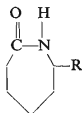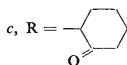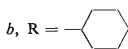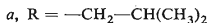
No substantial difference between both diastereoisomers of bislactam *Ib* on the course of anionic copolymerization of 6-caprolactam was observed; a smaller drop of polymerization rate in the presence of 3,7′-isomer of a bislactam having methylene bridge (*IV*) can be attributed to an unusually fast transamidation reaction[12] leading to a structurally different bicyclic monomer, which is less sterically hindered:

IV
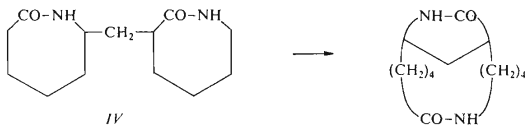
The ease of the addition of the anion derived from the bislactam type *II* on the imide bond is substantially higher, steric hindrance is not important even in the next step of the propagation reaction. The justification of these assumptions can be documented by the dependence of molecular weights of copolymers which are still soluble (formed at the beginning of copolymerization) on the time of polymerization or on the content of polymer (Fig. 1*b*): while the increase of molecular weight of the polymer with conversion is at the copolymerization of 6-caprolactam with bislactam *I* practically identical with the increase of molecular weight at the homopolymerization of 6-capro-lactam, or it is rather less steeper, the corresponding values of molecular weights of copolymers of 6-caprolactam with bislactam *IIb* are substantially higher, despite the fact that this monomer does not homopolymerise[7,9]. The differences in the effect of the type of bislactam on the rate of copolymerization are in this case also in good agreement with the quoted differences in the rates of hydrolytic polymerization of 7- and 5-substituted 6-caprolactams[19,20].

In contrast to 3- and 7-substituted compounds the 5-substitution on the capro-lactam cycle effects negatively the equilibrium monomer–polymer. This fact becomes evident, *e.g.* from the differences at homopolymerization of both types of bislactams[8,9], at their copolymerization with 6-caprolactam above the melting temperature. No large differences in the polymer content were found at the low-temperature anionic copolymerization of bislactam type *II* and type *I*, respectively, with 6-caprolactam. In both cases the final water-extractable portions are increasing with increasing concentrations of bislactams. The drop of polymer content in the case of bislactams type *II* may be, especially, due to the presence of cooligomers which are more soluble or, similarly as in case of hydrolytic polymerization[9], due to the presence of unreacted monomer. As we can assume that the competing base catalysed condensation reactions of N-acylcaprolactam structures proceed simultaneously with copoly-merization and independently of the presence of bislactams, these condensation reactions become relatively more important in those cases when copolymerization is markedly slowed down. The fall of the polymer content of bislactam *Ia* with its increasing concentration (the fall of the values t_{26} and p in Table I) can be explained by a premature decay of the catalytic system.

The crosslinking efficiency of bislactams at the anionic polymerization depends, analogously as in the case of hydrolytic polymerization[8,9] both on the position of the joining bridge and its character. In agreement with the present knowledge about the effect of the character and the position of substituents on polymerization capability of caprolactam cycle[21,22], the critical bislactam concentration at which the presence of three-dimensional polymer insoluble in m-cresol could be detected, decreases in the following series $IIb > IIa > Ib > Ia$ at the concentration range of $0.1 - 0.06$ . . 10^{-2} mol/mol of 6-caprolactam and the concentration of both catalyst components being $0.25 . 10^{-2}$ mol/mol of 6-caprolactam. The differences in the crosslinking efficiency of the individual bislactams defined in this way are markedly smaller than at the hydrolytic polymerization at higher temperatures[8,9]; with decreasing polymerization temperature the equilibrium content of acyclic structure increases in all cases in both reaction steps, $e.g.$:

$$(D)$$
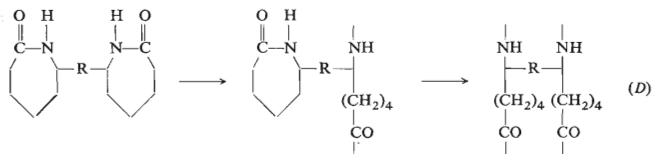
and therefore the crosslinking efficiency increases. A quantitative comparison with hydrolytic polymerization is difficult because of a different degree of polymerization of the basic linear chains and also because of the side reactions proceeding generally
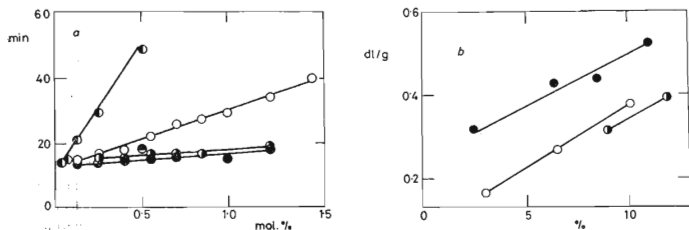

FIG. 1

Anionic Copolymerization of 6-Caprolactam with Bislactams under Adiabatic Conditions

a) Half-time of copolymerization (t_{26}) vs concentration and the type of bislactam: ◐ Ia, ○Ib, ◑ Ic, ◖ IIa, ● IIb, ◒ IV. b) Intrinsic viscosity of the polymer vs conversion of the polymerization reaction. Bislactam: ◑ Ib, ● IIb; ○ for the polymerization of caprolactam.

at the anionic polymerization of lactams. Most of these relations can explain the determined critical bislactam concentrations which are as much as by one order lower; this is true even if we assume that the real crosslinking efficiency of bislactams derived from the equilibrium tension of swollen samples[14] is lower than 50%, providing that the sequence is unchanged. However, it can be said, that the succession of the crosslinking efficiency of bislactams quantitatively agrees with that for hydrolytic copolymerization. Also, as it was expected, the crystallisation exotherm (ΔT_S) in the time-temperature dependence at an adiabatic process decreases with increasing bislactam concentration, which is in accord with the found lower content of the crystallinic phase and with lower density[14]. As the drop of ΔT_c values with increasing bislactam concentration is larger than it should be with respect to the real decrease of the crystallinic phase (Table I), it is evident, that due to crosslinking the crystallisation becomes more difficult and is slower and that it takes place, in these cases, during cooling. Largest decrease of ΔT_c is induced at the copolymerization of 6-caprolactam with bislactams type *Ia* and *IIa*, i.e. in cases when intermolecular cross-link points, because of steric reasons, are rigid.

The changes of polymer morphology, *i.e.* the size and the shape of birefringeting spherulites which together with the change of the crystalline phase portion influence mechanical properties of polymerizates, also depend on the concentration and the type of bislactam used[14].

EXPERIMENTAL

Bislactams were prepared by Schmidt's reaction of corresponding diketones, or by Beckmann's rearrangement of corresponding dioximes. Preparation of methylene-bis(1-aza-2-cycloheptanone) isomers (*Ib*,*IV*) is described in the paper[12]; preparation of 7,7'-bis(1-aza-2-cycloheptanone) (*Ia*) and 7,7'-tetramethylene-bis (1-aza-2-cycloheptanone) (*Ic*) is described in (ref. 8) and for the syntheses of 5,5'-bis(1-aza-2-cycloheptanone) (*IIa*) and 5,5'-isopropylidene-bis(1-aza-2-cycloheptanone) (*IIb*) see (ref. 9). Similarly was prepared 7-isobutyl-1-aza-2-cycloheptanone[23] (*IIIa*) and 7-cyclohexyl--1-aza-2-cycloheptanone[24] (*IIIb*). Syntheses of 7-(2-oxocyclohexyl)-1-aza-2-cycloheptanone (*IIIc*) and of 2,2'-bis(cyclohexanone) are described in ref.[15]. The monomers used were prior to polymerization dried for 12 hours at 50—80°C/2 Torr, bislactam *IIb* was freed from hydration water by drying for 12 hours at 130°C/2 Torr. The solubilities of bislactams in 6-caprolactam at 135°C are (mol %): 0·5 (*Ia*); 1·25 (*IIa*); 1·5 (*IIb*).

The anionic copolymerization was performed under adiabatic conditions[1]; the initial concentration of sodium caprolactam and also of N-acetyl-caprolactam was $0·25 . 10^{-2}$ mol/mol of 6-caprolactam, the initial temperature of the process was 135°C. Sodium salt of 6-caprolactam was prepared by reacting 6-caprolactam with sodium hydroxide in the presence of molecular sieve Nalsit 4A according to the procedure described in ref.[25]; some of the copolymerizations were simultaneously performed in the presence of sodium salt of 6-caprolactam which was prepared with the use of sodium hydride (no change of the course of copolymerization was observed). Copolymer content was determined by a repeated extraction of dried samples in boiling water[26]. Viscosity measurements of soluble copolymers were performed in a Ubbelohde viscometer equipped with capillary No II (ref.[26]). Solutions in *m*-cresol were measured at $25 \pm 0·005°C$.

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