The Structure and Physical Properties of Copolymers of Lactams

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Synopsis

Copolymers of caprolactam with caprylolactam and laurolactam were prepared by activated anionic copolymerization under adiabatic conditions, at an initial polymerization temperature of $T_0 = 130°C$. The drop of the crystalline phase content and changes of the copolymer morphological structure depending on the content of comonomers result in increasing toughness and deformability due to enhanced yielding ability. The dependences of the copolymer structure and properties on the concentration of comonomers are different for the two series of copolymers. This results from different courses of the polymerization and crystallization history as a consequence of a large difference between polymerization rates of caprylolactam and laurolactam.

INTRODUCTION

Physicomechanical properties of homopolyamides may be modified through their copolymerization. In a preceding work,[1] we paid attention to copolymers of caprolactam with bislactams, which were prepared by activated, anionic, low-temperature polymerization with an adiabatic course. Crosslinked products of enhanced toughness were obtained in this way.

During the last few years the production of laurolactam and caprylolactam has been growing. However, data in the literature concerning their polymerization have appeared only sparingly until now. Besides patents,[2,3] there are only isolated works[4,5] dealing with the anionic polymerization of these lactams. Even more scant are data on the copolymerization of higher lactams with caprolactam. The course of the anionic copolymerization of caprolactam with laurolactam was studied depending on the reaction mechanism, and conditions were established for the adiabatic copolymerization of the two lactams below the melting point of the products.[6] The preparation of the copolymers of caprolactam with caprylolactam through the anionic adiabatic copolymerization below the melting point of the copolymers encounters difficulties owing to a high polymerization heat of caprylolactam.[7]

The works aimed at properties of copolyamides agree in that the crystallinity and mp of original homopolymers drop by action of the copolymerization.[8-11] The statistical terpolymer nylon 6-66-610 was found to have more free amide groups as compared to homopolymers, the rate of the conversion of free amide

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groups to the bonded ones by tempering being lower for this copolyamide than those for homopolyamides.[12] The study of the copolymers of laurolactam with N-methyl-, N-ethyl, and N-benzyllaurolactam revealed that hydrogen bonds did not represent a necessary condition for the crystallization ability of polyamides with a low concentration of amide groups such as poly(N-methyllaurolactam) which contains 19% of the crystalline phase.[13,14]

As indicated by results of certain works,[15,16] the mechanical properties of crystalline polymers are not simply related to the degree of their crystallinity. The way of achieving the crystallinity and details of the morphologic structure play an essential role.

This work deals with relations between the structure and mechanical properties of the copolymers of caprolactam with caprylolactam and laurolactam prepared by the activated anionic copolymerization under adiabatic conditions.

EXPERIMENTAL

Materials

Copolymers of caprolactam (6-CL) with caprylolactam (8-CL) and laurolactam (12-LL) were prepared by the activated anionic polymerization under adiabatic conditions.[17] Sodium and potassium salts of caprolactam were used as catalysts in the case of copolymers of 6-CL with 8-CL (6-8) and 6-CL with 12-LL (6–12), respectively. N-Acetylcaprolactam was used as activator. The catalyst as well

TABLE I
Data on the Preparation of the Copolymers[a]

Comonomer concentration, mole-% 8-CL	Content of portions extractable with water, wt-%	T_{max}, °C	$[\eta]$, dl/g	T_m, °C	
				Nonextr.	Extr.
0	5.8	195.0	3.56	228	230
10	6.3	195.5	3.99	185	196
20	6.2	195.5	4.05	184	188
30	5.9	199.0	4.17	157	163
100	1.3	227.0	4.39	176	—

Comonomer concentration, mole-% 12-LL	Content of portions extractable with benzene, wt-%	T_{max}, °C	η_{red}, dl/g	T_m, °C	
				Nonextr.	Extr.
5	4.2	196.5	5.41	208	210
10	7.1	189.0	7.41	205	207
20	4.9	188.5	6.41	188	193
30	9.8	183.5	7.21	175	177
100[b]	—	177.0	6.46	173	—

[a] T_{max} = Maximum polymerization temperature; T_m = polymer melting point, $[\eta]$ = intrinsic viscosity, η_{red} = reduced viscosity at concentration c = 0.4 g/100 ml.
[b] Initial polymerization temperature T_0 = 160°C.

as activator concentrations were 0.25 mole-%. The initial temperature of the copolymerization was 130°C. The data on the composition of copolymers and on the copolymerization conditions are given in Table I.

Sample Preparation

Polymers in the form of cylindrical blocks, 100 mm high and 56 mm in diameter, were cut to plates. These plates were used to prepare test samples for determining mechanical properties as well as for the other tests. The samples for DSC measurements and for determining the viscosity and notched impact strength were extracted with water (copolymers 6–8) or benzene (copolymers 6–12) at room temperature to remove the monomer. Prior to measurement, all the samples were dried above phosphoric oxide at 40°C until constant weight and stored in a desiccator above phosphoric oxide.

Methods

The content of extractable compounds was determined by the extraction with water or benzene in the case of copolymers 6–8 and 6–12, respectively, at the boiling point on about 0.2-mm samples. Results are given in Table I. The viscosity of the copolymers determined in m-cresol at 25°C is also shown in the table.

The mp values of copolymers were established from DSC measurements and are presented in Table I. The crystalline phase content was determined from the area of endothermic melting peaks. A Perkin-Elmer DSC-1B differential scanning calorimeter was used for thermal analysis. The heating rate was 8°C/min. The crystallinity was calculated from the relation

$$C_{\text{DSC}}(\%) = \frac{\Delta H}{\Delta H_c} \cdot 100$$

where ΔH is the determined heat of fusion (cal/g), ΔH_c is the heat of fusion of the 100% crystalline polycaprolactam, and $\Delta H_c = 45$ cal/g.[18] The calculated value of the crystallinity of copolymers was related to the value ΔH_c of polycaprolactam under the assumption that the random copolymers are formed and comonomer is acting as an ingredient disturbing the original arrangement of the homopolymer.

The morphological structure was established on thin sections (5–10 μm) by a polarizing microscope.

The dynamic shear modulus G' and the mechanical damping tan δ were determined by the free vibration method on a torsion pendulum at a frequency of about 1 Hz and temperature of −30° to +80°C.

The notched impact strength a_k was determined by means of a Charpy pendulum testing machine according to DIN 53453 with a precision of ±10%. The embrittlement temperature T_b was measured according to the Czechoslovak standard ČSN 621555 with a precision of ±2°C.

The tensile properties (yield stress σ_y, rupture strain ϵ_r, and brittle strength σ_b) were determined on an adapted Schopper tensile testing machine with a device for tempering of samples. The cross-head speed was $v_0 = 50$ mm/min, the calculated strain rate was $\epsilon = 0.4$ sec^{-1}, the precision of measuring σ_y, ϵ_r, and σ_b was ±5%, ±10%, and ±10%, respectively.

RESULTS AND DISCUSSION

The Copolymer Structure

On the basis of the data from the DSC measurement (Figs. 1 and 2), we can suppose that block copolymers are absent.[13]

No melting peaks of copolymers at the same melting temperatures as the two individual homopolymers were found on the thermograms. The crystalline copolymers 6–8 and 6–12 exhibit only one melting peak at the new melting temperature, decreasing with comonomer concentration (Table I). Thus, we can assume that random copolymers are formed.

The crystalline phase content of copolymers drops with increasing concentration of comonomers 8-CL and 12-LL as determined by DSC measurement of nonextracted samples (Fig. 3). The crystallinity values determined on extracted samples are different from those for the nonextracted ones only within the precision range.

The decrease of the crystallinity by influence of the copolymerization is caused, first of all, by a lower concentration of the caprolactam segments in the copolymer. The crystallization ability is probably also limited by a drop in the concentration of hydrogen-bonded amide groups. In the case of random copolymers, more free amide groups remained because of their irregular placement.[12]

The shape of endothermic melting peaks in the DSC curves also offers information on the crystalline phase structure. A low and wide peak measured with the copolymers 6–8 as well as copolymers 6–12 (Figs. 1 and 2) suggests that the crystallites are characterized by a wide distribution of melting points, irregularly developed, and disturbed by high content of amorphous chains.

Over a temperature interval, where the dynamic modulus G' and mechanical damping tan δ were measured (−30° to +80°C), the polyamides are characterized
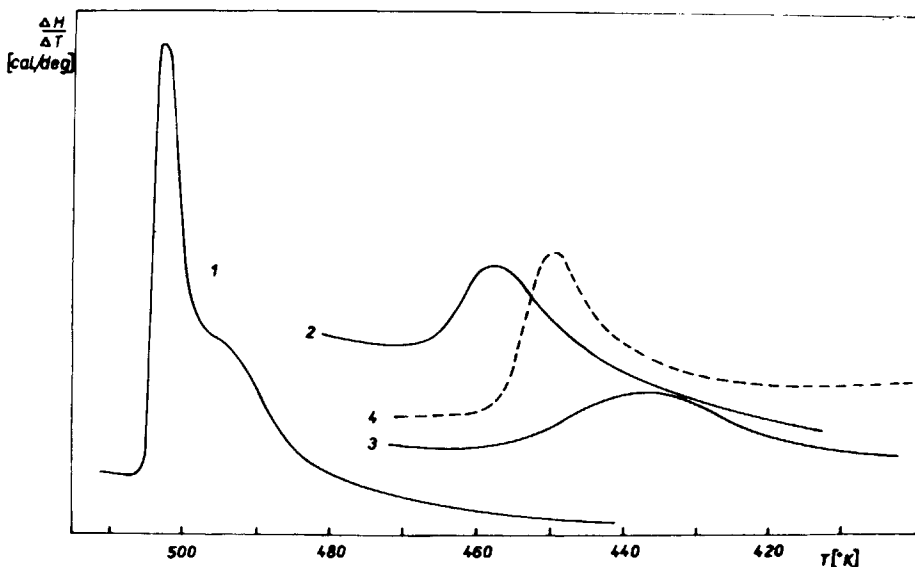

Fig. 1. DSC curves of copolymers 6–8: (1) 6-CL homopolymer; (2) 10 mole-% 8-CL; (3) 30 mole-% 8-CL; (4) 8-CL homopolymer.

by one relaxation process, α-maximum. This process is attributed to motions of hydrogen-bonded amide groups in the amorphous regions by action of the motion of long segments of the chain.[19] The moving chain segments are assumed to contain about 15 monomer units in the case of the polycaprolactam.[20]

From the measured temperature dependences of the mechanical damping tan δ, i.e., increase of the α-maximum intensity and from its shift to lower temperatures (Figs. 4 and 5), one can assume that the copolymerization leads not only to increasing the amorphous phase content,[11] but also to changing the structure of the amorphous phase where a lower concentration of hydrogen bonds makes possible a larger mobility of the chains.

The α-maximum temperature, T_α, varies with the concentration of comonomers, as shown in Figure 6. A remarkable decrease in α-maximum temperature, T_α, was found for the content of 10 mole-% of 8-CL or 12-CL in the copolymer. With further increase in comonomer concentration, the temperature T_α varied only slightly.

The above-mentioned results suggest that an addition of 10 mole-% of the comonomers shows a remarkable plasticizing effect on the polycaprolactam. Further increase in comonomer content does not lead to so remarkable a change in the amorphous phase structure.

Figure 7 shows a dependence of the α-maximum height on the comonomer concentrations. The character of these dependences for the two series of copolymers is similar to the character of the dependence of the crystalline phase content on the comonomer concentration as determined by the DSC measurement (Fig. 3). In the copolymers 6–12, the crystallinity decreases essentially continuously in the concentration region of 0–30 mole-% 12-LL. In the copolymers 6–8, there is the most remarkable decrease in crystallinity for the copolymer with 10 mole-% 8-CL. The crystallinity no longer decreases with further increase in caprylolactam concentration.
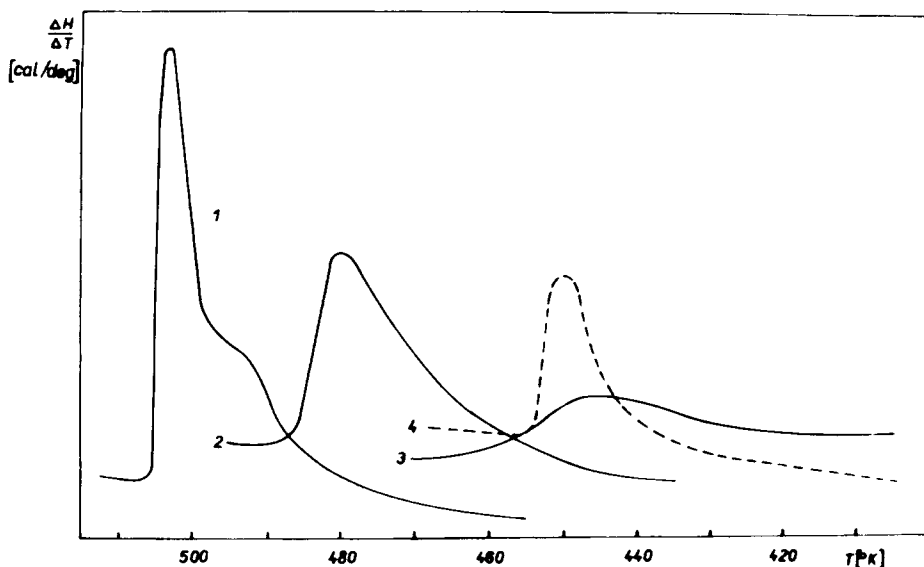

Fig. 2. DSC curves of copolymers 6–12: (1) 6-CL homopolymer; (2) 10 mole-% 12-LL; (3) 30 mole-% 12-LL; (4) 12-LL homopolymer.
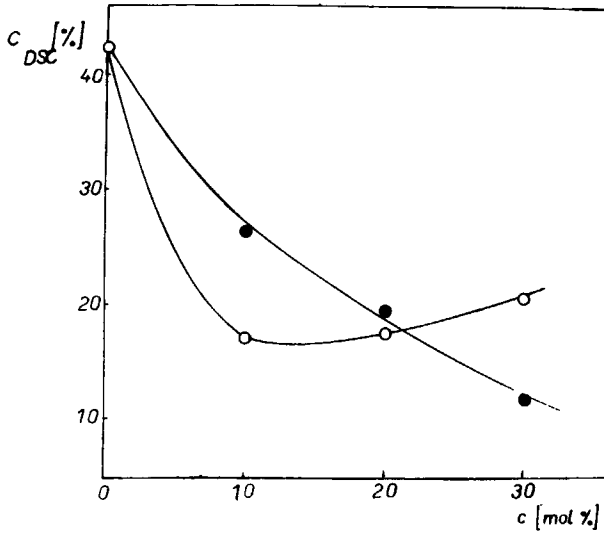
Fig. 3. Dependence of crystalline phase content as determined by DSC measurement, C_{DSC}, on concentration of comonomers in copolymers for nonextracted samples: (O) copolymers 6–8; (●) copolymers 6–12.
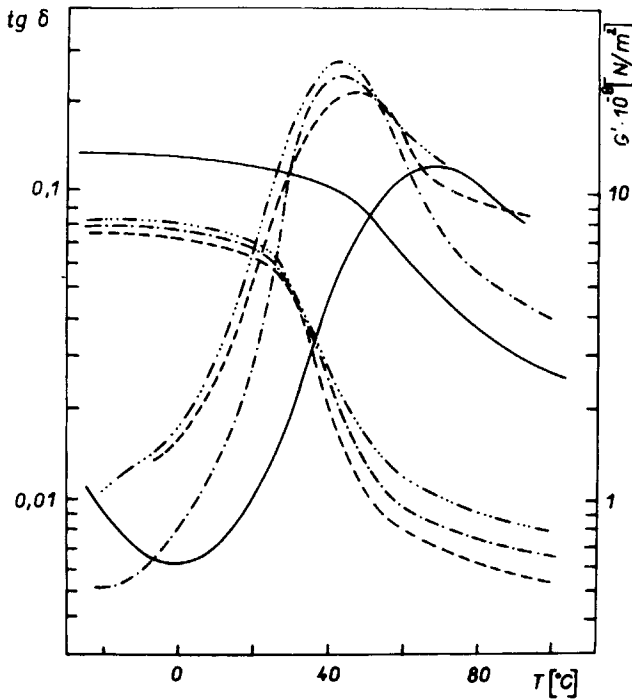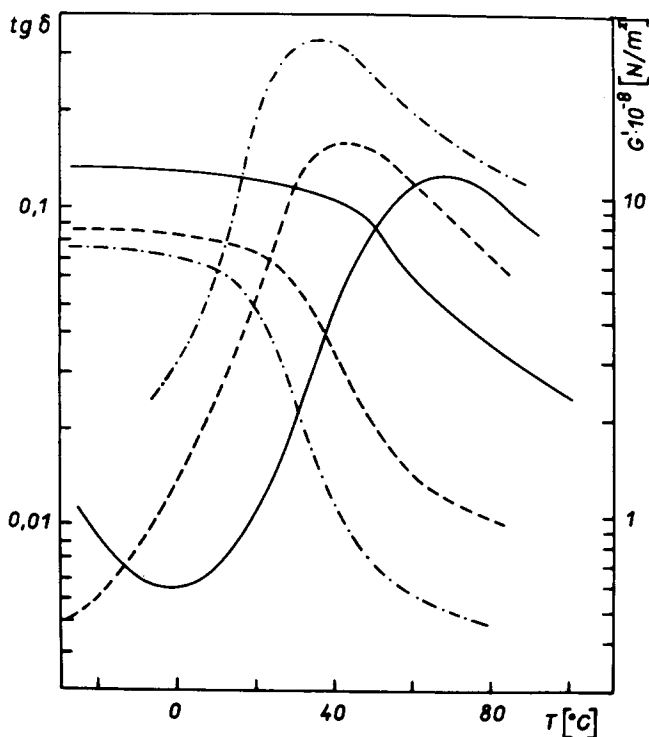

Fig. 4. Dependences of dynamic modulus G' and mechanical damping $\tan \delta$ on temperature for copolymers 6–8: (··) 6-CL homopolymer; (—·—) 10 mole-% 8-CL; (—·—·—·—) 20 mole-% 8-CL; (– – – –) 30 mole-% 8-CL.

Fig. 5. Dependence of dynamic modulus G' and mechanical damping tan δ on temperature for copolymers 6–12: (———) 6-CL homopolymer; (– – – –) 10 mole-% 12-LL; (— · — · —) 30 mole-% 12-LL.

Explanation of these differences is difficult because the crystallization histories for individual copolymers cannot be compared (Figs. 8 and 9). At a constant initial polymerization temperature, the final temperature also varies with changing monomer mixture composition, so that the temperature of the crystal–melt equilibrium transition is also varied. Nucleation and growth always occur at different degrees of the undercooling, which is manifested by various crystalline structures of the samples.

The Morphologic Structure of the Copolymers

It is obvious from our preceding work that the course of the polymerization has a significant effect on the way of crystallization and on the copolymer morphologic structure formation.[1] In the course of the low-temperature anionic polymerization under adiabatic conditions, the crystallization occurs either simultaneously with the polymerization or immediately after the polymerization.

The morphologic structure of homopolymers of the lactams used is relatively regular (Fig. 10a, b, c). Different sizes of spherulites result from different manners of the polymerization and crystallization. The comparison encounters difficulties with respect to remarkable differences between the values of the polymerization heat, melting point of polymers, and melting point of monomers. For the reasons mentioned here, under adiabatic conditions, it is essentially
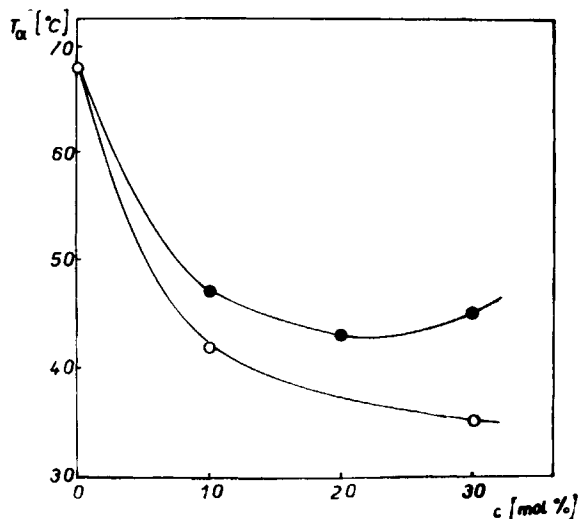
Fig. 6. Dependence of temperature of α-maximum, T_α, on concentration of 8-CL and 12-LL: (●) copolymers 6–8; (O) copolymers 6–12.

impossible to prepare samples with the same thermal history. The polymerization of 8-CL is proceeding fast, and the maximum polymerization temperature exceeds the polymer melting point remarkably at an initial polymerization temperature $T_0 = 130°C$.[7] During the melt cooling, spherulites of about 20–30μm are formed. The polymerization of 12-LL is proceeding at a relatively slower rate, and is characterized by a lower polymerization heat. However, owing to a high mp of the monomer, it is also impossible to accomplish its adiabatic
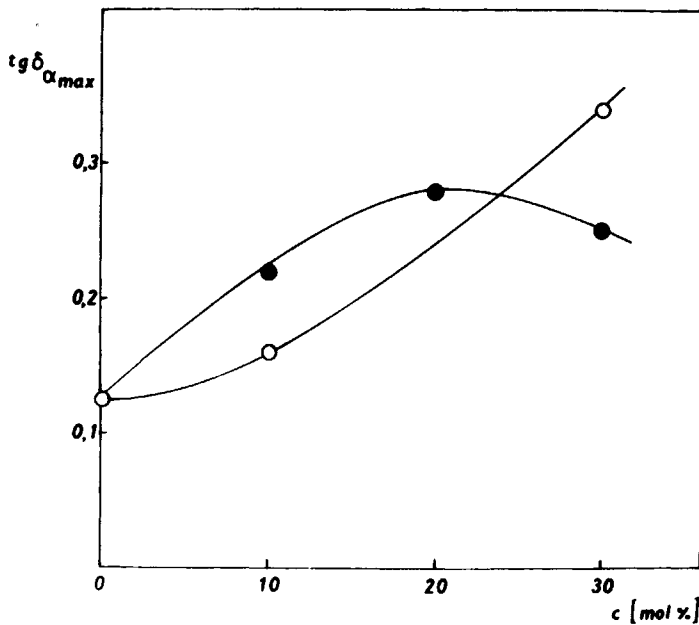

Fig. 7. Dependence of height of α-maximum, tan $\delta_{\alpha\text{-max}}$, of copolymers on concentration of 8-CL and 12-LL: (●) copolymers 6–8; (O) copolymers 6–12.
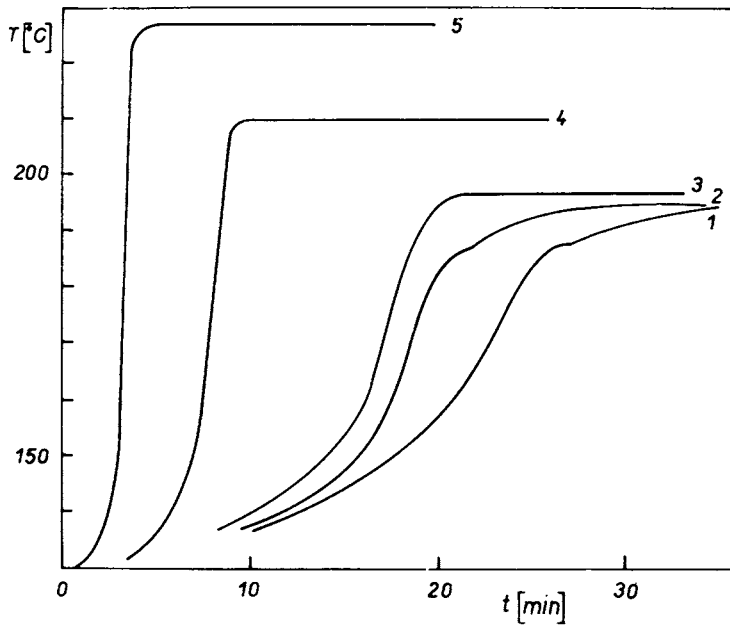
Fig. 8. Course of the anionic adiabatic copolymerization of 6-CL with 8-CL depending on the monomer mixture composition, $T_0 = 130°C$: (1) 6-CL homopolymer; (2) 10 mole-% 8-CL; (3) 30 mole-% 8-CL; (4) 50 mole-% 8-CL; (5) 8-CL homopolymer.
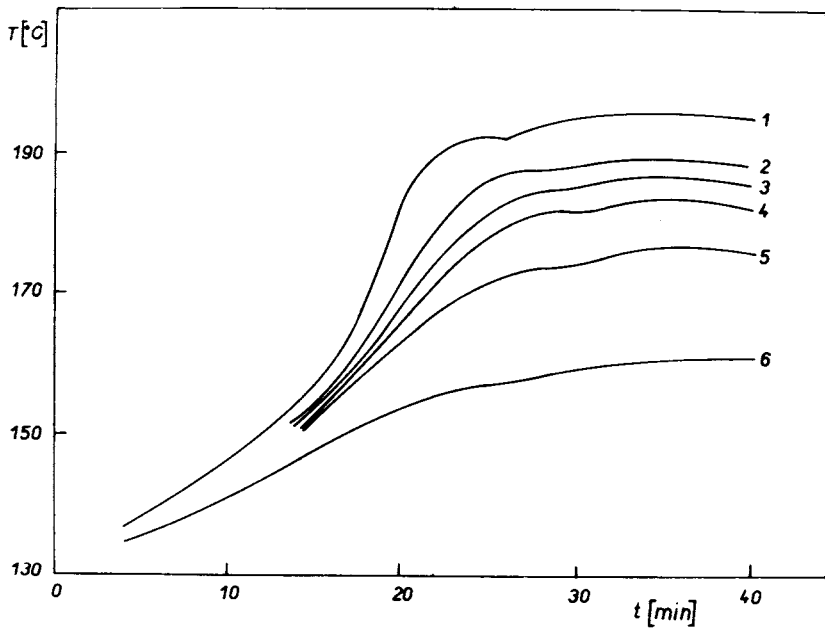

Fig. 9. Course of the anionic adiabatic copolymerization of 6-CL with 12-LL depending on the monomer mixture composition, $T_0 = 130°C$: (1) 6-CL homopolymer; (2) 5 mole-% 12-LL; (3) 10 mole-% 12-LL; (4) 20 mole-% 12-LL; (5) 30 mole-% 12-LL; (6) 60 mole-% 12-LL.

polymerization below the polymer melting point.[21]   The spherulites of the samples prepared at an initial temperature of $T_0 = 160°C$ are well developed, and their size is about 100 μm.

In the case of the copolymerization of caprolactam with caprylolactam, the total copolymerization rate is higher than the 6-CL homopolymerization rate (Fig. 8) thanks to a high polymerization rate of 8-CL in the course of the anionic polymerization.   It is impossible to find those reaction conditions that could provide the copolymerization to occur over the whole concentration region below the copolymer mp.[7]   The maximum copolymerization temperature exceeds the mp of the copolymer formed for a 8-CL content higher than 10 mole-% at the

(a)

(b)
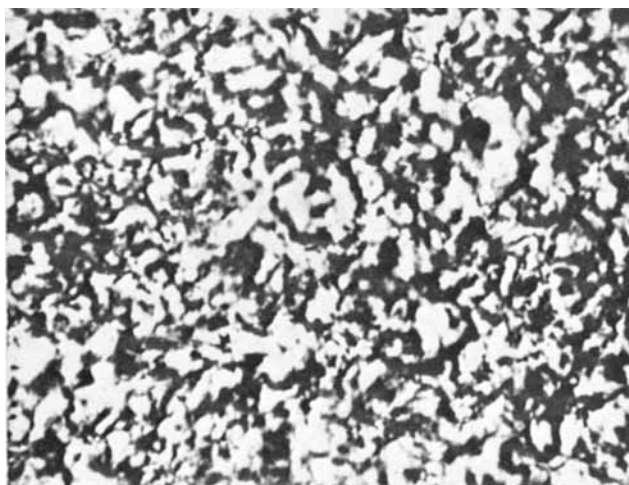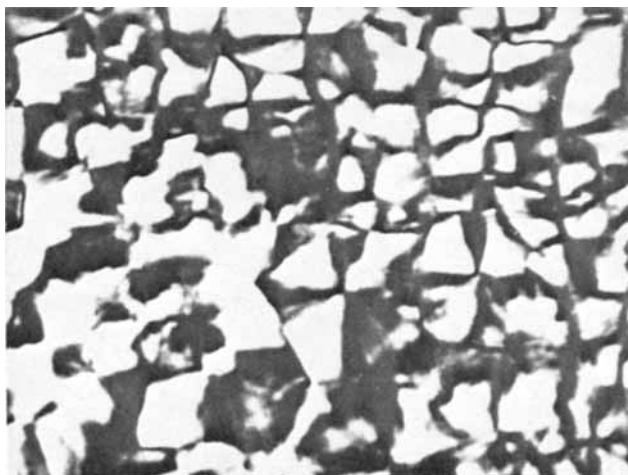
Fig. 10. Morpholigic structure of homopolymers and copolymers 6–8 and 6–12, magnified 1260×: (a) 6-CL homopolymer; (b) 8-CL homopolymer; (c) 12-LL homopolymer; (d) copolymer of 6-CL with 10 mole-% 8-CL; (e) copolymer of 6-CL with 30 mole-% 8-CL; (f) copolymer of 6-CL with 10 mole-% 12-LL; (g) copolymer of 6-CL with 30 mole-% 12-LL.

initial polymerization temperature of $T_0 = 130°C$ (Fig. 8, Table I). In this case, one can assume the crystallization and growth of spherulites to occur only after cooling down the copolymer melt after the completed polymerization.

By contrast, the anionic copolymerization of 6-CL with 12-LL, in the presence of N-acetylcaprolactam as activating agent, is slowed down as compared to the 6-CL homopolymerization, owing to a low polymerization rate of 12-LL (Fig. 9). The maximum copolymerization temperature at $T_0 = 130°C$ is always lower than the copolymer mp (Table I). The crystallization and growth of the spherulites occur either simultaneously with the polymerization or immediately after it.

Figure 10 (d)–(g) shows the spherulitic structure of the copolymers 6–8 and 6–12. The copolymer with 10 mole-% 8-CL (Fig. 10d) is characterized by a


(c)

(d)

Fig. 10 (continued)

structure consisting of two types of spherulites corresponding to the structure of the two homopolymers. In the copolymer with 30 mole-% 8-CL (Fig. 10e), the spherulitic structure is less regular. The copolymer with 10 mole-% 12-LL has very well-developed spherulites (Fig. 10f) and in the presence of 30 mole-% 12-LL in the copolymer (Fig. 10g), the spherulitic structure is disturbed remarkably by action of a high portion of amorphous regions that limit spherulite growth.

The structure of the copolymer with 10 mole-% 12-LL is similar to that of the copolymer of 6-CL with ϵ,ϵ'-methylenebiscaprolactam,[1] which is able, similar to 12-LL, to slow the polymerization rate and for which the crystallization already occurs during the adiabatic polymerization.
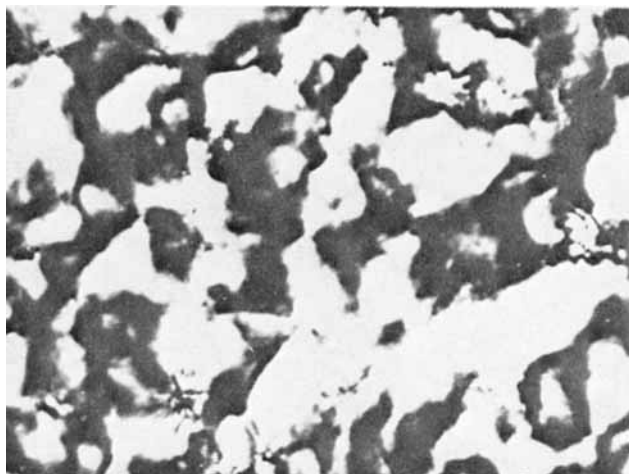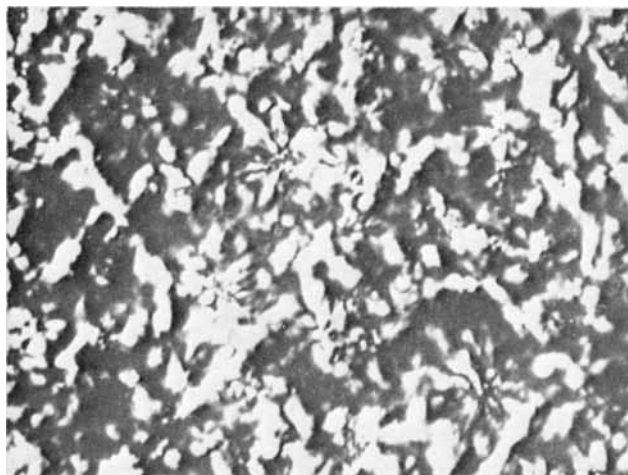

(e)

(f)

Fig. 10 (continued)

(g)

Fig. 10 (*continued*)

Mechanical Properties of Copolymers

Changes in mechanical properties occur as a result of the copolymerization of caprolactam with caprylolactam and laurolactam. These changes may be primarily attributed to an increase in the portion of amorphous regions with a higher mobility. The mobility of the amorphous phase of the lactam copolymers is probably even increased owing to a lower content of hydrogen bonds between chains.

The effect of the way of crystallization and of the type of the resulting morphologic structure is of the same importance for the deformation behavior. No generally valid rule is known for a dependence between the size and shape of spherulites and mechanical properties.

The most significant differences between the mechanical behavior of the

TABLE II
Mechanical Properties of Copolymers

| Comono-mer concentra-tion, mole-%	Notched impact strength, a_k, kJ/m²		yield stress σ_y, MPa			rupture strain ϵ_r, %			Brittle strength σ_b, MPa, at −80°C
	Nonextr.	Extr.	20°C	60°C	100°C	20°C	60°C	100°C	
8-CL									
0	4.0	4.1	77	55	42	10	30	150	161
10	8.6	5.5	61	25	11	80	540	460	138
20	7.9	5.9	63	25	13.5	150	515	560	143
30	8.9	5.1	61	19.5	13	90	650	700	128
100	13.6	—	—	—	—	—	—	—	—
12-LL									
5	5.1	4.8	—	—	—	—	—	—	—
10	5.7	8.0	57	33	17	60	420	360	139
20	8.0	9.2	—	—	—	—	—	—	—
30	17.0	11.4	35	21.5	10.5	160	790	810	115

(a)   (b)

(c)
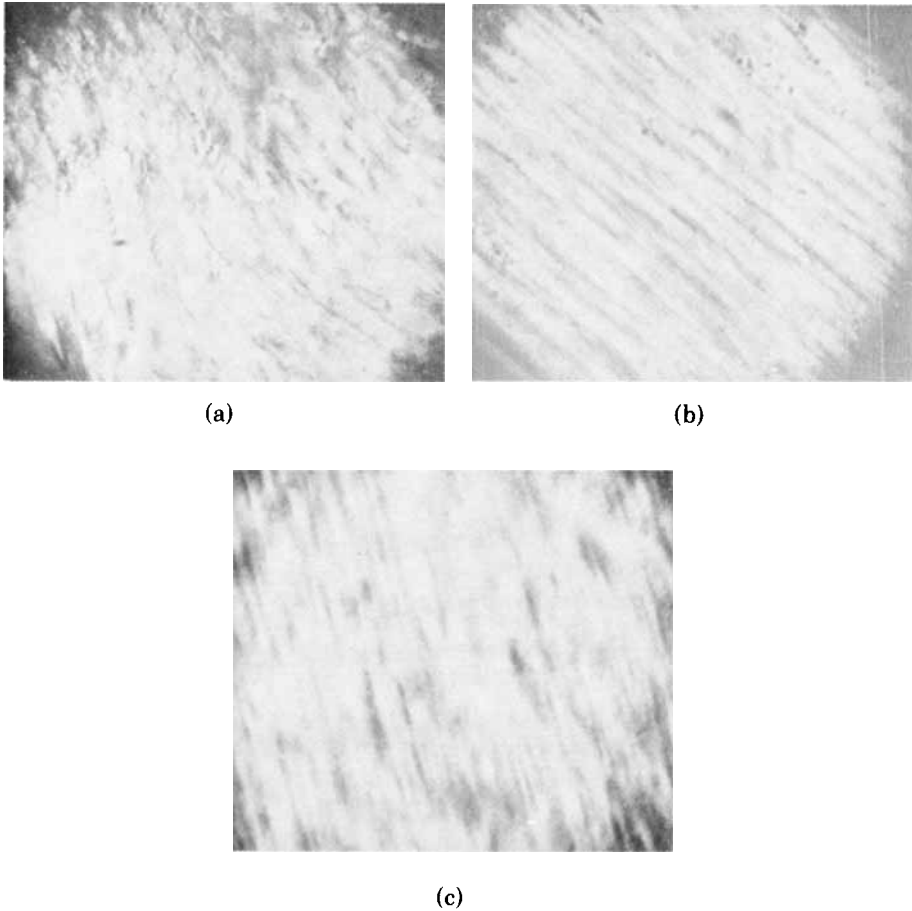
Fig. 11. Morphologic structure of strained samples, magnified 400X: (a) 6-CL homopolymer, 100°C; (b) copolymer of 6-CL with 10 mole-% 8-CL, 20°C; (c) copolymer of 6-CL with 10 mole-% 12-LL, 20°C.

caprolactam homopolymer and those of 6–8 and 6–12 copolymers were observed in the tensile tests (Table II). For a temperature of 20°C and deformation rate of $\dot{\varepsilon} = 0.4$ sec^{-1}, the homopolymer 6-CL is, according to the Vincent's terminology,[22] in a region between the brittle fracture and necking rupture. Only at temperatures sufficiently above T_α (at 100°C) do necking and cold drawing occur, accompanied by whitening which probably results from the crazing, similar to glass-like polymers. In crystalline polymers, the dispersed heterogeneous phase, which is very important for forming crazes,[23] is represented by crystalline formations. The existence of the crazing deformation in this case can be supported by the measured drop in density of a drawn part of a sample from its original value of 1.163 to 1.130 g/cm^3.

By contrast, the copolymers with all the measured concentrations of 8-CL and 12-LL exhibit, at a temperature below T_α (i.e., at about 20°C), cold drawing accompanied by necking, without whitening.

Figure 11 presents a comparison of the spherulite behavior in the course of the deformation of the 6-CL homopolymer and 6–8 and 6–12 copolymers. The

spherulitic structure of the homopolymer 6-CL when strained at 100°C, where its elongation is comparable with that of copolymers at 20°C, remains partially unaltered (Fig. 11a). By contrast, destruction of the spherulites occurs during the corresponding elongation of copolymers 6–8 and 6–12 at 20°C. This means that the originally radially oriented lamellae were oriented in the drawing direction with subsequent probable tearing to smaller blocks of folded chains[24] (Fig. 11b and c). This behavior may be explained by a markedly larger volume of the amorphous phase in interlamellar and interspherulitic spaces of the copolymers. This is manifested by an ability to be cold drawn. In the homopolymer, where the amorphous phase volume is remarkably lower, cold drawing is difficult. An increased deformability may be found at temperatures above T_α when the amorphous chains are in the rubber-like region and are characterized by larger mobility.

At temperatures above T_α, the copolymers are deformed by plastic flow. With respect to a high amorphous phase content, they behave like amorphous polymers above T_g.

The yield stress of copolymers drops with increasing concentration of comonomers and measuring temperature, in accordance with the decrease in the crystallinity (Table II). The brittle strength of the copolymers also decreases with increasing comonomer concentration (Table II). As is known from the literature,[25] the brittle strength is only slightly affected, whereas the yield stress drops with increasing amorphous phase portion. In our case, the drop in brittle strength probably results from changes of the crystalline phase structure. The copolymerization leads to forming defects of the crystalline structure as suggested by the results of the DSC measurements (Figs. 1 and 2) and by the spherulite structure (Fig. 10a–g). These defects are the reason for the drop in brittle strength of the copolymers.

In general, it can be said that the decrease in crystallinity shifts the ductile–brittle transition to more severe impact conditions, i.e., to a lower temperature or higher strain rate.

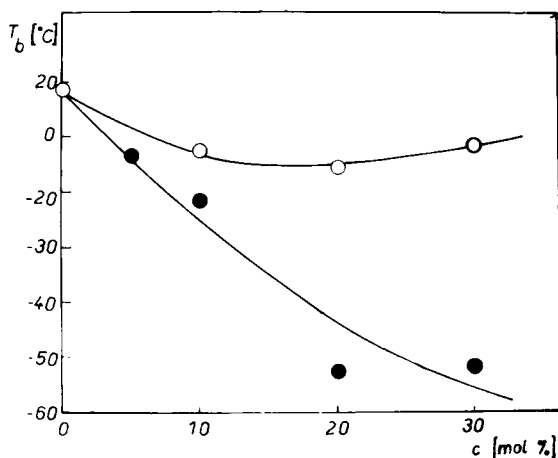The embrittlement temperature T_b may be considered as an approximate

Fig. 12. Dependence of embrittlement temperature T_b on 8-CL and 12-LL concentrations in copolymers: (O) copolymers 6–8; (●) copolymers 6–12.

temperature characterizing the ductile–brittle transition. The dependence of T_b on the comonomer concentration, as shown in Figure 12, indicates that the embrittlement temperature decreases by influence of the copolymerization as a result of the crystallinity decrease. This decrease is much more remarkable in the case of copolymers 6–12 in comparison with copolymers 6–8.

A similar character can be observed for the dependence of the notched impact strength a_k on the comonomer concentration (Table II). The toughness of the 6–8 and 6–12 copolymers increases thanks to an increased yielding ability. In the case of the copolymers 6–12, the increase of the notch impact strength with the 12-LL concentration is more remarkable, even for extracted samples.

Copolymers 6–8, as compared with copolymers 6–12, exhibit less remarkable changes in mechanical properties. This particularly holds for higher concentrations of 8-CL when the copolymerization temperature exceeds the mp of the product (Table I). In this case, an internal stress is probably developed in the course of the copolymer melt cooling, and defects in the structure of the crystalline and amorphous phases are formed.

The differences between properties of copolymers 6–8 and 6–12 are also influenced by a larger decrease in the crystalline phase content in copolymers 6–12 at a higher concentration of 12-LL (Fig. 3).

These differences between the two series of copolymers are similarly manifested in terms of all the properties determined.

CONCLUSIONS

Relations were studied between the structure and physicomechanical properties of copolymers of caprolactam with caprylolactam and laurolactam prepared by the activated, anionic, adiabatic polymerization at an initial temperature of $T_0 = 130°C$.

The copolymerization results in a decrease in crystalline phase content, changes in spherulitic structure, and a drop in the copolymer mp. The intensity of the α-relaxation is also increased, and the temperature of the α-maximum of the mechanical damping is decreased. These structural changes affect the mechanical properties. Notched impact strength and deformability are increased, embrittlement temperature, yield stress, and brittle strength are decreased.

Thanks to a higher content of the amorphous phase, and to changes in amorphous phase structure and morphologic structure, the ability to yield of the copolymer of caprolactam with caprylolactam and laurolactam is enhanced as compared to that of the homopolymer.

The differences between the structure and properties of copolymers 6–8 and 6–12 probably result from different courses of the polymerization which result in different crystallization histories. The copolymerization of caprolactam with caprylolactam is faster than the homopolymerization of caprolactam; and in the case of a caprylolactam content above 10 mole-% and initial polymerization temperature of $T_0 = 130°C$, the polymerization temperature exceeds the mp of the copolymers. By contrast, the copolymerization of caprolactam with laurolactam is slower and under the same conditions, it is accomplished surely below the mp. This means that different manners of the crystallization process are encountered in the two series of copolymers which are manifested by different

morphologic structures. It is not easy to compare effects of the spherulitic structure on the properties with respect to different thermal histories of the samples.

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