

## The Structure and Physical Properties of Anionically Polymerized Nylon 6 Crosslinked by Bislactams

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### Synopsis

Crosslinked polyamides prepared by copolymerization of  $\epsilon$ -caprolactam with bislactams under conditions of activated anionic polymerization proceeding adiabatically below their melting point show differences in physico-mechanical properties. Owing to varying copolymerization rates of bislactams, depending on the position of the connecting bridge of the bislactam in relation to the amido group, copolymers with different morphological structure are formed. The differences in the mechanical properties of the copolymers are explained on the basis of the differences in the morphological structure. This explanation is supported by results obtained by measuring the thermal and dynamic properties.

### INTRODUCTION

Polyamides prepared by the anionic polymerization of lactams possess outstanding tensile, flexural, and compressive strengths because of their high degree of crystallinity. In spite of these advantages polyamides prepared in such a way have some shortcomings, especially low impact strength, due to their high degree of crystallinity and low content of substances extractable by water. Some of these properties may be improved by structure interference, i.e., by copolymerization<sup>1,2</sup> or by the formation of intermolecular crosslinks. The three-dimensional structure is formed from linear polyamides either by physical methods, most frequently by radiation,<sup>3,4</sup> or by chemical reactions.<sup>5-9</sup>

In this paper we discuss the effect of the structure of crosslinked copolymers of  $\epsilon$ -caprolactam with bislactams prepared by activated anionic polymerization under adiabatic conditions on their physico-mechanical properties.

### EXPERIMENTAL

#### Materials

Copolymers of  $\epsilon$ -caprolactam (CL) with  $\epsilon,\epsilon'$ -methylenebiscaprolactam (MBCL),  $\gamma,\gamma'$ -isopropylidenebiscaprolactam (IBCL), and  $\gamma,\gamma'$ -biscapro-

lactam (BCL) were prepared by activated anionic polymerization under adiabatic conditions,<sup>10</sup> in the whole process of the reaction below the melting point of the product. The sodium salt of caprolactam was used as catalyst and N-acetylcaprolactam was used as activator, both in concentration of 0.25 mole %. The initial polymerization temperature was 135.0° C. Data referring to the composition of the copolymers and the conditions of the polymerization are shown in Table I. The value of the

TABLE I  
Data on Preparation of Copolymers<sup>a</sup>

<i>c</i>	<i>t</i> <sub>0.5</sub>	<i>T</i> <sub>max</sub>	Conversion, %
0	12.0	206.5	97.2
MBCL			
0.25	16.5	199.5	95.4
0.40	18.0	200.5	94.7
0.55	22.0	200.5	94.4
0.70	26.0	200.5	94.7
0.85	28.0	199.5	94.2
1.00	30.0	198.5	94.4
1.25	34.0	194.5	92.9
1.50	40.0	193.5	91.7
IBCL			
0.40	14.5	202.5	96.1
0.55	15.0	199.5	75.7
0.70	15.5	199.5	95.1
1.00	15.0	200.5	94.9
1.25	18.0	194.5	94.3
1.50	—	—	—
BCL			
0.25	15.5	202.5	97.2
0.40	15.0	200.5	96.6
0.55	17.0	197.5	96.8
0.70	17.5	194.4	96.2
0.85	17.0	191.5	95.4

<sup>a</sup> *c*, Concentration of bislactams (mole-%); *t*<sub>0.5</sub>, half-time of polymerization (min); *T*<sub>max</sub>, maximal temperature of adiabatic reaction (°C).

half-time of the polymerization, *t*<sub>0.5</sub>, was determined from the increase of the temperature under adiabatic conditions which is proportional to the change of conversion. The time *t*<sub>0.5</sub> corresponds to the time during which the reaction mixture temperature rises from the initial temperature *T*<sub>0</sub> by  $\Delta T/2$ .

$\Delta T$  is the temperature increase due to the exothermic reaction at the adiabatic polymerization of CL corresponding to a 100% conversion;  $\Delta T = 52^\circ\text{C}$ .<sup>11</sup> After the termination of the adiabatic polymerization, the temperature further increases owing to the adiabatic crystallization to the temperature *T*<sub>max</sub>, that is, the maximum reaction temperature. After the temperature *T*<sub>max</sub> is reached, the adiabatic process is terminated and the polymer is cooled slowly to room temperature. In Figure 1 are shown

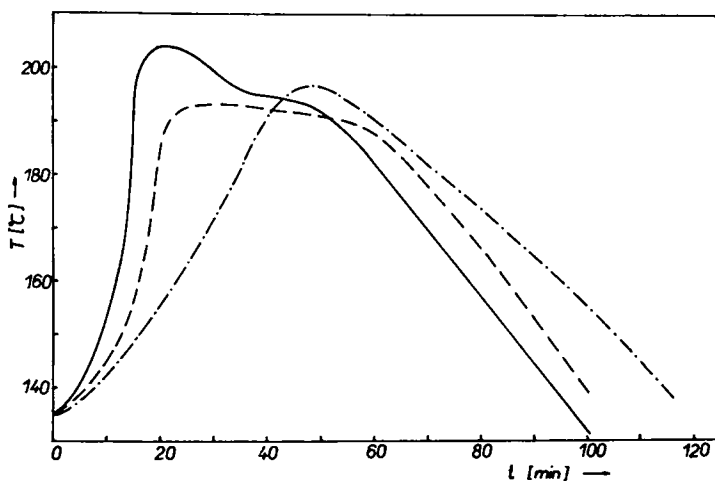


Fig. 1. Course of polymerization, crystallization, and cooling for PCL (—), copolymer with 1.0 mole-% MBCL (---), and copolymer with 1.0 mole-% IBCL (-·-·-).

the typical curves of polymerization, crystallization, and cooling for homopolymer of  $\epsilon$ -caprolactam and copolymers of CL with MBCL and IBCL.

### Sample Preparation

The materials prepared by anionic polymerization were in the form of cylindrical blocks with diameter 56 mm and height 145 mm. Samples for the determination of mechanical properties were prepared by cutting and milling. Samples with a thickness of about  $10\ \mu$  for determination of the spherulitic structure were prepared on a microtome. The low molecular weight fraction was removed from all samples by extraction in boiling water for 30 hr. The samples were dried at  $95^\circ\text{C}$  for 48 hr and stored in a desiccator over phosphoric oxide.

### Methods

The conversion was determined by extraction of samples in the form of saw dust dried in a desiccator to constant weight. Extraction was carried out by distilled water at the boiling point, and the conversion was calculated from the weight of the dry sample before and after extraction.

For the direct proof of the differences in the rate of building MBCL and IBCL in copolymers with CL, the values of the intrinsic viscosity  $[\eta]$  in *m*-cresol and of the conversion of samples taken successively in the initial phase of copolymerization were determined. All these operations were performed in an inert atmosphere.

The crystallinity was determined from the density measured by the flotation method in toluene and carbon tetrachloride mixture with an ac-

curacy of 0.001 g/cm<sup>3</sup>. The crystallinity was calculated according to the relation

$$\%C = [(V - V_a)/(V_c - V_a)] \times 100$$

where  $V$  is the specific volume of the sample;  $V_a$  is the specific volume of the amorphous polycaprolactam (PCL),  $V_a = 0.9225$  cm<sup>3</sup>/g; and  $V_c = 0.816$  cm<sup>3</sup>/g.<sup>12</sup>

The crystallinity was also determined from the heat of fusion by means of DSC measurement. The heating rate was 8°/min. Crystallinity was calculated according to the relation

$$\%C = (\Delta H/\Delta H_c) \times 100$$

where  $\Delta H$  is the observed heat of fusion,  $\Delta H = 45$  cal/g<sup>13</sup>; and  $\Delta H_c$  is the heat of fusion of perfectly crystalline PCL.

The degree of crosslinking was determined from equilibrium swelling in *m*-cresol. The values  $v_r$ , i.e., of the volume fraction of the polymer in the swollen network and of the sol content were determined.<sup>14</sup>

The crosslinking density  $\nu_e$  was determined by measuring the equilibrium tension of the swollen samples.<sup>15</sup> It was calculated according to the relation

$$f/A_0 = \nu_e RT v_r^{-1/3} \cdot (\alpha - \alpha^{-2})$$

where  $f/A_0$  is the elastic force per unit cross section of unswollen and unstrained test piece,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\alpha$  is the relative deformation.

The morphological structure was ascertained by means of a polarizing microscope.

The notched impact strength was measured by means of the Charpy pendulum testing machine according to DIN 53453 with an accuracy of  $\pm 10\%$ .

The embrittlement temperature was determined according to Czechoslovak Standards (ČSN 621555) with an accuracy of  $\pm 2^\circ\text{C}$ .

The brittle strength was ascertained on the tensile testing machine on samples tempered in liquid nitrogen at a cross-head speed of 50 mm/min. The accuracy of the measurement amounted to  $\pm 20\%$ .

The dynamic shear modulus  $G'$  and the mechanical damping  $\tau \tan \delta$  were determined by means of the free vibration method on the torsion pendulum in the frequency range of 0.6–1.3 Hz at temperatures from  $+20^\circ$  to  $+120^\circ\text{C}$ .

## RESULTS

### The Structure of Crosslinked Polyamides

The crosslinking efficiency of the bislactams used was determined by measuring the equilibrium swelling and the equilibrium tension on the swollen samples. In Table II are listed the values  $v_r$  and the sol content

TABLE II  
 Data on Structure of Copolymers\*

C	$C_d$	$C_{DSC}$	$v_r \times 10^2$	Sol fraction, %/100	$\nu_e \times 10^5$
0	58.9	54.5	—	—	—
MBCL					
0.25	58.1	—	1.36	0.24	0.084
0.40	56.1	52.2	3.03	—	—
0.55	55.4	—	3.32	0.084	2.390
0.70	54.6	52.1	4.30	—	—
0.85	53.8	—	4.72	—	—
1.00	53.8	48.7	5.28	0.033	6.492
1.25	53.0	—	5.64	—	—
1.50	51.6	44.7	6.30	—	—
IBCL					
0.40	56.8	—	—	—	—
0.55	56.1	—	1.87	0.204	0.293
0.70	55.4	53.7	—	—	0.925
1.00	55.4	51.2	3.28	0.104	1.789
1.25	53.8	—	—	—	—
1.50	51.6	45.8	—	—	—
BCL					
0.25	57.6	—	1.77	0.132	0.272
0.40	56.8	—	—	—	—
0.55	56.8	—	3.10	0.124	1.647
0.70	55.4	49.3	3.65	—	2.530
0.85	55.4	48.1	—	—	—

\* C, Concentration of bislactams (mole-%);  $C_d$ , crystallinity determined from density (%);  $C_{DSC}$ , crystallinity determined from DSC measurement (%);  $v_r$ , volume fraction of polymer in the swollen system;  $\nu_e$ , number of elastically active network chain per unit volume (moles/cm<sup>3</sup>).

determined by swelling and the crosslink density  $\nu_e$  obtained by measuring the equilibrium tension of swollen samples on the basis of the kinetic theory of rubber elasticity.<sup>15</sup> From the dependence of the sol content on the bislactam concentration, the critical concentration of the crosslinking agent  $c_s$  at the gel point (Fig. 2) was determined by linear extrapolation toward the value  $S = 1$ , i.e., 100% of sol. At the gel point, the critical concen-

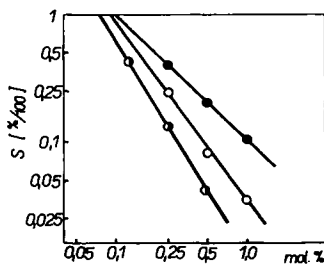


Fig. 2. Relation between sol fraction  $S$  (%/100) and concentration of bislactams in log-log scale: (O) MBCL; (●) IBCL; (●) BCL.

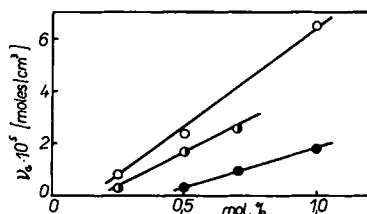


Fig. 3. Relation between physico-effective degree of crosslinking  $\nu_e$  and concentration of bislactams: (O) MBCL; (●) IBCL; (◐) BCL.

tration of the crosslinks  $c_k = d/2\bar{M}_w$ , where  $d$  is the density and  $\bar{M}_w$  is the weight-average molecular weight of the uncrosslinked polymer.  $\bar{M}_w$  was determined from the viscosity measurement and calculated by relations<sup>16</sup>

$$[\eta] = 5.26 \times 10^{-4} \cdot \bar{M}_w^{-0.745}$$

and  $\bar{M}_w/\bar{M}_n = 0.93$  for  $a = 0.7$ , if we suppose the most probable molecular weight distribution, i.e.,  $\bar{M}_w/\bar{M}_n = 2$ . For the measured value of the intrinsic viscosity in *m*-cresol,  $[\eta] = 2.94$  dl/g was determined the weight-average molecular weight  $\bar{M}_w = 116200$ .

The crosslinking efficiency may be estimated as  $k = c_k/c_s$ . The crosslinking efficiency ( $k \times 100$ ) was determined from the experimental data: MBCL, 54%; IBCL, 49%; BCL, 71%. From the slope of the straight lines,  $d\nu_e/dc$  (Fig. 3), we may estimate the crosslinking efficiency  $k$  on the basis of the kinetic theory, and we obtain the approximate values for  $k \times 100$ : MBCL, 40%; IBCL, 15%; BCL, 30%. The values of the crosslinking efficiency obtained from the equilibrium tension may be regarded as the more likely ones.

The determined order of the crosslinking efficiency of bislactams is in agreement with the order of the crosslinking efficiency of bislactams copolymerized hydrolytically with CL above the melting point of polymer (at 260°C).<sup>17</sup> In this case, the crosslinking efficiency decreases in the order  $\epsilon, \epsilon'$ -MBCL  $>$   $\gamma, \gamma'$ -BCL  $>$   $\gamma, \gamma'$ -IBCL and the critical concentration of the crosslinking agent is of the order in the range  $0.75$ – $1.0$ – $2.0 \times 10^{-2}$  mole/mole CL. In the case of anionic polymerization, the critical concentrations are in the range of  $0.07$ – $0.10 \times 10^{-2}$  mole/mole CL.

The differences in the crosslinking efficiency of the bislactams in the case of anionic polymerization are not large. This is also evident from the values of the volume fraction of the polymer in the swollen network ( $\nu_r$ ) in the dependence on the bislactam concentration (Table II).

By determining the morphological structure it was found that changes occur in the size and regularity of the spherulites (Figs. 4–7) depending on the type and concentration of the bislactam used. In the case of copolymers with MBCL, the formed spherulites are regular and their size increases with the concentration of MBCL from the original 5–15  $\mu$  for uncrosslinked PCL to 70–100  $\mu$  at a concentration of 0.7–1.0 mole-% MBCL. At a concentration of 1.25–1.50 mole-% MBCL, the formed spherulites are smaller, irregular, and defective.



Fig. 4. Spherulitic structure, PCL.

In copolymers with IBCL and BCL, the formed spherulites are smaller, more irregular, and less developed. The size of the spherulites increases (to 20–40  $\mu$ ) only at the highest concentration of IBCL (1.25 mole-%) and of BCL (0.85 mole-%). In comparison with the morphological structure of homopolymer CL, the structure of copolymers with IBCL and BCL is more irregular and defective.

The degree of crystallinity was determined from the density and from the heat of fusion by DSC measurements (Table II, Figs. 8 and 9). It was found that the change in degree of crystallinity as a function of the concentration of various bislactams is approximately the same for all types and is relatively slight (from 59% to 52% by the density and from 55% to 45% from the heat of fusion). We can say that the influence of copolymerization with bislactams on the decrease of the content of the crystalline phase in PCL is not a significant one and that the proved changes are independent of the bislactam type used.

By the DSC measurements on copolymers with MBCL at higher concentrations (over 0.7 mole-%), another endothermic secondary maximum

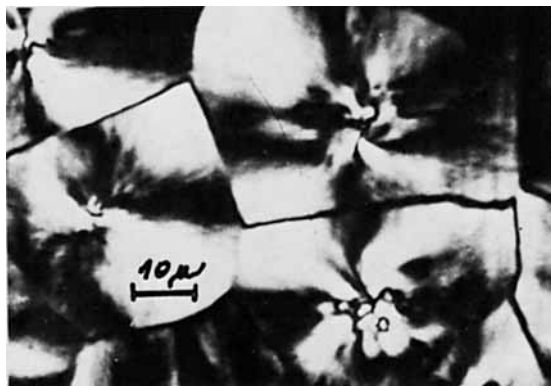


Fig. 5. Spherulitic structure, 0.7 mole-% MBCL.

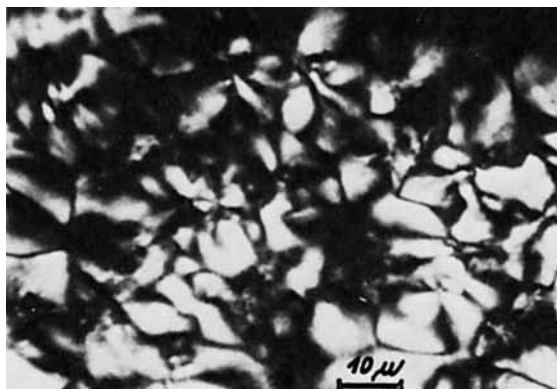


Fig. 6. Spherulitic structure, 0.7 mole-% IBCL.

at a lower temperature was found. This maximum increases in magnitude and shifts to a lower temperature with increasing concentration of MBCL by 10°–25°C from the main melting peak (Fig. 9).

#### Mechanical Properties of Crosslinked Polyamides

The notched impact strength of copolymers with all bislactams types increased. The notched impact strength of copolymers with MBCL was more than doubled at the highest concentration; for IBCL and BCL it increased slightly but was insensitive to concentrations above a 0.5–0.7 mole-% range (Fig. 10).

Remarkable differences were found for the embrittlement temperature (i.e., brittle–ductile transition) and brittle strength (Figs. 11 and 12). In the case of copolymers with IBCL and BCL, these properties deteriorate, whereas copolymers with MBCL show a marked increase of brittle strength and decrease of embrittlement temperature. Both these properties reach maxima approximately in the same concentration region which was ascertained for the maximum size of spherulites.

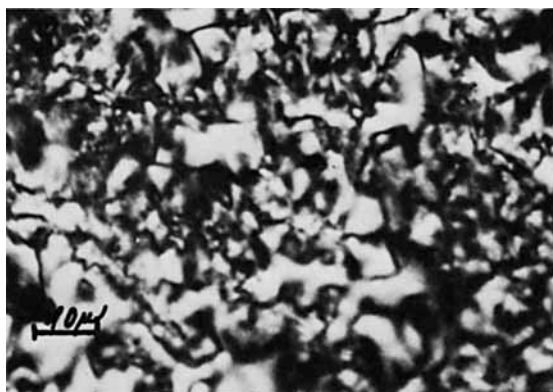


Fig. 7. Spherulitic structure, 0.7 mole-% BCL.



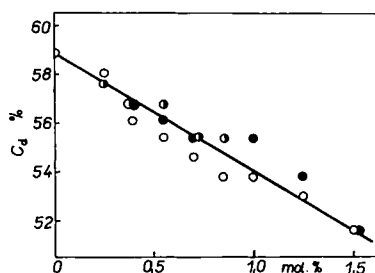


Fig. 8. Relation between crystallinity determined from density  $C_d$  and the concentration of bislactams: (O) MBCL; (●) IBCL; (◐) BCL.

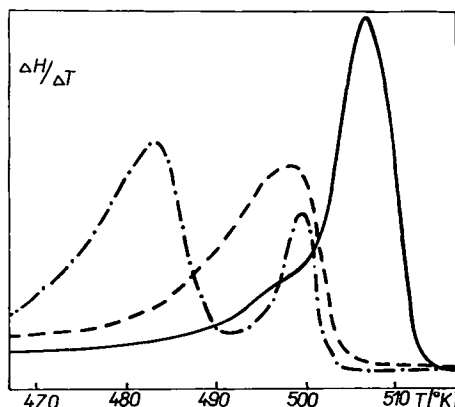


Fig. 9. Melting curves of PCL (—), copolymer with 1.5 mole-% MBCL (-·-·-) and copolymer with 1.5 mole-% IBCL (- - -).

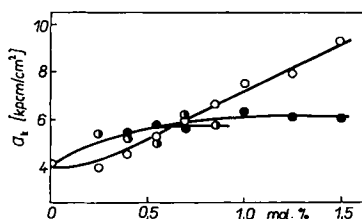


Fig. 10. Dependence of notched impact strength  $a_k$  on the concentration of bislactams: (O) MBCL; (●) IBCL; (◐) BCL.

The dynamic shear modulus  $G'$  and the mechanical damping ( $\tan \delta$ ) were determined in the temperature range from  $+20^\circ$  to  $+120^\circ\text{C}$ . Changes were observed in the  $\alpha$ -transition region caused by the copolymerization with bislactams. We see from Figure 13 that at high concentration of MBCL (1.25 mole-%) the height of the  $\alpha$ -maximum is increased and that the modulus in the  $\alpha$ -transition region decreases more steeply. The  $\alpha$ -maximum for the copolymers with 1.25 mole-% of IBCL and with 0.85 mole-% of BCL does not increase but shifts to a higher temperature, approximately by  $16^\circ$  and  $18^\circ\text{C}$ , respectively.

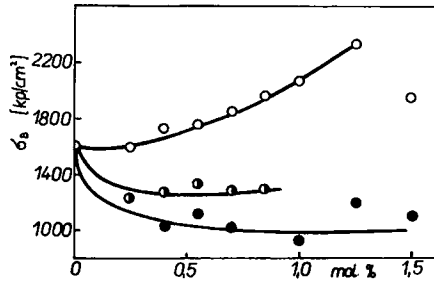


Fig. 11. Dependence of the brittle strength  $\sigma_B$  on the concentration of bislactams: (O) MBCL; (●) IBCL; (◐) BCL.

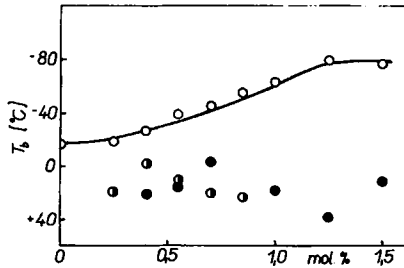


Fig. 12. Dependence of embrittlement temperature  $T_b$  on concentration of bislactams: (O) MBCL; (●) IBCL; (◐) BCL.

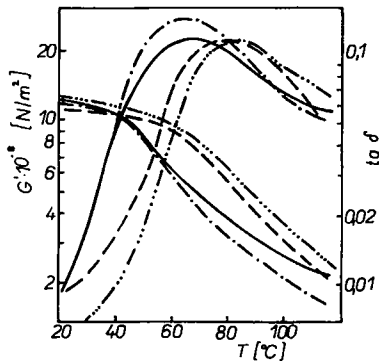


Fig. 13. Dependence of dynamic shear modulus  $G'$  and mechanical damping  $\tan \delta$  on temperature: PCL (—); copolymer with 1.25 mole-% MBCL (---); copolymer with 1.25 mole-% IBCL (-·-·-); copolymer with 0.85 mole-% BCL (····).

## DISCUSSION

The explanation of the influence of bislactams on the structure and the properties of their copolymers with CL can be found in the varying course of copolymerization with the various types of bislactams used.

It is evident from the dependence of the polymerization half-time  $t_{0.5}$  on the concentration and on the bislactam type (Table I, Fig. 14) and from the curves of the temperature course of polymerization, of crystallization,

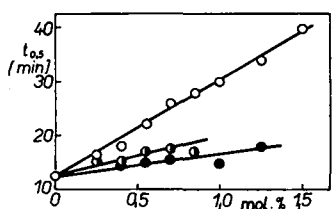


Fig. 14. Dependence of half-time of polymerization  $t_{0.5}$  on the concentration of bislactams: (○) MBCL; (●) IBCL; (◐) BCL.

and of cooling (Fig. 1) that the copolymerization of CL with MBCL is proceeding at a slower rate than the homopolymerization of CL. The polymerization rate as well as the polymerization ability of the bislactams can be deduced by analogy of the polymerization rate and the ability of C-alkyl-substituted CL<sup>18</sup> derivatives. The lowered polymerization rate of  $\alpha$ - and  $\epsilon$ -derivatives, respectively, in comparison with  $\gamma$ -derivatives is accounted for by the vicinity of the substituent and the amide bond.<sup>19</sup>

This assumption is in agreement with the ascertained order of the polymerization rate of bislactams with CL in the anionic polymerization (Table I, Figs. 1 and 10) decreasing in the order of  $\gamma, \gamma'$ -IBCL  $>$   $\gamma, \gamma'$ -BCL  $\gg$   $\epsilon, \epsilon'$ -MBCL.

In contrast to this, the polymerization ability of derivatives of CL decreases with the distance of the substituent from the amide bond and with the volume and length of the substituent chain.<sup>17</sup> It was found that in anionic adiabatic low-temperature copolymerization of bislactams with CL, the equilibrium content of copolymer decreases with the bislactam concentration (Table I), particularly at the highest MBCL concentrations where the conversion decrease may be attributed to the premature disappearing of the catalytic activity of the system due to unusually long polymerization times.

The polymerization ability of bislactams in the copolymerization with CL may be assessed from the values of their crosslinking efficiency. The found order of the crosslinking efficiency of bislactams in the anionic copolymerization with CL (see Section on the structure of crosslinked polyamides) complies with the above-mentioned influence on the polymerization ability of derivatives CL.<sup>17</sup>

$\epsilon, \epsilon'$ -MBCL with the connecting bridge between the lactam cycles in the vicinity of the amide bond, probably from steric reasons, is slowing down copolymerization already in the initial phase of polymerization owing to the fact that it is blocking the propagation intermolecular transacylation reaction. Copolymerization is slower the higher the concentration of MBCL used. The viscosity increase of the system is slower. As it may be concluded from the temperature course of polymerization and cooling (Fig. 1), crystallization proceeds most likely simultaneously with polymerization at relatively low temperatures and hence the formation of a regular spherulitic structure sets in. It is evident from Figure 1 that in the case of copolymerization with MBCL, there is not a plateau in the re-

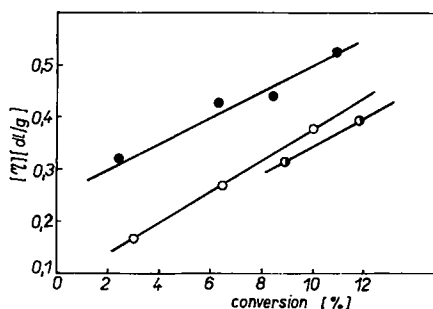


Fig. 15. Dependence of intrinsic viscosity  $[\eta]$  on conversion in the first stages of polymerization: (O) PCL; (●) copolymer with 1.0 mole-% IBCL; (●) copolymer with 1.0 mole-% MBCL.

gion  $T_{\max}$  and that there appears another exothermic process in the polymer cooling at a temperature of about 175°C. This process may be attributed to the postcrystallization of the polymer in less arranged regions.

The secondary maximum on DSC curves corresponds probably with the crystalline phase formed at a lower temperature. This explanation is supported by the results of Illers<sup>20</sup> who investigated nylon 6 annealed from a near-amorphous state at temperatures of 100°–180°C and found on DSC curves the secondary maxima at temperatures 25° higher than the annealing temperature. These maxima are attributed by the author to the less perfect crystalline structure, to the  $\gamma$ -phase.

Copolymerization with  $\gamma, \gamma'$ -BCL and  $\gamma, \gamma'$ -IBCL proceeds substantially quicker, almost comparable with homopolymerization of CL (Table I, Figs. 1 and 10) in agreement with the above-mentioned assumption about the dependence of polymerization rate of substituted lactams on the distance of the substituent from the amido group. The viscosity increase of the system caused by the building of  $\gamma$ -bis lactam in the chain already from the beginning of polymerization and the subsequent branching and later also on crosslinking bring about the formation of a defective, irregular spherulitic structure. This claim is proved by Figure 15 from which it is evident that the intrinsic viscosity  $[\eta]$  of the polymer solution in dependence on the conversion increases more steeply in the case of copolymer with IBCL than in the case of homopolymer of CL, and even of copolymer with MBCL. The dependence was determined only for the initial phase of polymerization, where viscosity could be determined.

It is possible that in the further phase of copolymerization this dependence is changed, as the low final crosslinking efficiency of IBCL points to.

The mechanical properties of crystalline polymers are, as a rule, determined by the content of the crystalline phase and by the character of the amorphous regions. In our case, it was found that the content of the crystalline phase remains almost unchanged with the type of bis lactam used and shows a slight decrease with the concentration of the bis lactams.

Therefore, it became necessary to look for an explanation of the differences in the mechanical properties in the varying structure of the amorphous phase.

We may assume that with increasing size of the spherulites in copolymers with MBCL (Fig. 5), the interlamellar and interspherulitic spaces increase at the same content of the crystalline phase. The lower embedding of the chains of the amorphous phase into the adjacent lamellae results in their higher mobility.<sup>21</sup>

The increased mobility of the amorphous phase and probably the higher mobility of the  $\gamma$ -phase causes the material to absorb more impact energy. Corresponding to this are the increased values of notched impact strength and the shift of ductile-brittle transition to lower temperatures. The high values of brittle strength, caused by the regularity of structure or by the low concentration of defects, influence the low temperature of ductile-brittle transition, too (Figs. 12, 13, and 14). Minimal values of embrittlement temperature and maximum brittle strength are roughly reached in the region of maximally developed spherulites. At higher MBCL concentrations (1.25–1.50 mole-%), a decrease in size of the spherulites was found, probably caused by the higher degree of crosslinking. Simultaneously at higher MBCL concentrations, the brittle strength decreases and the embrittlement temperature becomes approximately constant.

In the case of copolymers of CL with IBCL and BCL, a decrease was found in brittle strength and a shift of brittle-ductile transition to higher temperatures whereby the measured values showed large dispersion. An explanation can be found above all in the character of the morphological structure. The small, irregular, and defective spherulites, formed after polymerization during the cooling process in the range of 190°–193°C (Fig. 1), are surrounded by small interspherulitic spaces of the amorphous phase where the mobility of the chains is restrained by the more pronounced embedding into the neighboring lamellae.<sup>21</sup>

In this way we cannot explain the deterioration of the mechanical properties of copolymers with  $\gamma, \gamma'$ -bisactams in comparison with homopolymer of CL. There is not any great difference between the morphological structure of PCL and its copolymers with  $\gamma, \gamma'$ -bisactams. The structure of copolymers is only more defective. The deterioration of the mechanical properties of copolymers with  $\gamma, \gamma'$ -bisactams is probably due to the crosslinking of the amorphous phase which in the case of homopolymer of CL remains unaffected by crosslinking.

The above-mentioned considerations are also supported by the conclusions based on the temperature dependence of the mechanical damping  $\tan \delta$  in the  $\alpha$ -transition region (Fig. 11) for copolymers of CL with bisactams. The  $\alpha$ -maximum of polyamides is caused by the motion of the chain segments in the amorphous regions.<sup>22</sup> The slight increase of the  $\alpha$ -maximum while its temperature position is preserved in the case of copolymers with MBCL is evidence of the increased mobility of the amorphous phase. The overall crystallinity and the crosslinking degree that

are factors which may affect the  $\alpha$ -process remain approximately the same in the case of copolymers with  $\epsilon, \epsilon'$ - and  $\gamma, \gamma'$ -bislactams.

In the case of copolymers with  $\gamma, \gamma'$ -bislactams, the crystalline regions are smaller, and there is a greater number of crystallites which also means a shorter amorphous sequence. We may assume that the amorphous chains will be under greater restraint and  $T_\alpha$  will be higher.<sup>21</sup>

## CONCLUSIONS

Property changes caused by the copolymerization of CL with bislactams are due to the difference in the copolymerization rates of the bislactams in which the position of the connecting bridge exerts an influence.

$\epsilon, \epsilon'$ -MBCL slowing down copolymerization with CL significantly forms copolymers with a regular morphological structure and a higher content of  $\gamma$ -phase. At the optimal MBCL concentration, large spherulites are formed, which means also larger interspherulitic spaces. This results in the higher mobility of the amorphous phase which is suggested by the increase of the  $\alpha$ -maximum of the mechanical damping. The greater values of impact strength, brittle strength, and the shift of the ductile–brittle transition to lower temperatures may be probably attributed to the higher mobility of the amorphous phase and the regularity of the structure. The negative effect of the crosslinking on the chain mobility of the amorphous phase remains negligible up to a concentration of 1.25 mole-% of MBCL.

$\gamma, \gamma'$ -BCL and  $\gamma, \gamma'$ -IBCL do not considerably slow down copolymerization with CL. They form copolymers with an irregular and defective morphological structure with small spherulites. The interspherulitic spaces are small, and the mobility of the amorphous chains is restrained. The mobility of the amorphous regions is also decreased by the crosslinking. Thanks to this, the  $\alpha$ -maximum of the mechanical damping shifts to a higher temperature. The mechanical properties (brittle strength and embrittlement temperature) are poorer than those of MBCL copolymers and even of CL homopolymer.

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