Structure of Poly(ε-caprolactam) Obtained in Anionic Bulk Polymerization

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SYNOPSIS

The nascent structures of poly(ε-caprolactam) (N6), obtained during anionic polymerization in bulk in the presence of different additives, were investigated. The experimental data show that both the type and the quantity of activator influence significantly the process of polymerization as well as the chemical and the physical structures of N6. By means of WAXD, DSC, IR, light and transmission microscopy (TEM), and electron microdiffraction (ED) the changes in the morphological and the crystal structure were followed. The observed alterations in the physical structures of N6 samples are explained on the base of changes in the chemical structure and mobility of the polymer chains. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

For the aliphatic polyamides based on poly(ε-caprolactam) (nylon 6, N6), obtained in bulk, three basic phases are observed: amorphous and (α monoclinic and γ monoclinic) crystalline.[1-4] The two modifications of the crystal structure are determined by the position of hydrogen bonds between NH and CO groups of adjacent chains.[1-4] The existence of several intermediate phases have also been reported: two are amorphous δ_1, δ_2, β hexagonal, paracrystalline monoclinic α, and γ pseudohexagonal.[5,8]

The annealing of the crystallized samples or exposure to water can cause partial or entire transformation from one crystalline phase to another, without requiring any drastic rearrangement of the chain, except for the twist of amide groups.[8] The two crystalline forms have different structure and density and they can be reliably determined by means of wide-angle X-ray diffraction (WAXD)[8] and IR spectroscopy.[6,8] The main stable phase of N6 in bulk is α. Normally, N6 in bulk possesses a spherulite structure. The spherulites retain their form during annealing and swelling in water even after transition from one modification to another.[9]
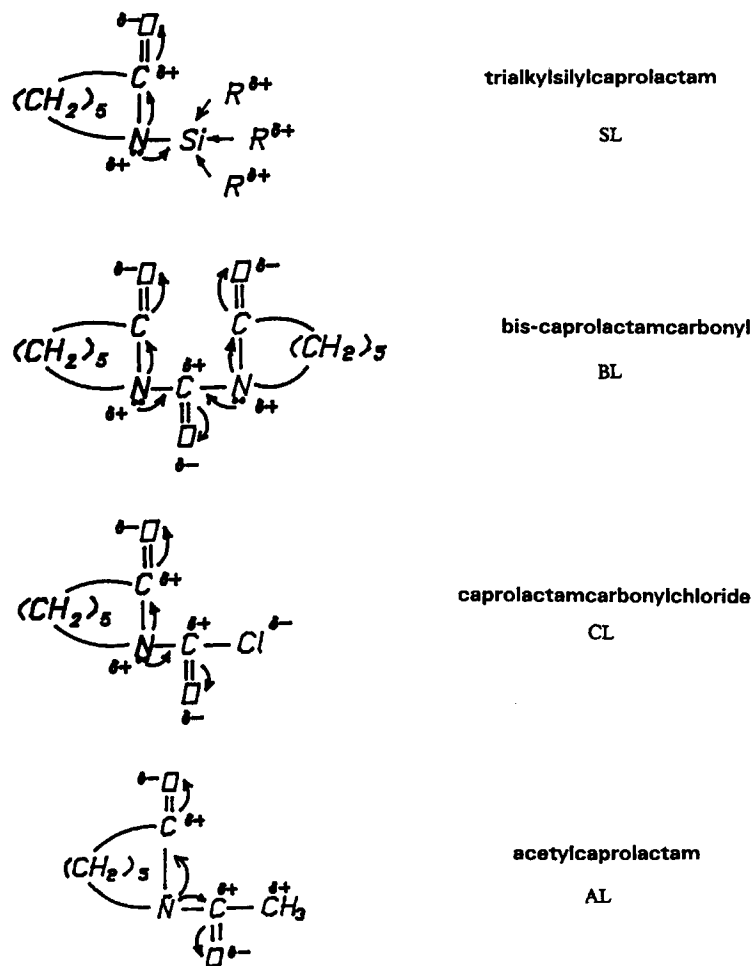
The spherulite structures were investigated by means of several methods: replication of fracture surfaces,[10-13] replication of liquid and ion-etched surfaces,[14-16] and by observing a milling of bulk samples in order to obtain fine grains[15] and ultramicrotomy.[16]

Both the morphology and structure of good quality ultrathin sections from N6 bulk samples obtained by the reaction injection molding (RIM) method, were thoroughly studied by Galeski et al.[3] They developed a special technique for direct investigation of details of the morphology of N6 in bulk. In the samples obtained by RIM, crystallization occurred during polymerization. They suggest a theoretical explanation for the formation of ribbon shaped lamellae and their growth in width. There are no publications about the nascent structure of N6 in bulk occurring during the anionic bulk polymerization in the presence of different activating agents.

The aim of this work was to study the influence of some activating additives on the type and degree of crystallization of N6. Some activators with structures shown in Scheme 1 were synthesized for the anionic polymerization of ε-caprolactam.

It is well known that the anionic polymerization of lactams beings with the activators that influence the induction period[17-20] as well as the rate of polymerization. In this way they could also change the chemical structure of polyamides.[18-20] In bulk polymerization the process of crystallization begins after the start of the polymerization and depends on the reaction conditions.

trialkylsilylcaprolactam

SL

bis-caprolactamcarbonyl

BL

caprolactamcarbonylchloride

CL

acetylcaprolactam

AL

Scheme 1

It is worthwhile to investigate the formation of nascent structures under various polymerization conditions. While studying their action and influence on the structure of poly(ε-caprolactam), they were compared as a rule with the most widely used activator.

EXPERIMENTAL

The anionic polymerization in bulk was carried out in the presence of initiator, Na-caprolactam, and activators synthesized for this purpose (Scheme 1). The conditions of activator synthesis as well as the conditions of polymerization are given in Mateva and Delev.[21] The samples of N6 bulk were investigated by WAXD on a Philips apparatus at 40 kV, 30 mA. The electron micrographs and electron microscope investigations were made on a Philips ap-

paratus at 80-kV operating voltage. Polarizing microscopy was carried out on an Opton–Karl Zeiss apparatus. The IR spectra were recorded on a Specord M80 in KBr pellets using fine grains of N-6 obtained in a disintegrating mill with liquid nitrogen. The chain branching of the polymer was determined as $g' = [\eta/\eta e]$ where, $[\eta]$, $(d1/g)$ is the characteristic viscosity calculated on the determined $\bar{M}_v$. $[\eta e]$, $(d1/g)$ is the characteristic viscosity determined by light scattering according to Kondelikova and Kralicek.[22] The calorimetric investigations as well as the degree of crystallization were determined on a Mettler apparatus using a special program operating at heating and cooling rates of 10°C/min, under nitrogen atmosphere. The average molecular weight, $\bar{M}_v$, was estimated by the method given in Ivanova et al.[23] In order to avoid the effect of knife cutting on the thin N6 sections, the sections were done at 0–5°C.

(a)
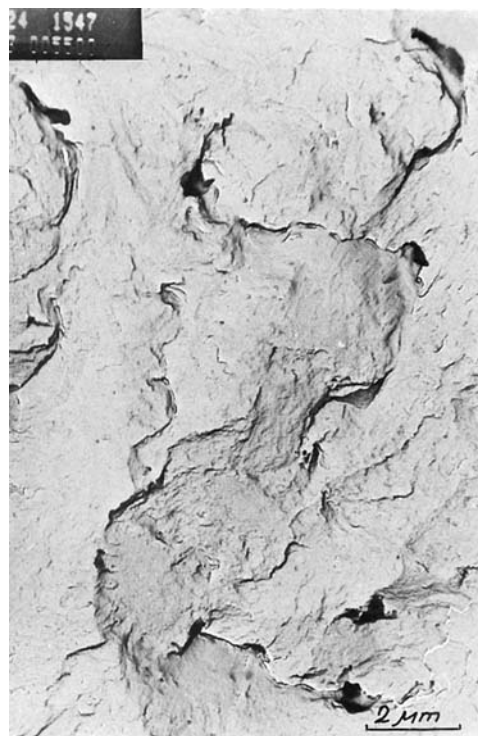
(b)

(c)

Figure 1 Electron microscope replica of N6 in bulk, obtained in the presence of different activators: (a) SL, 1%; (b) AL, 1%; (c) BL, 1%.

Table I Influence of Type of Activators on Polymerization of ε-Caprolactam and Corresponding Polymer Structures

Activator (mol %)	V, Rate of Polym. (%/min)	α, Degree of Branching (%)	$\bar{M}_v$ (×10⁻³)	α, WAXD Degree of Crystal. (%)	L-Crystal Size (Å)
AL	4.8	0.80	35.4	60.5	51
LC	3.5	0.79	34.0	48.0	37
BL	4.1	0.74	36.2	51.0	38
SL	1.8	0.61	38.5	52.1	58
—	1.1	—	14.0	56.0	54

RESULTS AND DISCUSSION

As mentioned above, the process of crystallization begins after the start of polymerization. There are successive processes that depend on the induction period, rate of polymerization, $\bar{M}_v$, and gel fraction. All these parameters are functions of the temperature of polymerization as well as of the quantity of activators.
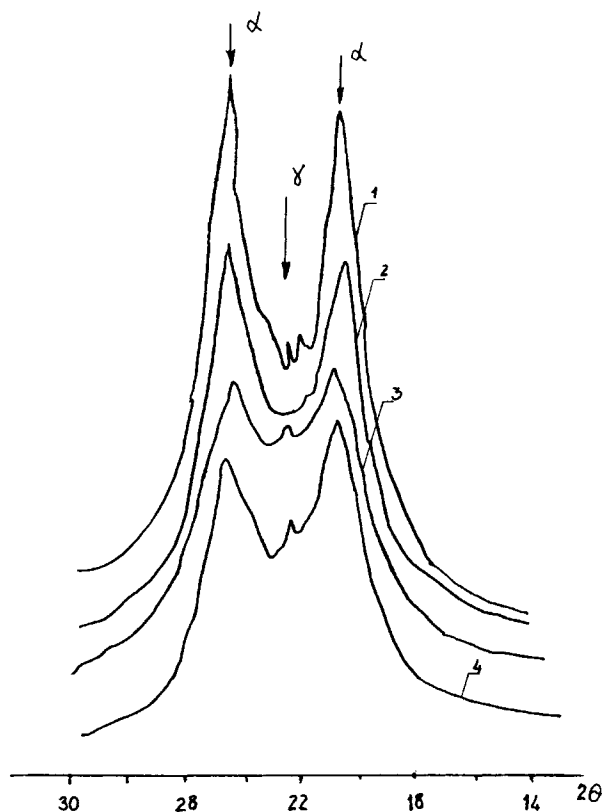
The activators influence the structure of N6 in bulk due to incorporation into the polymer chain. The polymer chain formation starts with activators.[19,20] The side reactions and the branching of the

Figure 2 Diffractograms of N6 obtained at 180°C with: (1) SL, (2) BL, (3) CL, (4) AL.
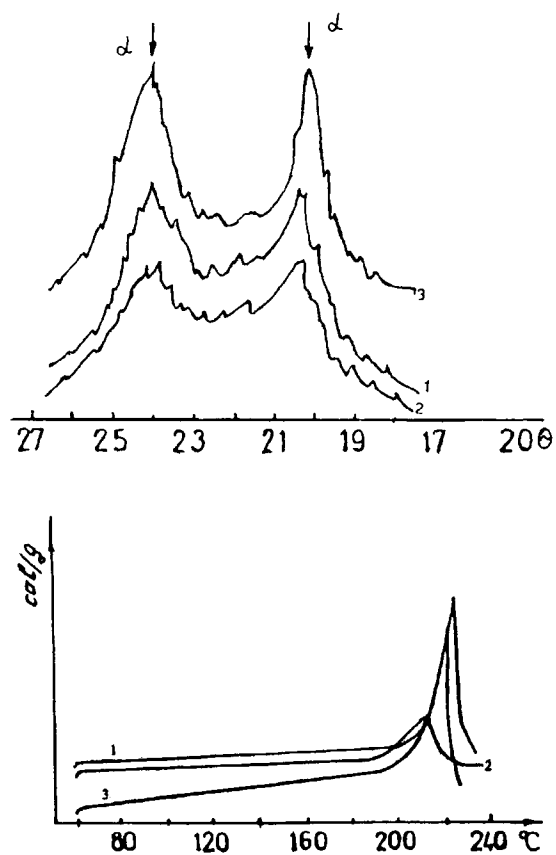
Figure 3 (a) Diffractograms of N6 samples with the following activators, at the indicated temperature of polymerization: (1) Activator, AL 180°C; (2) SL, 180°C; (3) SL, 135°C. (b) Differential scanning calorimetry diagram of N6, obtained at: (1) AL, 180°C; (2) SL, 180°C; (3) SL, 135°C.

Table II   Influence of the Temperature on the Polymerization and Crystallization of N6, Synthesized in the Presence or Activator SL
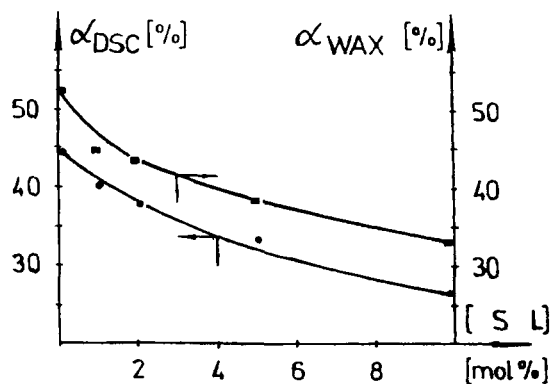
Activator	T_m of Polym. (°C)	V, Rate of Polym. (% min)	$\bar{M}_v$	T_m (°C)	α_{DSC} (%)	α_{WAX} (%)
SL	135	1.5	12,600	234	44	38.0
SL	180	2.3	27,555	210	25	24.2

Table III   Changes of Some N+6 Parameters in Dependence on the SL Activator Amounts

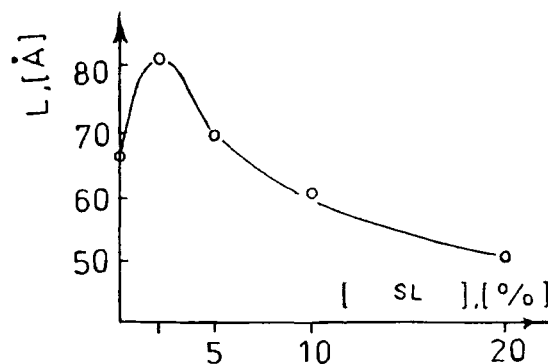| Activator (mol%)	$\bar{M}_v$ ($\times 10^{-3}$)	ΔH (cal/g)	T_m (°C)	ΔT_m (°C)	Gel Fraction (%)	g (degree of branch.)
0	225	19.8	225.0	7	—	—
1	385	18.4	223.0	9	0.5	0.79
2	360	17.5	222.3	10	1.2	0.83
5	—	15.4	221.5	18	5.1	—
10	—	12.0	220.5	20	12.5	—

main chain significantly affect both the chemical and the physical structure of poly(ε-caprolactam).

Our experimental data demonstrated that the degree of crystallinity and the crystal size of the nascent N6 in bulk depends on the type of activator (Table I), as well as other polymerization conditions (initiator, temperature, time of polymerization). From these data we can conclude that the stronger the activator, the higher the degree of conversion and degree of crystallinity. The steric hindrance of the substituent at the N-atom in ε-caprolactam plays an important role too. It influences the kinetics of polymerization $\bar{M}_v$, degree of branching (g'), and also the structures of polymers (Table I).

The prepared N6 samples in the presence of all activators (Scheme 1) possess a spherulitic structure, but they differ from each other depending on the type of activator (Fig. 1). The spherulites are positive with respect to the light breaking coefficient. As seen in the diffractograms (Fig. 2), the α form prevails when AL and SL (Scheme 1) activators were used.

The activator SL with —SiR$_3$ substituent at N in ε-caprolactam (Scheme 1) has the greatest volume. The experimental data shows that the concentration of SL exerts significant changes on the physical structure of N6 in the bulk (Figs. 5–7). The temperature of polymerization influences significantly the rate of polymerization and the average molecular weight ($\bar{M}_v$). That is why we com-

Figure 4   The degree of crystallinity vs. content of SL, additives in mol % of ε-caprolactam monomer (WAXD-αWAXD; DSC-αDSC).

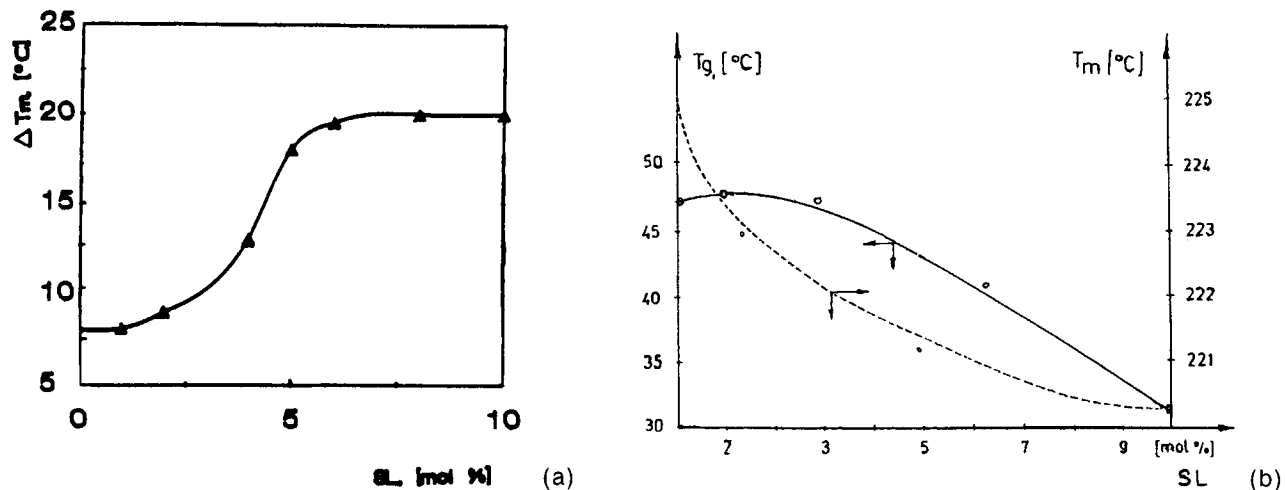**Figure 5**   Dependence of the crystallite size of N6 samples on the content of SL.

Figure 6 (a) Changes in the value of melting interval, ΔT_m of samples, obtained at different contents of SL at 180°C. (b) Changes in the value of glass temperature T_g and the maximum melting temperature of samples, obtained at different contents of SL at 180°C.
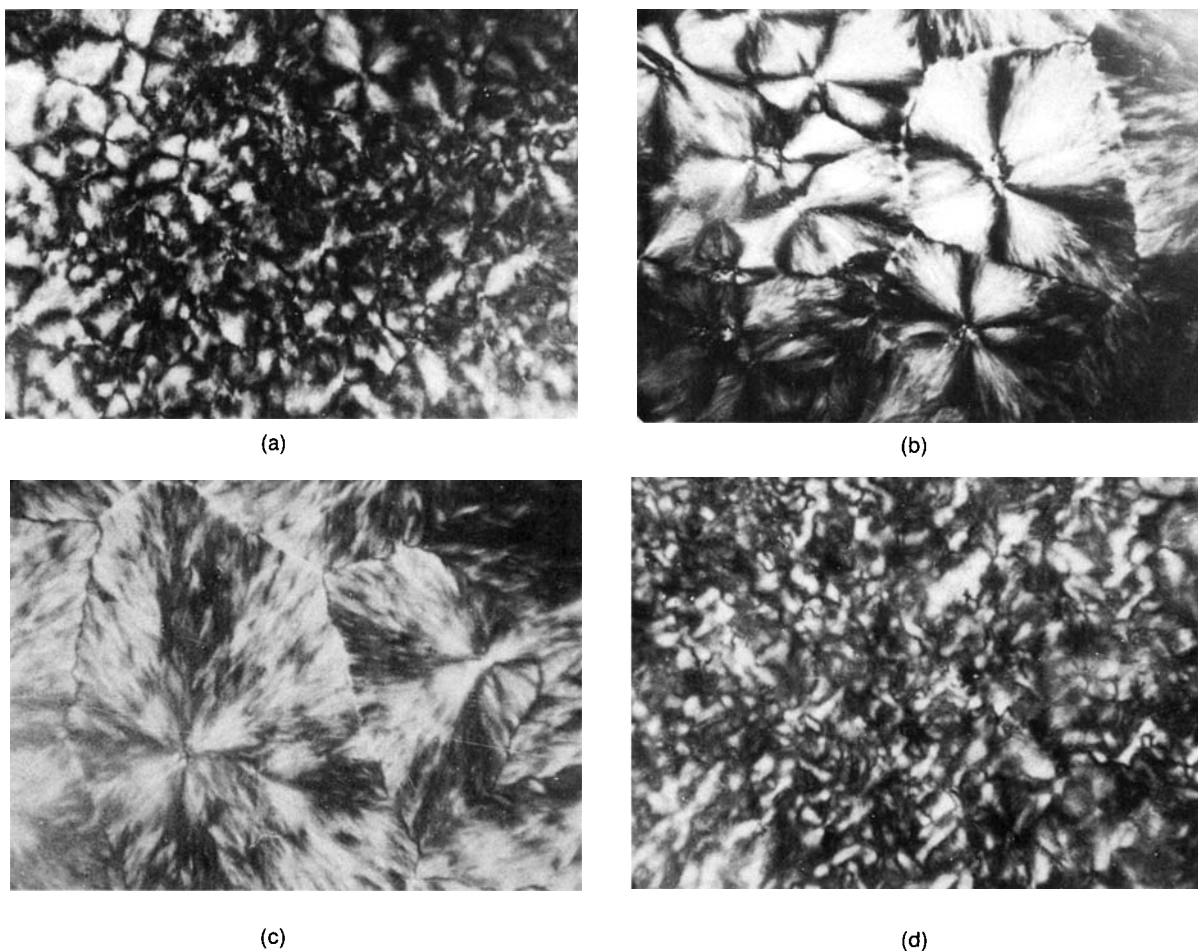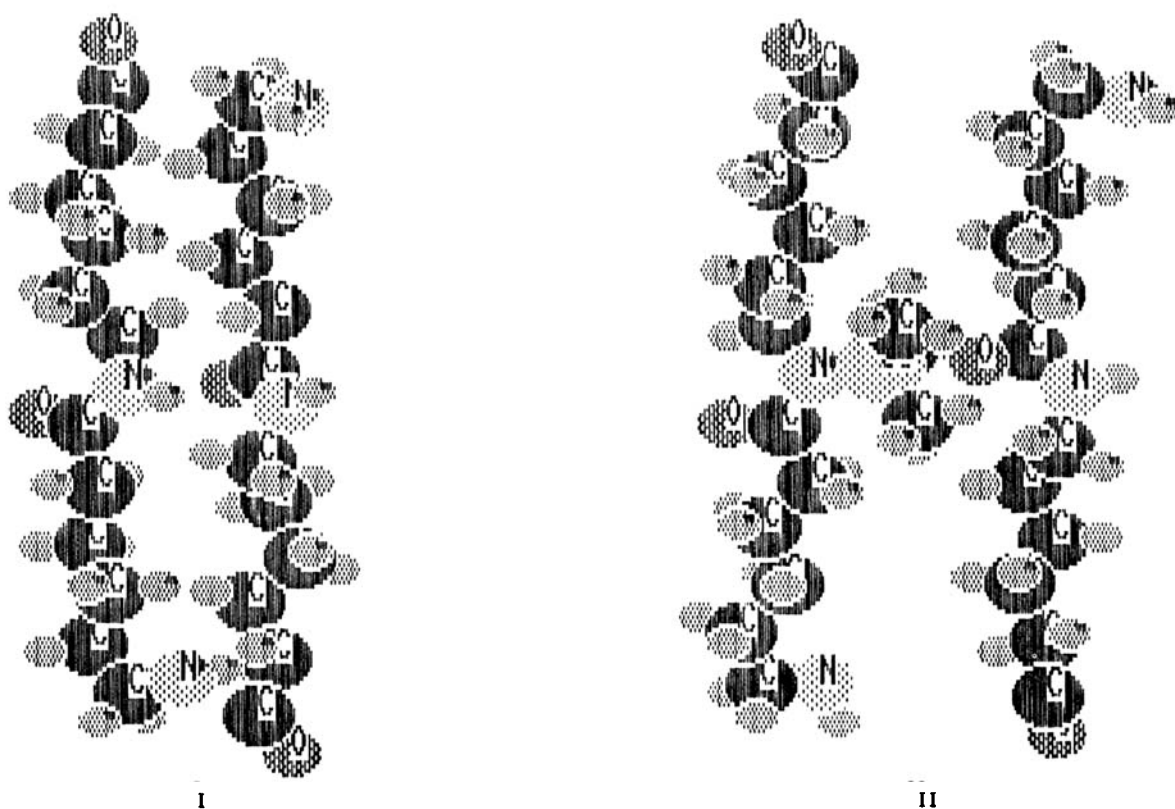

(a)

(b)

(c)

(d)

Figure 7 Morphology of N6 samples taken with a polarizing microscope at different contents of SL, by the same magnification, before melting: (a) 0% SL, (b) 1% SL, (c) 2% SL, (d) 5% SL.

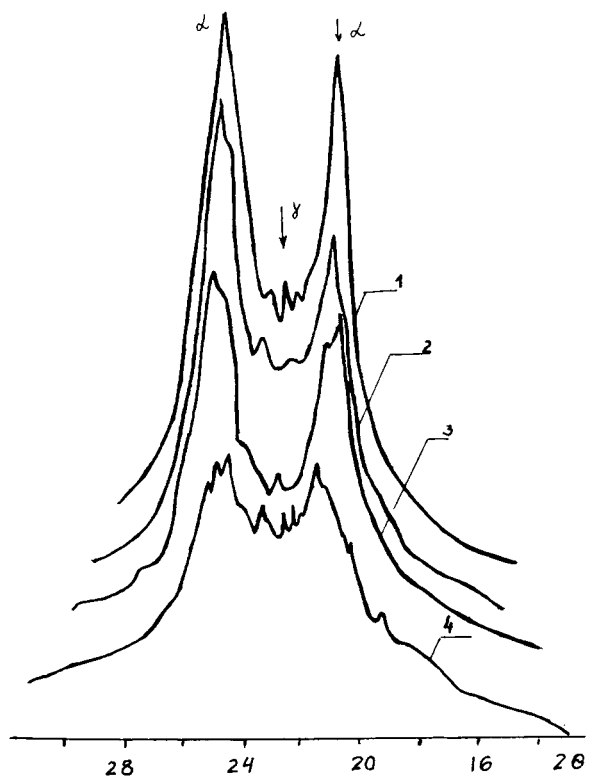**Scheme 2** H-bonds of N-6 (I) and N-6/SL (II).

Figure 8 Diffractograms of N6 obtained with different amounts of SL: (1) 1 mol, (2) 0%, (3) 2 mol, (4) 10 mol.
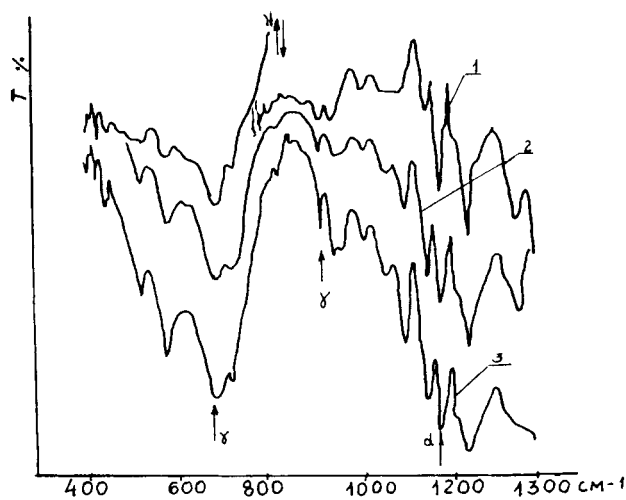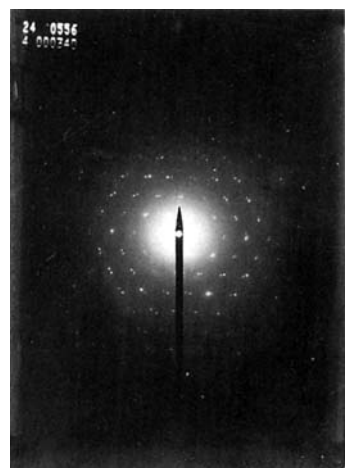

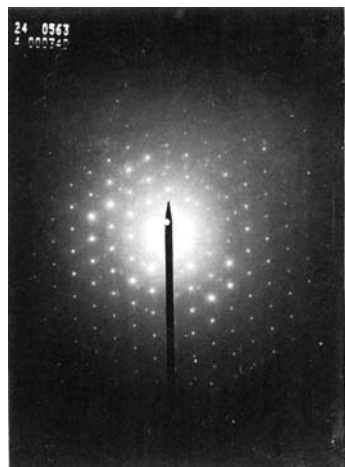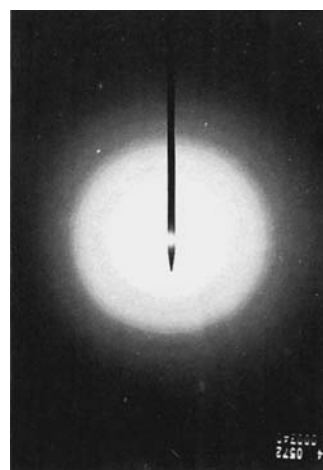**Figure 9** IR spectra of N6 samples in bulk, obtained in the presence of SL vs. monomer ε-caprolactam: (1) 2% SL, (2) 5% SL, (3) 10% SL.

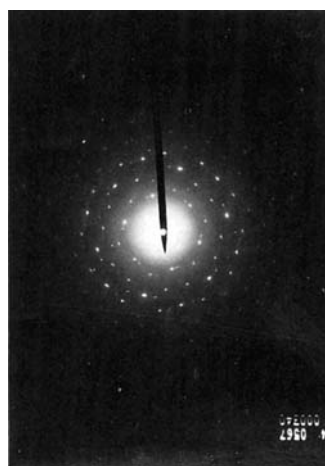**Figure 10** Electron microdiffractions of N6 samples prepared with different contents of SL: (a) 0% SL, (b) 1% SL, (c) 2% SL, (d) 5% SL, (e) 10% SL.

(a)

(b)

(c)

(d)

Figure 11 Electron micrographs of N6 samples obtained in the presence of activator SL at: (a) 1% SL, (b) 2% SL, (c) 5% SL, (d) 10% SL.

pared the samples prepared at different temperatures of polymerization in the presence of the mentioned activators. On the diffractograms [Fig. 3(a)] and DSC-gram [Fig. 3(b)] it can be seen that decreasing the polymerizing temperature increases the tendency of crystallization and the degree of crystallinity.

For N6 samples T_m decreases and $\bar{M}_v$ increases with increasing reaction temperature (Table II). The experimental data show that SL influences the structure of N6. For this reason it is interesting to study this process in more detail.

With the increase in amount of SL to ε-caprolactam, a significant change in the degree of crystallinity was observed (Table III, Fig. 4). The crystal sizes (Fig. 5) and the degree of crystallinity diminish, the melting interval, T_m, [Table III, Figs. 4, 6(a)] enlarges, and the glass temperatures, T_g, goes down [Fig. 6(b)]. Both the chain mobility and the amount of gel fraction also increase with increasing SL content.[21] The dependence of crystal size vs. SL content passes through a maximum at 2% (Fig. 5). If the content of SL activator is more than 2%, the gel fraction grows rapidly. This causes insolubility of the N6 samples and the determination of $\bar{M}_v$ is impossible (Table III). The morphological investigations show that the largest spherulites with average diameter of 10 μm are found in the nylon samples obtained in the presence of 2% SL (Fig. 7). In this case the macromolecular chain probably possesses very significant mobility because of reduced hydrogen bonds between NH and CO groups and the presence of the bulky substituent SiR_3 (Scheme 2). Usually the most stable form of N6 is α, with the typical reflection in WAXD at $2Q = 20.6$ and 24.8 (Fig. 8). In parallel with them could be observed the reflection at $2Q = 22.8$ (Fig. 8).[3] These are characteristics for γ modification. IR spectra also give evidence for the existence of the γ form. With the increase of the SL content (Fig. 9), the content of γ modification also goes up (Figs. 8, 9).[6,7] It was found that the existence of intermediate phases for the synthesized samples of N6 in bulk is evident (Fig. 10). The electron micrographic investigation shows (Fig. 10) that with the increase of the SL content an amorphization process took place. The crystalline size d (Å) was measured by electron micrographic diffraction (Table IV, Fig. 10). The estimated d value shows a tendency to decrease with increasing SL content. The micrograph replicas from the surface of the N6 samples obtained at different contents of SL (Fig. 11) were observed. Different structures, depending on the amounts of SL,

Table IV Crystalline-size Changes of N6 in Dependence on the SL Content

N	Content of SL (mol%)	d_1 (Å)	d_2 (Å)	d_3 (Å)
1	0	4.374	—	—
2	1	4.356	—	3.772
3	5	4.355	4.133	3.754
4	10	4.311	4.114	3.738

were observed. They all possess spherulitic structure. The size of the spherulitic formations are bigger than the maximum magnification of the electron microscope. For this reason a small part of a spherulite could be seen that resembles a lamella structure. With the increase of the content of SL in the polymer, an amorphization of the samples was noted with an increase in the degree of microheterogeneity.

CONCLUSION

The results of our investigations show undoubtedly that the influence of both the type and quantity of the activating additives is of great importance for the structural formation of N6 in bulk.

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