

Polyamides from lactams by centrifugal molding via anionic ring-opening polymerization

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Abstract

This paper deals with a study of some properties of the polymers obtained by centrifugal molding via activated anionic ring-opening polymerization of ϵ -caprolactam and copolymerization of ϵ -caprolactam with lauro lactam. Ethyl magnesium bromide, as initiator and *N*-benzoyl ϵ -caprolactam and *N,N'*-isophthaloyl-bis- ϵ -caprolactam, as activators were used. The initial mold temperature (initial polymerization temperature) was kept constant at 160°C. Our experimental data demonstrated that the degree of crystallinity depends on the activator type and concentration. The incorporation of lauro lactam into nylon 6 chain depresses both in the degree of crystallinity and the melting temperature of nylon 6/12 copolymers. The notched Izod impact strength of the copolymers increased as the lauro lactam content was increased, while the flexural modulus and the water absorption decreased. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It is well known that the anionic 'activated monomer' polymerization of ϵ -caprolactam occurs at a significantly faster rate, reaching equilibrium conversion in only a few minutes, compared to the classical hydrolytic polymerization process which takes about 12–24 h [1–3]. This fact, associated with the good mechanical properties of nylon 6 resulted in important applications of this polymer such as: reaction injection molding (RIM) [4], rotational molding [5,6], centrifugal molding [7–12], and monomer casting [13,14]. For these processing methods, the activated anionic polymerization of lactams proceeds rapidly at 120–160°C well below the melting temperature of nylon 6, 220°C [4], permitting direct manufacturing of products. Consequently, these processes have significant advantages and one can avoid conventional processing methods of polymer which used previously synthesized polymer [9–11,15].

The centrifugal molding of nylons via activated anionic polymerization of lactams is a processing method widely used in the manufacture of tubes [7–11,16], pulleys, discs and wheels, calender rollers [16] and other articles. The polymerization system consists either of one monomer

component or of a combination of two monomers which can form nylon (co)polymers or more layers of the polymer with different qualities. The anionic polymerization of lactams requires the use of a strong basic catalyst capable of generating the lactam anion (initiator) and a co-catalyst (activator) capable of generating the polymerization growth center (polyamidoacyl lactam) [17,18]. The fast catalyst systems for the anionic polymerization, based on Grignard reagents and their reaction products with the lactam are widely used in the reactive processing of lactams, e.g. Nylon-RIM [19], reactive extrusion [2]. The incorporation of a comonomer into the nylon 6 chain leads to modification of its physico-chemical and mechanical properties. The anionic copolymerization of ϵ -caprolactam with lauro lactam has been investigated and the results are published in patents [20–22] and other reports [23–28]. However, the studies directed toward centrifugal molding of nylon 6/12 copolymers via anionic ring-opening polymerization were not reported.

The present work deals with the centrifugal molding of nylon 6 and nylon 6/12 copolymers via anionic ring-opening polymerization in the presence of Grignard reagent as initiator. Both a monofunctional, *N*-benzoyl ϵ -caprolactam and difunctional, *N,N'*-isophthaloyl-bis- ϵ -caprolactam, activator were employed. Also, we have studied the influence of activator type and concentration on the characteristics of

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nylon 6 and the effect of lauro lactam content on nylon 6/12 copolymer properties.

2. Experimental

2.1. Materials

The purification of ϵ -caprolactam (technical grade, Fibrex S. A. —Savinesti, Romania) and lauro lactam (technical grade, Huls Germany) have been described elsewhere [9,11]. Ethyl magnesium bromide, (EtMgBr, Aldrich Chemical Co., Inc.) as initiator in 3.0 mol l^{-1} in diethyl ether solution was used without further purification. As polymerization activator we have used *N*-benzoyl ϵ -caprolactam (monofunctional activator) and *N,N'*-isophthaloyl-bis-caprolactam (difunctional activator) of the structures (Fig. 1a and b):

N-benzoyl ϵ -caprolactam and *N,N'*-isophthaloyl-bis- ϵ -caprolactam were prepared by reaction of benzoyl chloride, 98% (Aldrich Chemical) and isophthaloyl dichloride, 98% (Aldrich Chemical), respectively, with ϵ -caprolactam in anhydrous toluene in the presence of an equivalent amount of triethylamine [29]. The products were repeatedly crystallized from dry diethyl ether; m. p. (DSC), *N*-benzoyl ϵ -caprolactam, 68.3°C (Ref. [29]: 68.2°C) and m. p. (DSC), *N,N'*-isophthaloyl-bis- ϵ -caprolactam, 141°C (Ref. [25]: 139.2°C). Sulfuric acid (97% Ishizu Seiyaku) as solvent for viscosity measurements and hexafluoro-2-propanol (HFIP, Ishizu Seiyaku) as the mobile phase in gel permeation chromatography were of reagent grade and used as received. Other chemicals were of reagent grade and used without further purification.

2.2. Sample preparation

The material prepared by centrifugal molding via anionic polymerization of ϵ -caprolactam or ϵ -caprolactam–lauro lactam mixtures was in the form of a tube with diameter 101 mm and length 210 mm. For the determination of monomer conversion, molecular weight and molecular weight distribution, the samples were obtained by cutting and grinding up the dry polymer and then carrying out a Soxhlet extraction with methanol for 16 h. The samples were dried at 95°C for 48 h and stored in a desiccator over phosphoric oxide. For X-ray measurements we used ‘as centri-

fugal molded’ samples (approximately $25 \times 25 \times 3 \text{ mm}$) of each polymer. Samples for the determination of mechanical properties were prepared by cutting and milling to dimensions required by the standards (see below). Then the samples were dried at 60°C , to constant weight and stored in a desiccator over phosphoric oxide. For the FT-IR measurements the films were obtained by casting the formic acid polymer solutions (5 wt%) on glass plates followed by drying in an oven at 120°C for 15 min.

2.3. Measurements

The viscometric weight-average molecular weight (\bar{M}_w) of the nylons was determined by intrinsic viscosity measurements ($[\eta]$, 97% sulfuric acid) at a concentration of 0.2 g dl^{-1} with a suspended level Ubbelohde viscometer thermostatted at $25 \pm 0.1^\circ\text{C}$. Densities of the samples were evaluated by means of a density gradient column. The 1 m-high column, covering the range from 1.000 to 1.200 g cm^{-3} , was filled with a mixture of toluene and carbon tetrachloride (dried by 5 \AA molecular sieve). All density measurements were performed at 23°C . Gel permeation chromatography (GPC TSK gel GMH_{HR}-H) measurements were carried out with HFIP as the mobile phase at 40°C column temperature. The system was calibrated with PMMA standards whose molecular weights were 135,000, 69,000, 49,000, 36,000, 13,500, and 6,000, respectively. The flow rate chosen was 0.4 ml min^{-1} . Differential scanning calorimetry (DSC) was performed by METTLER DSC 112E, at a heating rate of $20^\circ\text{C min}^{-1}$, with a temperature range from 20 to 250°C in the first scan and sample weight of about 7–10 mg under nitrogen atmosphere, considering the heats of fusion the crystalline region of nylon 6 and nylon 12 to be 45.6 [30,31] and 53.7 cal g^{-1} [31], respectively. The values of the heat of fusion for the 100% crystalline nylon 6/12 copolymers were calculated based on the contributions of the mole percent of each homopolymer in the respective copolymer. The melting temperature, T_m of each sample was evaluated from the maximum of the endothermic peak. The moisture absorption was determined as the weight gain in % after dipping of sample in water according to ASTM 570-63 (variant D). The notched Izod impact strength and flexural modulus were determined according to ISO-180-1982 and ASTM D790-86, respectively [9]. The X-ray diffraction data were performed on a PW 1830 Philips diffractometer (Ni-filtered Cu- K_α radiation of wavelength 0.1542 nm) in the reflection mode over the range of diffraction angles (2θ) from 5 to 35° , at room temperature. The voltage and tube current were 40 kV and 30 mA, respectively. Infrared spectra were recorded on a Bomem-MB-104 Type FT-IR spectrometer, over a range $500\text{--}4000 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} and co-addition of 100 scans, using the thin film technique.

2.4. Polymerization–centrifugal molding

The polymerization–centrifugal molding process was

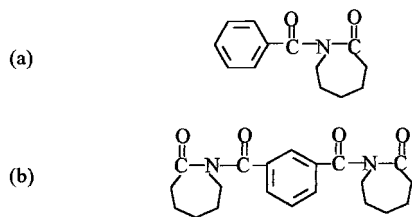


Fig. 1. Structure of activators used (a) *N*-benzoyl ϵ -caprolactam and (b) *N,N'*-isophthaloyl-bis-caprolactam.

Table 1
Influence of activator type and concentration on monomer conversion, molecular weight and polydispersity index

Activator ^a (mol%)	Conversion (%)	$[\eta]^b$ (dl g ⁻¹)	\bar{M}_w^c	\bar{M}_w^d	\bar{M}_n^d	\bar{M}_w/\bar{M}_n^d
<i>N</i> -Benzoyl ϵ -caprolactam						
0.2	65.5	2.16	79 600	13 100	59 800	4.57
0.4	96.5	2.04	73 400	14 500	69 100	4.80
0.6	97.7	1.56	51 100	8 700	34 900	4.01
<i>N,N'</i> -Isophthaloyl-bis- ϵ -caprolactam						
0.2	97.1	3.07	128 000	15 400	182 100	11.83
0.4	98.0	2.55	99 500	18 200	212 900	11.70
0.6	98.3	1.71	57 500	16 300	101 700	6.24

^a mol% based on the total monomer feed.

^b 0.2 g dl⁻¹, 97% H₂SO₄, 25°C (intensity method) [32,34].

^c \bar{M}_w was calculated from equations in Ref. [32,34] $\bar{M}_w = 2.81 \times 10^4 [\eta]^{1.35}$.

^d By GPC measurements, PMMA standards with molecular weights: 135,000, 69,000, 49,000, 36,000, 13,500 and 6,000.

carried out as described in Ref. [9–11], which is as follows.

(a) Preparation of polymerization mixture by mixing, while stirring for 30–40 s of two melts: one melt containing the initiator dissolved in half of the total amount of the monomer (141.5 g ϵ -caprolactam or ϵ -caprolactam–lauro lactam mixture, respectively) and the other containing the other half of monomer amount (141.5 g) and activator. The initiator (EtMgBr) solution (3.0 mol l⁻¹ in diethyl ether) was injected into anhydrous molten ϵ -caprolactam or ϵ -caprolactam–lauro lactam mixture at 90°C under a nitrogen atmosphere via a syringe, while simultaneously distilling off the volatiles. The concentration of initiator was kept constant at 0.5 mol% based on the total monomer feed. The amount of activator ranged from 0.2 to 0.6 mol% of the monomer feed for homopolymerization and it was kept at 0.6 mol% in the case of the copolymerization process (see Table 1 and Section 3.4).

(b) Transfer of well mixed melts into the previously heated mold at 160 ± 2°C (initial mold temperature).

The molding–polymerization time was 20 min in all cases.

3. Results and discussion

3.1. Influence of activator (chain initiator — source of growth centres) type and concentration on monomer conversion, molecular weight and polydispersity of nylon 6

The anionic ring-opening polymerization of ϵ -caprolactam by centrifugal molding was carried out in the presence of EtMgBr, as initiator and mono- and difunctional activators, *N*-benzoyl ϵ -caprolactam and *N,N'*-isophthaloyl-bis- ϵ -caprolactam, respectively synthesized for this purpose. The initial mold temperature (initial polymerization temperature) was 160 ± 2°C. The results are presented in Table 1.

At the same concentration of activator (0.2 mol%) the monomer conversion was much lower for monofunctional activator (65.5%) than in the case of difunctional activator

(97.1%). This result may be attributed to the fact that in the case of *N*-benzoyl ϵ -caprolactam the corresponding concentration of acyllactam (0.2 mol%) is far too below the equivalent ratio requirements [32] for the initiator (EtMgBr) concentration of 0.5 mol%. However, at 0.2 mol% of difunctional activator, *N,N'*-isophthaloyl-bis- ϵ -caprolactam the concentration of acyllactam being 0.4 mol% (twice the concentration of monofunctional activator) the monomer conversion is close to that obtained when a monofunctional activator is used at 0.4 mol%. There is a slight increase in the monomer conversion as the activator content (acyllactam) in the system was increased. The weight-average molecular weight of samples, \bar{M}_w was estimated by intrinsic viscosity measurement (intensity method) [33] using Eq. (1) [32,34]:

$$\bar{M}_w = 2.81 \times 10^4 [\eta]^{1.35} \quad (1)$$

Typical results are given in Table 1. Calculations (see Table 1) show that the viscometric weight-average molecular weight (\bar{M}_w) decreases when the activator concentration increases, in both cases of the presence of mono- and difunctional activator (*N*-benzoyl ϵ -caprolactam and *N,N'*-isophthaloyl-bis- ϵ -caprolactam, respectively) in the polymerization mixture. For a given concentration of activator the weight-average molecular weight (\bar{M}_w) of sample obtained with monofunctional activator is much lower than in the difunctional activator case. Also, number-average molecular weight (\bar{M}_n), weight-average molecular weight (\bar{M}_w) and polydispersity index (\bar{M}_w/\bar{M}_n) obtained from GPC measurements are reported in Table 1. Surprisingly, all samples are characterized by very small values of \bar{M}_n and high values of \bar{M}_w . This conducted to high values of polydispersity. The GPC curves of the polymers studied indicated that the *N,N'*-isophthaloyl-bis- ϵ -caprolactam activated nylon 6 show highest polydispersity (from 6.24 to 11.83) whereas the polydispersity of samples obtained in presence of *N*-benzoyl ϵ -caprolactam are much lower (between 4.01 and 4.80). It is well known that the

polydispersity index of a polymer is a record of the history of the reactions which occurred during its formation. The results obtained can be correlated with the observations made by Udipi et al. [25] and Kim et al. [35,36]. Data in the literature [25,35,36] indicates that the branching or crosslinking (by Claisen-type condensation) in the activated anionic polymerization of ϵ -caprolactam, has been suggested as being an important reaction as high conversion is approached. The effect of branching reaction of ϵ -caprolactam polymerization has been reflected on the \bar{M}_w and polydispersity index of nylon 6.

3.2. Crystallinity of nylon 6

It is well known that at room temperature the aliphatic polyamides are semicrystalline polymers. Data in the literature [37] indicate that polymerization and crystallization in the anionic ring-opening polymerization of ϵ -caprolactam are simultaneous parallel processes under certain reaction conditions. In the centrifugal molding of nylon 6, via anionic polymerization performed below the melting temperature of polymer, the formed polymer shows only limited solubility in the reaction mixture [14] the open monomer units being retained by hydrogen bonds between amide groups in the crystalline structure [18].

The crystalline structure of the nylon 6 which is developed during the molding-polymerization process is affected by processing conditions, particularly initial mold temperature as well as by type and quantity of activator [38]. The enthalpies of fusion, degree of crystallinity and melting points of nylon 6 were determined by differential scanning calorimetry and their values are presented in Table 2. The degree of crystallinity of nylon 6 was calculated from the ratio of the measured enthalpy of fusion of the sample and the enthalpy of fusion of a completely crystalline polymer by using the following equation:

$$\alpha_{\text{DSC}}\% = \frac{\Delta H_f}{\Delta H_{f,c}} \times 100, \quad (2)$$

where ΔH_f is the enthalpy of fusion of the sample, and $\Delta H_{f,c}$ is the enthalpy of fusion of 100% crystalline sample of the same polymer.

WAXS is an alternative method to evaluate the crystallinity of polymers. From the WAXS patterns in Fig. 2 it was found that the samples of homopolymers display peaks at double scattering angles (2θ) of 20.5 and 23°, corresponding to the reflections of the crystalline planes (200) and combined (002)/(202), respectively, indicative of monoclinic α -phase morphology.

The percent of crystallinity determined by X-ray method are shown in Table 2. There is an excellent agreement between the X-ray and DSC estimates of crystallinity for all the nylon samples.

Also, the level of crystallinity was evaluated from density measurements. Values recorded for density were computed from three determinations and were converted to degree of crystallinity (see Table 2) by using the following equation:

$$\alpha_d\% = \frac{\rho_c}{\rho} \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100, \quad (3)$$

where ρ is density of sample, g cm^{-3} , $\rho_a = 1.1 \text{ g cm}^{-3}$ is the density of completely amorphous sample, $\rho_c = 1.23 \text{ g cm}^{-3}$ is the density of completely crystalline sample [39].

The values of the degree of crystallinity obtained from density measurement for all samples were slightly greater as compared with those calculated from DSC analysis as has also been reported in the literature [26,40]. This fact can be interpreted as resulting from either the enthalpic contribution of disordered overlayer (which appears because the crystallization process takes place in the bulk, in the case of the centrifugal molding of the nylon 6 via anionic polymerization of the lactam) or the fact that the density measurements include interfacial contribution [41].

From the results obtained by DSC, X-ray and density measurements presented in Table 2, it can be observed that the degree of crystallinity of nylon 6 samples depends on

Table 2
Characteristics of nylon 6 samples obtained with EtMgBr as initiator and various activators

Activator ^a (mol%)	α_{DSC} , ^b (%)	α_x , ^c (%)	α_d , ^d (%)	Density, (g cm^{-3})	T_m^c , (°C)	Notched Izod Impact strength, (kJ m^{-2})	Flexural modulus, (MPa)	
<i>N</i> -benzoyl ϵ -caprolactam	0.2	36.0	35.1	36.9	1.1443	221	5.08	2340
	0.4	44.0	42.2	46.9	1.1575	225	4.30	2860
	0.6	46.0	45.0	47.2	1.1578	226	4.11	2990
<i>N,N'</i> -Isophthaloyl-bis- ϵ -caprolactam	0.2	47.0	46.0	50.5	1.1621	226	4.01	3055
	0.4	43.0	41.8	45.6	1.1558	220	4.40	2795
	0.6	42.3	41.2	44.7	1.1546	218.5	4.50	2730

^a mol% based on the total monomer feed.

^b Degree of crystallinity by DSC measurements.

^c Degree of crystallinity by X-ray measurements.

^d Degree of crystallinity by density measurements.

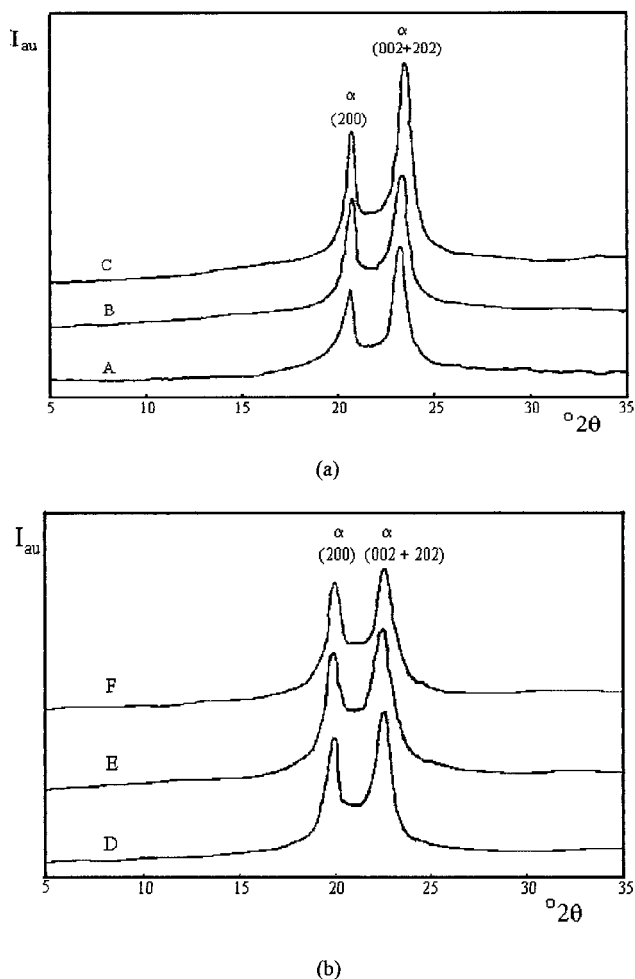


Fig. 2. X-ray diffraction patterns of nylons 6. (a) Activator: *N*-benzoyl ϵ -caprolactam A — 0.2 mol%, B — 0.4 mol%, C — 0.6 mol% and (b) *N,N'*-isophthaloyl-bis- ϵ -caprolactam D — 0.2 mol%, E — 0.4 mol%, F — 0.6 mol%.

both the type and content of the activator used. A slight increase in degree of crystallinity was observed as the content in monofunctional activator (*N*-benzoyl ϵ -caprolactam) increased from 0.2 to 0.6 mol% based on the total monomer feed. The increase in content in difunctional activator (*N,N'*-isophthaloyl-bis- ϵ -caprolactam) caused a decrease in crystallinity. The activator *N,N'*-isophthaloyl-bis- ϵ -caprolactam being difunctional will allow initiation of polymerization by two or less acyllactam functions. The macromolecular chains are not able to reorganize into perfect crystalline structure due to differences in length of chains, steric influence of isophthaloyl group and probably higher mobility of chains because of reduced protonic interaction between NH and CO groups.

The melting temperatures, T_m of homopolymers (see Table 2) found in the first DSC scan seems to show a small increase with the content of monofunctional activator in mixture feed, but T_m displays an opposite tendency as concentration of difunctional activator increases.

The notched Izod impact strength and flexural modulus of nylon 6 are found to decrease and increase, respectively, as degree of crystallinity is increased.

3.3. FT-IR Spectroscopic characterization of nylon 6

It is known that FT-IR spectroscopy is one of the most established methods for characterization of nylons and makes it possible to obtain information regarding the crystalline phase of the (co)polyamide samples [42,43]. The essential structural element of polyamides, the amide group (CO–NH) is a complex vibrational unit in IR range and involves stretching and bending vibrations. It is well known that nylon 6 generally shows α -type in the case of extended chain conformation or γ -type crystal structures in which the chains are twisted [44] depending on the thermal and processing conditions [45,46]. As seen in the Fig. 3a the IR spectrum of obtained homopolymer presents the strong absorption bands at 3299 cm^{-1} (amide A, =N–H stretch vibration), 1640 cm^{-1} (amide I, =C=O) and 1547 cm^{-1} (amide II, =N–H deformation) which are characteristic of the amide groups existing in the *trans* planar conformation.

These results also agree with previous data reported in the literature for nylon 6 [42,43]. Clearly, hydrogen-bonding exists between the NH and C=O groups, because it is known that free NH and C=O groups generate absorption bands at $\approx 3400\text{ cm}^{-1}$ (3460 cm^{-1} – *trans*, non-bonded amide group; 3420 cm^{-1} – *cis*, non-bonded amide group) [3]. The amide II band is especially sensitive to the crystalline structure corresponding to α -phase [42,43]. Also, the out-of-plane bends of the NH (amide V) and C=O (amide VI) groups which appear at 692 and 579 cm^{-1} , respectively are polymorph sensitive and indicate that the form of the crystalline phase of homopolymer is α -type [42,43,47]. The IR bands at 1476 and 1417 cm^{-1} are associated with $-\text{CH}_2-$ units adjacent to NH and C=O groups in the extended conformation of the chain in the α crystal modification of the obtained nylon 6. In the doublet band between 1202 and 1170 cm^{-1} the former band present in IR spectra indicates that amide group is in *trans* structure in α -form crystallinity and latter band corresponds to amorphous state [43,48]. For the amorphous phase bands at 1462 and 1438 cm^{-1} associated with $-\text{CH}_2-$ group are observed.

3.4. Anionic copolymerization of ϵ -caprolactam with lauro lactam

Incorporating a comonomer into the nylon 6 chain, the amide density is changed, the crystallinity decreases and melting point depresses. Also, one can modify properties of polymer such as: water absorption, moduli, impact strength and chemical resistance [26,49]. It is known that poly(lauro lactam) (nylon 12) possesses a lower water absorbance (1.8%) [50] as well as significant chemical and impact resistance and better electrical properties than nylon 6. However, nylon 12 has a lower melting point (172°C) [25] compared to nylon 6 (220°C) [4] due to the presence of

longer aliphatic segments between the amide group. The density of nylon 6/12 copolymers decrease as the initial concentration of lauro lactam in the reaction mixture increases.

The purpose of copolymerizing ϵ -caprolactam with lauro lactam, by centrifugal molding was to study the effect of the concentration of lauro lactam in the feed composition on the monomer conversion, water absorption, degree of crystallinity and mechanical properties (Izod impact strength and flexural modulus) of nylon 6/12 copolymers. A series of nylon 6/12 copolymers containing 0, 5, 10, 20, 30 and 50 wt% lauro lactam were obtained by centrifugal molding via the anionic activated copolymerization of ϵ -caprolactam with lauro lactam. Ethyl magnesium bromide as initiator (at 0.6 mol% of reaction mixture) and N,N' -isophthaloyl-bis- ϵ -caprolactam as activator (at 0.4 mol% of reaction mixture) were used for copolymerization process. The initial temperature of copolymerization was

kept constant at $160 \pm 2^\circ\text{C}$. The polymerization was allowed to proceed for 20 min, the mold was then cooled at $40\text{--}50^\circ\text{C}$ and the sample removed.

It is known that anionic polymerization mechanism of lactams involves nucleophilic attack on endo- or exo-cyclic carbonyl group of the growing chain by a lactam anion. The locus of nucleophilic attack has no significant implications in the homopolymerization, but it has a significant influence over copolymerization mechanism, and consequently on the copolymer structure [25]. The rate of copolymerization of ϵ -caprolactam with lauro lactam is determined by the rate of reaction between the N -acyllactam and the lactam anion [25]. In case of copolymerization of ϵ -caprolactam with lauro lactam the reactivities of monomers are close, because their relative acidities and their nucleophilicity, respectively, are also relatively close [25]. Consequently it is expected that nylon 6/12 copolymers would be more random than block [23,25]. The effect of variation in

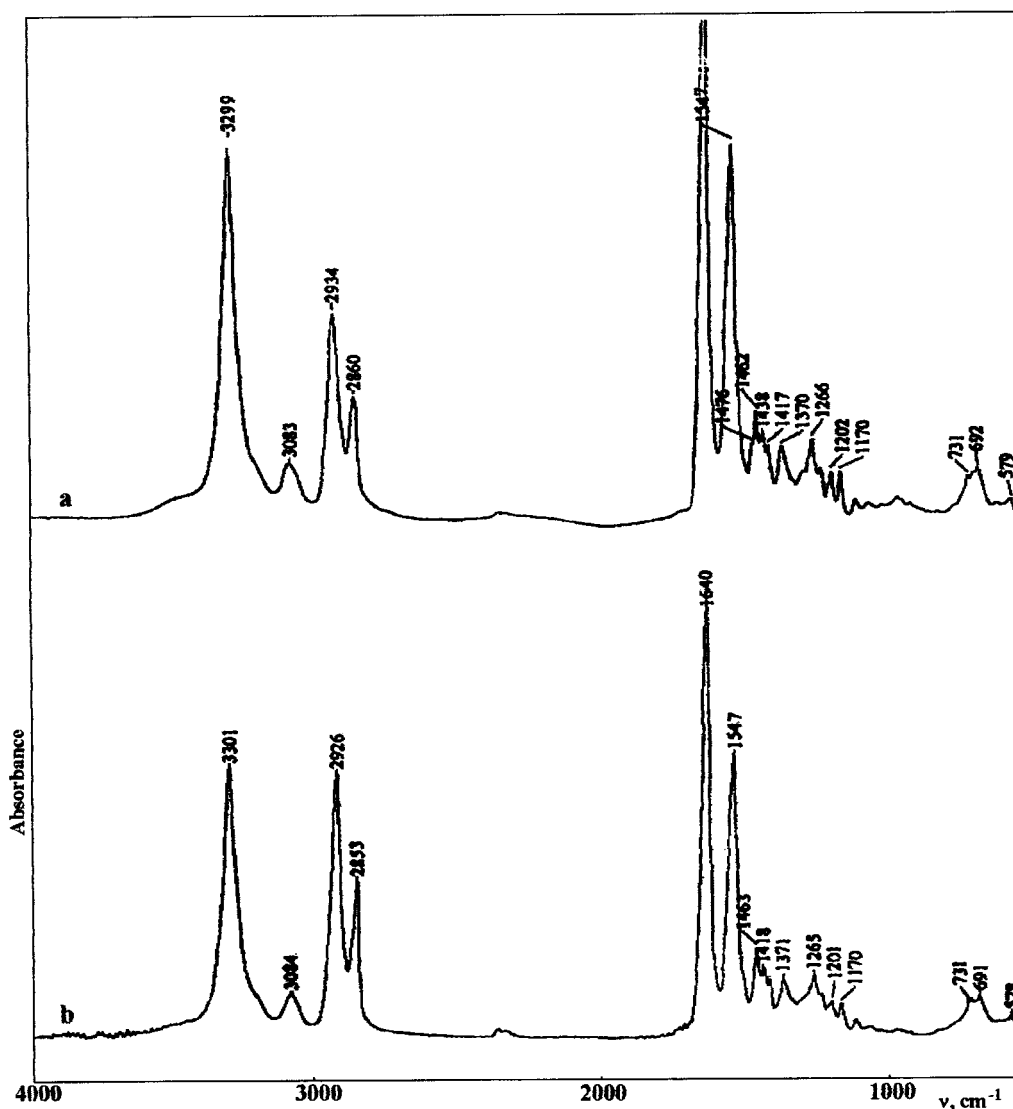


Fig. 3. FT-IR spectra of (a)nylon 6 (b) and nylon 6/12 copolymer with 50 wt% lauro lactam.

Table 3

The effect of variation in initial lauro lactam concentration on conversion, reduced viscosity and density of the nylon 6/12 copolymers

Copolymer composition CL/LL ^a	Conversion (%)	η_{sp}/c (g dl ⁻¹)	Density (g cm ⁻³)
100/0.0	98.1	2.5725	1.1546
95/5.0	98.0	2.5240	1.1455
90/10	97.2	2.4915	1.1316
80/20	93.3	2.2330	1.1230
70/30	89.8	2.0710	1.0889
50/50	83.4	1.5850	1.0653

^a CL = ϵ -caprolactam, LL = lauro lactam, composition by weight.

lauro lactam initial concentration on conversion, reduced viscosity and density are surveyed in Table 3.

It is observed that the conversion, reduced viscosity and density of nylon 6/12 copolymers decrease with the increase in initial comonomer concentration.

3.5. FT-IR Spectroscopic characterization of nylon 6/12 copolymers

The IR characteristic bands of copolymer with 50 wt% lauro lactam is given in Fig. 3b. It is difficult to determine the co-unit contents of copolymers from their IR absorption spectra because of the general similarity between the spectra of poly(ϵ -caprolactam) and poly(lauro lactam) [51]. The strong absorption band at 3300 cm⁻¹ (ν_{NH}) indicated that the amide NH groups of copolymer are substantially of *trans* form and completely hydrogen-bonded [52]. The presence of a band around 690 cm⁻¹ indicated that the nylon 6/12 copolymer is substantially in the crystalline α -form [47]. The bands characteristic of poly(lauro lactam) (at 1080, 1190 cm⁻¹) are not given by copolymers with less than 50 mol% of lauro lactam units. The maximum content of lauro lactam into the copolymers obtained by centrifugal molding is about 50 wt%, i.e. 36 mol%. If content of lauro lactam in total monomer feed is above 50 wt% some problems appear due to the higher reactivity coupled with the high temperature needed to melt the lauro lactam. Also, the incorporation of lauro lactam into nylon 6 chain depresses the degree of crystallinity and demolding process becomes difficult [6].

3.6. Influence of initial lauro lactam concentration on the crystallinity and melting temperature of the nylon 6/12 copolymers

Incorporating structural units of other monomers into the anionic nylon 6 chains act as an internal plasticizer and the degree of crystallinity of the copolyamide decreases. The decrease in crystallinity results from the disruption of chain packing due to the presence of longer flexible aliphatic hydrocarbon chain segments of lauro lactam. Therefore, the melting temperature decreases while the flexibility and

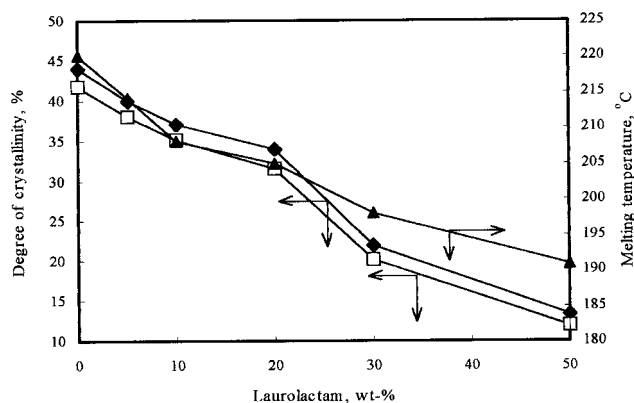


Fig. 4. Dependence of the degree of crystallinity determined by DSC of nylon 6/12 copolymers and their melting temperature, T_m on the concentration of lauro lactam (Δ) T_m ; (\blacklozenge) degree of crystallinity by X-ray; (\square) degree of crystallinity by DSC.

clarity of copolymers increase with increasing comonomer content (lauro lactam). Nylon 6/12 copolymers containing 20 wt% lauro lactam crystallize well since the ϵ -caprolactam segments are high enough in number and length to form hydrogen bonds, have strong dipole–dipole interaction and force the lauro lactam random sequences into the amorphous phase [25]. Data in the literature [25,53] indicates that the degree of crystallinity decreases continuously up to about 50 mol% lauro lactam and again one observes adverse effects on crystallization. The nylon 6/12 copolymers crystallinity was measured by DSC and X-ray on six samples. In the DSC thermograms of nylon 6/12 copolymers the peak areas decreases with increasing lauro lactam content. This means that crystallinity is reduced, because the areas are proportional to the degree of crystallinity. Fig. 4 shows that the degree of crystallinity of nylon 6/12 copolymers decreased as the initial concentration of lauro lactam was increased.

Fig. 5 shows the X-ray diffractograms of nylon 6/12 copolymers containing 5, 10, 20, 30 and 50 wt% lauro lactam. It is known that the crystal structure of copolymers with <20 mol% lauro lactam is in the α -phase [54].

All samples except copolymers containing 50 wt% lauro lactam, i.e. 36 mol% display a close similarity of peaks to those reported for nylon 6 homopolymers in α -form (see Fig. 5). The intensity of the X-ray diffraction curves drastically decreases as the lauro lactam content increased to 50 wt% based on the total monomer feed and a peak characteristic of the γ -phase was detected, between the two α -peaks at about $2\theta = 21.3^\circ$, corresponding to the reflection of the crystalline plane (100).

The variation in the melting temperature T_m of copolymers determined from the DSC curves (first run) is shown in Fig. 4. The melting temperature decreases as the lauro lactam content in the reaction mixture increases and the degree of crystallinity decreases.

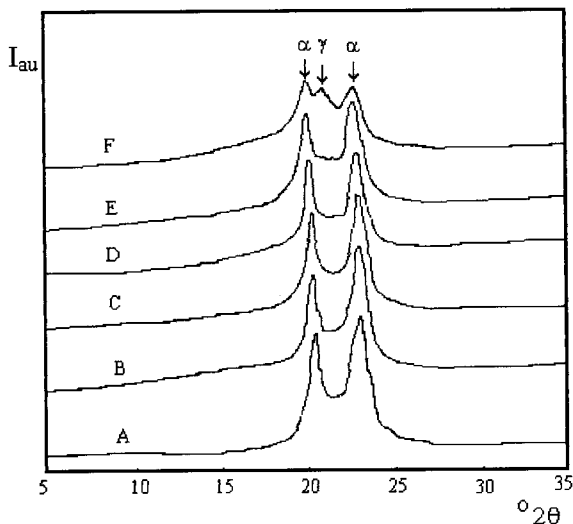


Fig. 5. X-ray diffraction patterns of nylons 6/12 copolymers. (A) 0 wt%; (B) 5 wt%; (C) 10 wt%; (D) 20 wt%; (E) 30 wt% and (F) 50 wt% lauro lactam.

3.7. Influence of initial lauro lactam concentration on water absorption of nylon 6/12 copolymers

At room temperature polyamides are semicrystalline and extremely sensitive to water absorption because of the existence of interchain H-bonding sites between amide groups [55,56]. The interaction between water and aliphatic polyamides is one of the most important characteristics of all nylons and has been studied by several researchers [55,42] in order to define the mechanism of water absorption and the associated changes in properties. The absorbed water has been shown to act as an effective plasticizer (which increases chain mobility) and thus will cause modification of the physico-mechanical properties (dimensional stability, T_g , tensile strength, flexural modulus) [6,50,57]. The water absorption depends on the degree of crystallinity of the copolymer, as the crystallinity increases the amount of water being absorbed decreases. Water molecules diffuse into the

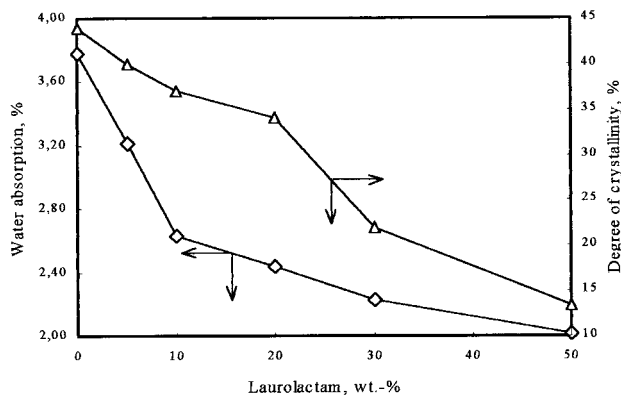


Fig. 6. Influence of initial lauro lactam content on water absorption of nylon 6/12 copolymers.

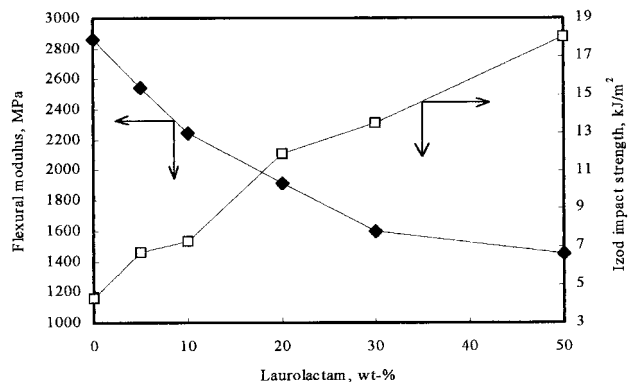


Fig. 7. Influence of initial lauro lactam content on Izod impact strength and flexural modulus of nylon 6/12 copolymers.

amorphous phase and only later displace 'disordered' amide–amide H-bonds, but they cannot penetrate into the crystal domain and break apart existing amide–amide bonds in this phase [39,43]. As the initial content of lauro lactam increases a decrease in the degree of crystallinity and water absorption occur, because the number of amide groups (responsible for water absorption) decreases while the length of aliphatic sequences between amide groups in polymer chains increases. At 50 wt% lauro lactam composition, the percent absorbed water is about 2.02% — close to that of nylon 12 which has a water content of 1.8%. The percent by weight of absorbed water for nylon 6/12 copolymers is plotted in Fig. 6.

3.8. Influence of initial lauro lactam concentration on notched Izod impact strength of nylon 6/12 copolymers

By changing the amide density, one can modify the crystallinity of nylon 6/12 copolymers. This effect may result from the introduction of longer aliphatic segments that cause a reduction in the intermolecular forces between chains. This reduction corresponds with plasticization, because lauro lactam units act to soften the polymer by making the polyamide chains more mobile. The crystallinity is important for the mechanical properties of the articles produced from nylon 6/12 copolymers. An increase in the percentage crystallinity generally leads to a decrease in the Izod impact strength [53]. As shown by DSC results in Fig. 4 the crystallinity of nylon 6/12 copolymers is lower than that of pure nylon 6. The values of Izod impact strength of the copolyamides obtained by using lauro lactam as a comonomer is better than that of pure nylon 6 and increases with increasing lauro lactam content. Consequently the impact strength of nylon 6/12 copolymers studied increases with decreasing degree of crystallinity of the moldings. The effects on notched Izod impact strength of incorporating the lauro lactam in copolymers are given in Fig. 7.

The Izod impact strength decreases with increase in

crystallinity, because outside effort which acts on the sample is rapidly propagated into crystalline region and caused breaking at interface of the crystallites.

3.9. Influence of initial lauro lactam concentration on flexural modulus of nylon 6/12 copolymers

Fig. 7 shows the influence of initial lauro lactam concentration on flexural modulus for nylon 6/12 copolymers. The flexural modulus of polymers increases, generally, by increasing the degree of crystallinity [58]. From Fig. 7 it can be seen that increasing the lauro lactam content indeed reduces the flexural modulus. This fact is due to the reduction in crystallinity. The decrease in the crystallinity with increasing co-unit (lauro lactam) content is a consequence of the reduced number of amide groups available for crystallization.

4. Conclusions

We have studied some properties of polymers obtained by the centrifugal molding of nylons via activated anionic ring-opening polymerization of ϵ -caprolactam and copolymerization of ϵ -caprolactam with lauro lactam. The initial mold temperature (initial polymerization temperature) was $160 \pm 2^\circ\text{C}$.

DSC, X-ray and density measurements showed that the degree of crystallinity of nylon 6 samples depends on both the type and content of the activator used. Also, for a given concentration of activator the weight-average molecular weights (\bar{M}_w), of samples obtained with a monofunctional activator are much lower than in the difunctional activator case.

The incorporation of a comonomer into the nylon 6 chain leads to modification of its physico-chemical and mechanical properties. The density and melting temperature of nylon 6/12 copolymers decrease with an increase in the comonomer content of the polymer. From DSC analysis and X-ray, it is shown that nylon 6/12 copolymers obtained by incorporating lauro lactam into the nylon 6 chain exhibit a degree of crystallinity lower than that of the pure nylon 6. Consequently, the notched Izod impact strength increases and flexural modulus of nylon 6/12 copolymers decreases progressively as the content of lauro lactam is increased.

The information derived from X-ray and infrared analysis indicates that the samples are predominantly in the α form. Both the polar amide groups and polymethylene sequences of obtained polymers are in *trans* conformation.

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