



## Evaluation of thermal and dielectric behaviour of some anionic nylon 612 copolymers

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### ABSTRACT

The anionic nylon 612 copolymers consisting of  $\epsilon$ -caprolactam and 0.0–50.0 wt.% of lauro lactam comonomer were synthesized and some of their characteristics were compared. The melting temperature, degree of crystallinity (first and second heating scan) and crystallization temperature of the nylon 612 copolymers are influenced by the presence of comonomer (lauro lactam) decreasing proportionally to the amount of the lauro lactam in the initial monomer mixture. The thermal stability of the copolyamides is good and equal to that of PA 6. Dielectric measurements performed on the polymers under study, over a frequency range of  $10^0$ – $10^6$  Hz, at temperatures from 173 to 373 K have evidenced that modification of the dielectric permittivity and dielectric loss values occur in concordance with increase/decrease of the homogeneity in the polymer chains structure induced by incorporation of lauro lactam segments.

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### 1. Introduction

The challenge to perform materials with tailored properties has focused the interest of researchers toward aliphatic polyamides (nylons) due to their excellent physico-chemical and mechanical features. A great variety of nylons and composites based on nylons can be obtained due to opportunity to choose the fraction and type of the components (monomers and matrix/filler, respectively) and the preparation method. These materials have gained a great importance for many field such as textile fibres, packaging, implants, membranes, biosensors, automotive, electrical/electronic and consumer applications [1–4].

The semicrystalline character and the attractive properties of nylons stem from intra- and interchain hydrogen bonds (specific to  $\alpha$ - and  $\gamma$ -crystalline phase, respectively) constituted between amide groups separated by methylene repeat unit with variable lengths [5]. The changing of the homogeneity in the structure of nylons by heating, copolymerization or addition of other compound as well as the slow crystallization seems to favour the  $\gamma$ -crystalline form. In the even nylons, such as nylon 6 all the NH and CO groups can establish hydrogen bonds between the adjacent molecular chains and a predominant *trans* conformation ( $\alpha$ -form) of the macromolecular chains is present. In the same time, even-even nylons have the different crystal structures that even ones when methylene segments have not same lengths, as in the case of nylon 612. The *gauche* conformation of the molecular chain, namely  $\gamma$ -form, appear in the crystal lattice of these type of nylons

to allow all the NH and CO groups to establish hydrogen bonds in the neighbouring molecular chains [6].

It is well known that nylon 6 has both desirable (high strength, stiffness, and resistance to nonpolar solvents) and undesirable (poor low-temperature toughness, moisture-sensitive) properties [7–9]. The anionic copolymerization of  $\epsilon$ -caprolactam (CL) with another lactam (i.e. lauro lactam, LL) is one promising pathway to modifying the properties of nylon 6 [7,10–13]. It is expected that the new nylon 612 copolymers with different content of the comonomer to combine the characteristics of the homopolymers.

The revealing of changes in the nylon properties needs knowledge of structural characteristics and understanding of the molecular dynamics in these polymers.

The survey of the literature has not yet revealed too many information about anionic nylon 612 copolymers obtained from corresponding lactams [13–15].

Taking into account all these it is of interest to contribute to evaluation of nylon 612 copolymers characteristics.

We focused our attention on the characterization of a series of nylon 612 copolymers based on lactams (CL and LL) with 0.0, 10.0, 20.0, 30.0, and 50.0 wt.% LL, denoted PCLL0–PCLL50 obtained by anionic copolymerization–rotational moulding combined technique.

The investigations were based on the fact that nylons are semicrystalline and rich in molecular dynamics and the amide groups have in FTIR spectra many characteristic bands (amide A, I–VII) especially related to chemical bonding and structure of materials [16,17].

Properties of the nylon 612 copolymers have ascertained through the combined use of Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, X-ray spectroscopy (WADS) and broadband dielectric spectroscopy (BDS) measurements.

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The thermal behaviour of the nylon 612 copolymers was also investigated by differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

The experimental results were correlated with initial content of LL and literature data and reported herein. For comparison of our results related to samples nylon 6 and nylon 612 copolymers with behaviour of other aliphatic polyamides reported in the literature one must take account that they were carried out on different polymers (obtained by anionic polymerization–rotational moulding process) and in different experimental conditions.

## 2. Materials

The monomers:  $\epsilon$ -caprolactam (CL) (technical grade, Sigma–Aldrich Chem. GmbH) and laurolactam (LL) (Huls – Germany) were used after purification in similar fashions to those described in the literatures [13,18].  $\epsilon$ -Caprolactam magnesium bromide (1.6 mol/kg concentration in  $\epsilon$ -caprolactam) as initiator, was obtained in our laboratories according to the procedure described in the literatures [19]. The activator, *N,N'*-isophthaloyl-bis- $\epsilon$ -caprolactam was synthesized in our laboratories [10,18]. Formic acid (98%) supplied by Merck–Germany and other chemicals were of reagent grade and used as received.

## 3. Experimental details

### 3.1. Synthesis of anionic nylon 612 copolymers

Anionic nylon 6 and nylon 612 copolymers were prepared by reactive rotational moulding process via anionic ring opening copolymerization of CL with of various weight content of LL comonomer. The process was performed in a laboratory scale rotational moulding installation. The content of LL was varied between 0.0 and 50.0 wt%. With respect to CL and LL mixture the content of *N,N'*-isophthaloyl-bis- $\epsilon$ -caprolactam, as activator and  $\epsilon$ -caprolactam magnesium bromide, as initiator, were kept constant at 0.4 mol% and 0.6 mol%, respectively. The initial polymerization temperature was kept constant at  $160 \pm 2$  °C for all tests. The details related to the synthesis of anionic nylon 6 and nylon 612 copolymers were presented in previously published articles [13,15].

### 3.2. Sample preparation

ATR-FTIR and dielectric properties measurements were performed on thin and transparent film samples. In this sense the anionic nylon 6 and nylon 612 copolymers were dissolved in formic acid to a concentration of 10 wt%. The films with compact structure and uniform thickness (about 20  $\mu$ m) obtained by casting the resulted solutions onto flat glass substrates and following were dried in vacuum at 60 °C until constant weight was reached. The X-ray spectral measurements were performed on cut sample of approximately  $25 \times 25 \times 4$  mm.

### 3.3. Characterization

#### 3.3.1. Fourier transform infrared spectroscopy (ATR-FTIR)

The ATR-FTIR spectra of the films of nylon samples were recorded at 25 °C over the range  $4000\text{--}400$   $\text{cm}^{-1}$  using a Bruker Vertex70 spectrometer. The internal reflection element was a single reflection diamond ATR crystal with an incidence angle of 45°. Hundred scans at a resolution of  $2$   $\text{cm}^{-1}$  were averaged to obtain each spectrum.

#### 3.3.2. Differential scanning calorimetry (DSC)

The nonisothermal crystallization and melting behaviour of nylon 6 and nylon 612 copolymers (coming directly from synthesis) was examined using differential scanning calorimetry (DSC) (Mettler DSC 12E) under nitrogen atmosphere in order to protect the nylons from degradation. Specimens were heated to 250 °C (first heating scan) and then cooled down to 25 °C. The crystallized specimens were reheated to 250 °C (second heating scan) to investigate the melting behaviour of nylon 6 and nylon 612 copolymers. The heating and cooling rates for all runs were 10 °C/min. Thus the crystallization occurs under nonisothermal conditions. The degree of crystallinity of nylon 6 and nylon 612 copolymers was calculated from ratio of the measured enthalpy of fusion of the sample ( $\Delta H_f$ ) and the enthalpy of fusion of a completely crystalline sample ( $\Delta H_{f,c}$ ). In this sense was taken into account the enthalpy of fusion ( $\Delta H_{f,c}$ ) for 100% crystalline of nylon 6 and nylon 12, considered to be  $191$   $\text{J g}^{-1}$  [10,13], and  $225$   $\text{J g}^{-1}$  [13,20], respectively and the contributions of the mol% of each homopolymer in the respective copolymer. The following equation was used:

$$\alpha_{\text{DSC}} (\%) = \frac{\Delta H_f}{\Delta H_{f,c}} \times 100 \quad (1)$$

where  $\Delta H_f$  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 copolymer.

#### 3.3.3. Thermogravimetric analysis (TGA)

The thermal stability of the extracted samples (nylon 6 and nylon 612 copolymers) was investigated by recording the mass loss as a function of temperature by thermogravimetric analysis (ATG) with a Paulik Derivatograph Q-1500D. Each sample was heated from 50 to 600 °C at a scanning rate of  $10$   $^\circ\text{C min}^{-1}$  in air atmosphere.

#### 3.3.4. Wide-angle X-ray diffraction

The crystal structures of nylon 6 and nylon 612 copolymers samples coming directly from synthesis was determined by means of Wide-angle X-ray diffraction (WAXD) as a function of LL content, on diffractometer PW 1830 Philips using nickel filtered  $\text{Cu K}\alpha$  radiation of wavelength 0.1542, in the range of diffraction angles ( $2\theta$ ) from 5° to 35° at a speed  $2^\circ \text{min}^{-1}$ . The voltage and tube current were 40 kV and 30 mA, respectively.

#### 3.3.5. Dielectric measurements

The dielectric spectroscopic experiments were run on a Novo-control ALPHA 40 Broadband Dielectric Spectrometer in controlled atmosphere. The sample was located between two horizontal gold plated metallic electrodes, and a permanent gaseous dry nitrogen jet was purged. The measurements were conducted over a broad frequency range,  $10^0 < F$  (Hz)  $< 10^6$  with a 1 V applied voltage, and at temperature between 173 and 373 K with a heating rate of 2 K/min. The dielectric behaviour was evaluated taking in account the well known expression of the complex relative permittivity ( $\epsilon^* = \epsilon' - i\epsilon''$ ) that contain the two terms, namely the relative permittivity–real part,  $\epsilon'$  (i.e., energy storage term, dielectric constant) and the relative loss–imaginary part,  $\epsilon''$  (i.e., absorptive term, dielectric loss) associated with the polarization or capacitance and the conductance of the polymer, respectively [21–24]. The results obtained under our experimental conditions were the typical values of reproduced experiments.

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