

# Synthesis and characterization of Nylon3

## Naylon3 sentezi ve karakterizasyonu

Research Article

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### ABSTRACT

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Nylon3 was prepared through base-catalyzed hydrogen transfer polymerization of acrylamide. The polymer was fully characterized by FTIR, FT-Raman, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, DSC, TGA, XRD, MALDI-MS, and end-group analyses. Glass transition temperature, thermal degradation temperature, d-space values, crystallinity, average molecular weights and polydispersity of nylon3 obtained were determined. Initiation, propagation and termination mechanisms of base-catalyzed hydrogen transfer polymerization of acrylamide were proposed using the structural analyses of nylon3 obtained.

### Key Words

Nylon3, hydrogen transfer polymerization, poly( $\beta$ -alanine).

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### ÖZET

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Naylon3 akrilamitin baz katalizli hidrojen transfer polimerizasyonu ile hazırlandı. Polimer FTIR, FT-Raman, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, DSC, TGA, XRD, MALDI-MS ve uç grup analizleri ile tamamen karakterize edildi. Camı geçiş sıcaklığı, termal bozunma sıcaklığı, kristal yüzdesi, d-boşluk değerleri, ortalama molekül kütlesi ve polidispersitesi belirlendi. Akrilamitin hidrojen transfer polimerizasyonunun başlama, büyüme ve sonlanma basamakları elde edilen naylon3 polimerinin yapısal analizi kullanılarak önerildi.

### Anahtar Kelimeler

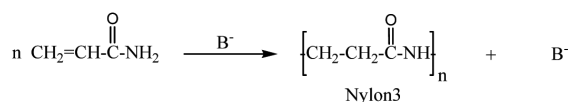
Naylon3, hidrojen transfer polimerizasyonu, poli( $\beta$ -alanin).

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## INTRODUCTION

The smallest member of polyamides, nylon3, is a highly crystalline polymer with a high thermal and mechanical resistance [1]. Because of high amide concentration, nylon3 shows properties of an excellent formaldehyde scavenger [2]. Nylon3 has been reported to have some applications such as heat stabilizer for polyacetal resins, soil conditioner, an additive for polymers, a coating material, a textile auxiliary and a printing agent [3]. Nylon3 (sometimes described as poly- $\beta$ -alanine or polyamide3) was obtained by several groups [4-10] using hydrogen transfer polymerization of acrylamide in the presence of an anionic catalyst ( $B^-$ ) according to the reaction below.



Initiation step of the polymerization was discussed in the literature [6-8]. Furthermore, alternative methods [11-12] have been proposed to prepare nylon3. Hydrogen transfer polymerization is the cheapest and easiest method for preparation of nylon3.

Detailed characterization of nylon3 was conducted with regard to thermal, structural and spectroscopic properties. Moreover, similarity of repeating unit of the polymers to structure of alanine, which is a well established ESR radiation dosimeter material, prompted us to perform a study on radiation chemistry of the polymer. This paper describes in detail the preparation and characterization of nylon3 with the anticipation of its use as a potential dosimetric material.

## Materials and Methods

Acrylamide (Sigma, 99%), potassium chloride (Carlo Erba 99%) and lithium chloride (Merck 98%) were obtained from their manufacturers. Sodium tert-butoxide (Aldrich 97%) obtained commercially was used without any purification. O-dichlorobenzene was redistilled in presence of  $\text{CaCl}_2$  before use.

## Polymerization

Nylon3 was prepared by hydrogen transfer polymerization of acrylamide using sodium tert-butoxide as a basic catalyst. The polymerization was carried out in a three-necked flask with continuous stirring under argon atmosphere at  $100^\circ\text{C}$  for 6 hours. O-dichlorobenzene was used as solvents. Potassium chloride was added into the reaction medium to increase the degree of polymerization by increasing the solubility of propagating chains. Hydroquinone was added to reaction medium to prevent possible thermally initiated vinyl polymerization of acrylamide. Monomer, catalyst, KCl and hydroquinone concentrations were adjusted by following Masamoto's procedure [5]. Water-insoluble fractions of the polymers were separated and used for characterization.

## Characterization

FTIR spectrum of nylon3 in KBr pellets was recorded on a Shimadzu FTIR Spectrometer in the range of  $400-4000 \text{ cm}^{-1}$  wavelength.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of nylon3 were recorded using Bruker 400 MHz in 10 M LiCl solution. DSC thermogram of nylon3 was recorded in the range of  $20-400^\circ\text{C}$  under  $\text{N}_2$  atmosphere using TA Instruments Q10 series DSC. TGA thermogram of nylon3 was recorded in dynamic nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$  using Perkin Elmer Pyris 1 model TGA. FT-Raman spectrum of the powder polymer sample was recorded by a Renishaw 1000B micro-Raman spectrometer. Powder XRD spectra of the polymer was obtained by Rigaku Multiflex spectrometer at a  $3^\circ/\text{min}$  rate in the range of  $3-60^\circ$ . End-group analysis of the polymer was carried out by conversion of primary amide group ( $\text{NH}_2$ ) to ammonia by extraction of the polymers with potassium hydroxide and titration of ammonia evolved [Yamamoto et al, 3], Dithranol (1,8-dihydroxy-10H-anthracen-9-one) (40 mg/mL in tetrahydrofuran) matrix for nylon3 was prepared. MALDI sample was prepared by mixing polymer solutions (10 mg/mL in 80 mM LiCl solution) with the matrix solution (1:10 v/v) in a 0.5 mL eppendorf® micro tube. Finally 1  $\mu\text{L}$  of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. Mass spectrum was acquired on a Voyager-DE™

PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectrum was recorded in linear mode with average of 50 shots.

## Results and Discussion

### FTIR Spectroscopy

The FTIR spectrum of nylon3 shows characteristic secondary amide absorption bands: 3298  $\text{cm}^{-1}$  (NH stretching), 3080  $\text{cm}^{-1}$  (overtone of NH in plane bending), 1640  $\text{cm}^{-1}$  (C=O stretching, amide I), 1540  $\text{cm}^{-1}$  (N-H bending, amide II), 1230  $\text{cm}^{-1}$  (C-N stretching, amide III) and 975  $\text{cm}^{-1}$  (C=O bending in-plane, amide IV) as shown in Figure 1.

### FT Raman Spectroscopy

FT Raman spectrum of nylon3 is given in Figure 2. Raman spectrum of nylon3 has been reported before by Hendra et al [13]. Most characteristic raman bands of nylon3 was assigned to 2932  $\text{cm}^{-1}$  (asymmetric  $\text{CH}_2$  stretching), 1637  $\text{cm}^{-1}$  (Amide I C=O stretching), 1443  $\text{cm}^{-1}$  ( $\text{CH}_2$  bending), 1366  $\text{cm}^{-1}$  ( $\text{CH}_2$  wagging), 1291  $\text{cm}^{-1}$  ( $\text{CH}_2$  twisting), 1200  $\text{cm}^{-1}$  (NH wagging), 1113  $\text{cm}^{-1}$  (C-C stretching) and 974  $\text{cm}^{-1}$  (C-CO stretching).

### NMR Spectroscopy

$^1\text{H}$ -NMR spectrum of nylon3 was obtained in 10 M LiCl- $\text{D}_2\text{O}$  solution (Figure 3). Two triplets

were observed at about 2.6 and 3.5 ppm having almost equal intensities. These signals belong to methylene hydrogens  $\text{CH}_2$ -CO (at 2.6 ppm) and  $\text{CH}_2$ -NH (at 3.5 ppm). As an exchange has been expected to occur between  $\text{D}_2\text{O}$  and amide protons, amide protons (NH and  $\text{NH}_2$ ) were not observed on the spectrum. Instead, a signal, belonging to HOD [14], has been shown at about 4.72 ppm. The small peaks 2.75 and 3.66 ppm were attributed to olefinic protons at the end-group. As the small peaks overlap with the methylene peaks, degree of polymerization could not be estimated using the intensities of the peaks.

$^{13}\text{C}$ -NMR spectrum of nylon3 was obtained in 10 M LiCl- $\text{D}_2\text{O}$  solution (Figure 4). Three signals were observed in the spectrum. The signals belong to methylene carbon adjacent to carbonyl group (at 35.8 ppm), methylene carbon adjacent to amide group (at 36.4 ppm) and carbonyl carbon (at 174.3 ppm).

### XRD Spectroscopy

XRD spectrum of nylon3 is given in Figure 5. Upper curves show the original spectrum. The lower curves show the diffraction due to crystalline regions as obtained from the subtraction of amorphous region from the upper curve. The two strong maxima at  $19^\circ$  and  $23.5^\circ$  (d spaces, 4.56 and 3.81) in X-ray diffraction curve of nylon3 have been

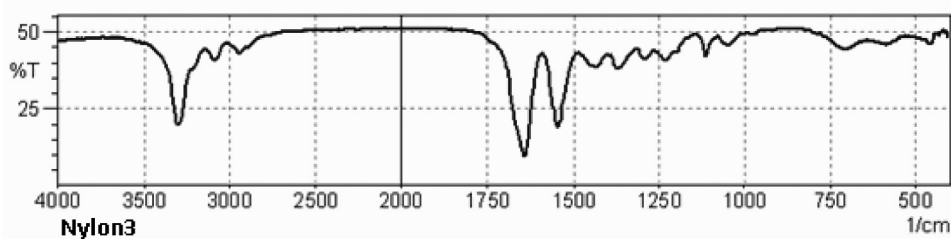


Figure 1. FTIR spectra of nylon3

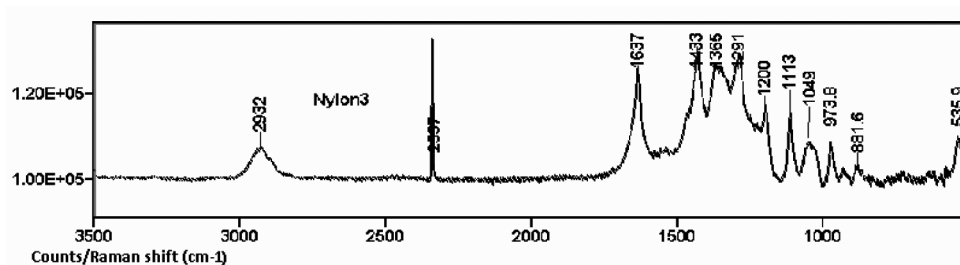


Figure 2. FT-Raman spectrum of nylon3

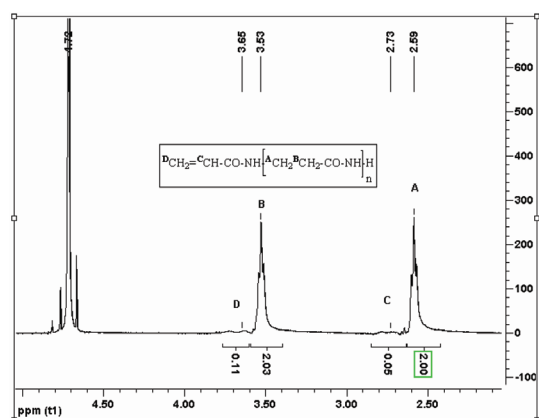


Figure 3. <sup>1</sup>H-NMR spectrum of nylon3

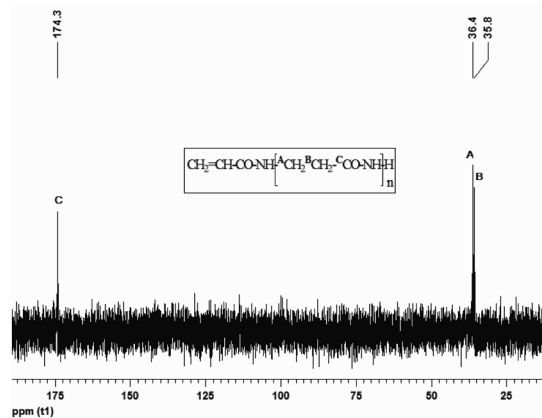


Figure 4. <sup>13</sup>C-NMR spectrum of nylon3

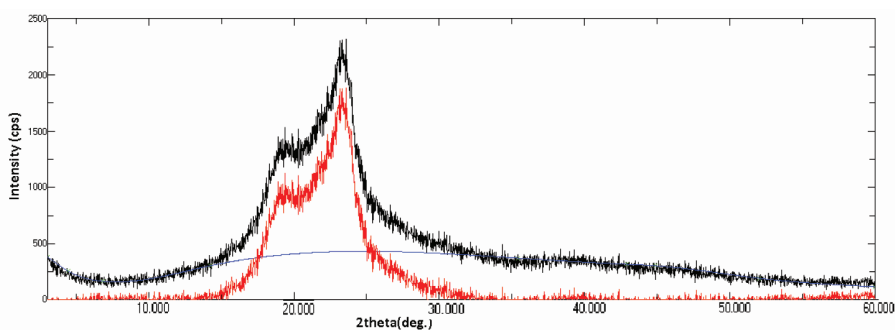


Figure 5. XRD spectrum of nylon3. (Black line: original spectrum, Red line: subtracted spectrum)

also observed at 22.0° and 23.5° (2θ) by Camino and Guaita [15]. Degrees of crystallinity of the polymers have been determined from ratio of the area under the lower curve to that of upper curve. Crystallinity of nylon3 was found to be 37%.

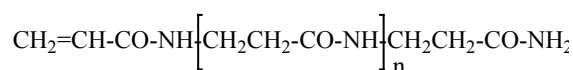
### Differential Scanning Calorimetry

Glass transition temperature ( $T_g$ ) of nylon3 has been observed at about 124°C (reported as 111°C by Wexler [16], 73-121.2°C by Berger [10]) (Figure 6). The exothermic peak centered at about 224°C is attributed to crystallization [15]. The polymer started to melt at about 250°C with an endothermic peak centered at 343°C (reported as 340-350°C by Berger [10] and 350-355 °C Wexler [16]). Before the melting process was completed, the polymer started to decompose at about 350°C (Figure 7).

### End-group Analysis

End-group analysis of nylon3 sample was carried out just by determination of  $\text{NH}_3$  evolved by hydrolysis of primary amide group ( $\text{NH}_2$ ). When <sup>1</sup>H-NMR spectrum and the contents of  $\text{NH}_2$  were

evaluated, the molecular structure of synthesized nylon3 has been estimated as;



Nylon 3

**Scheme 1.** Structure of nylon3 obtained from base-catalyzed hydrogen transfer polymerization

### MALDI mass spectrometry

MALDI mass spectrum of nylon3 was obtained using positive ion and linear mode in various novel MALDI matrices. But the high resolved MALDI mass spectra was obtained in dithranol matrix for nylon3. Inset in Figure 8 shown the expanded of the spectrum between 950 and 1550 Da masses. The mass difference between the most intense peaks were calculated to be 71 Da which was represented the monomer mass. For nylon3, molecular masses ( $M_n$ ,  $M_w$ ,  $M_z$ ) and the heterogeneity index (HI) were calculated to be 2002, 2619, 3087, and 1.31 using software which was available on Applied Biosystem mass spectrometric software. In the MALDI-MS

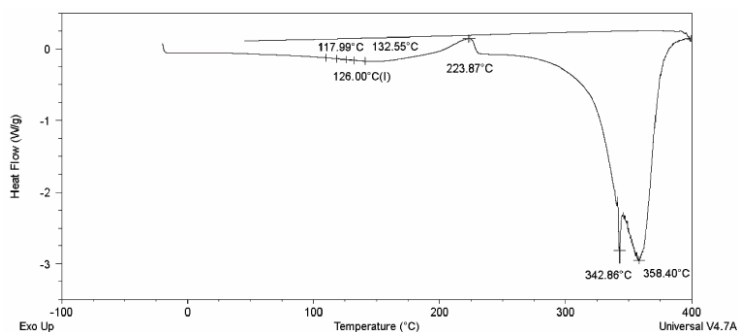


Figure 6. DSC thermogram of nylon3.

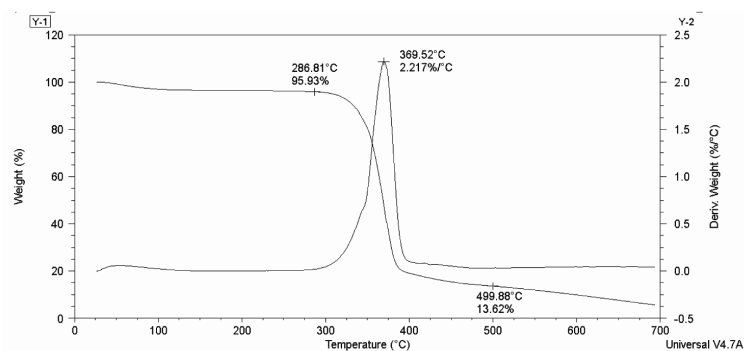


Figure 7. TGA Thermogram of nylon3.

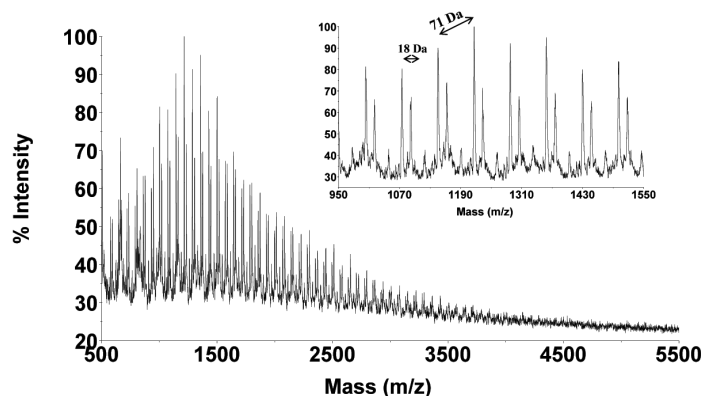


Figure 8. Positive ion and linear mode MALDI-MS spectrum of nylon3 was obtained in Dithranol (1,8-dihydroxy-10H-anthracen-9-one) (40 mg/mL in tetrahydrofuran), MALDI matrix using nitrogen laser accumulating 50 laser shots. Inset spectrum shows expanded mass region of the polymer between 950 and 1550 Da.

spectrum of nylon3, beside the repeating polymer chains which increase 71 Da mass differences, other peak groups with reasonable high peak intensities corresponding to the intensity of main polymer chains were also observed. These peak groups have higher masses than the main polymer units about 18 Da. This mass difference corresponds the water adducts of the cationized polymer chains. This means that polymer chains could generated the water adducts in the gas-phase because of the water sensitivity of the

amine groups onto the polymer chains.

Table 1. Molecular weights and heterogeneity indices characteristics of the three polymers synthesized in this study

Polymer	Mn	Mw	Mz	HI	N
Nylon3	2002	2619	3087	1.31	28-29

MALDI-MS spectrum of the studied polymer showed single nice distribution. No other polymeric mass distribution was observed at the other

**Table 2.** Properties of nylon3 prepared through hydrogen transfer polymerization. **a)** water-insoluble fraction, **b)** Analysis of amount of NH<sub>2</sub> at the end-groups, **c)** Obtained from DSC thermograms, **d)** % crystallinity from XRD spectrum, **e)** from MALDI-MS spectra

	<sup>a</sup> Yield (%)	DP <sup>b</sup>	<sup>c</sup> Tg (°C)	<sup>c</sup> Tm (°C)	<sup>c</sup> Td (°C)	<sup>d</sup> X %	Mn <sup>e</sup>	DP <sup>e</sup>
Nylon3	37-40	24	124	348	359	37	2002	28

masses even if at high masses up to 150 kDa. This and the clearness of the spectrum showed that one type polymer was synthesized only in our experimental conditions.

Table 2 summarizes some properties of the nylon3 obtained. When the data obtained from <sup>1</sup>H-NMR spectrum of nylon3, MALDI, and end-group analysis was considered the mechanism (Scheme 2) may be proposed for base-catalyzed hydrogen transfer polymerization of acrylamide.

## Conclusion

This paper describes in detail the synthesis and characterization of nylon3 with the anticipation of its use as a potential dosimetric material. The structural analyses revealed that the polymer obtained was linear nylon3 (poly-β-alanine) with low-molecular weight, neither branched [9] nor a copolymer of polyacrylamide and nylon3 [9].

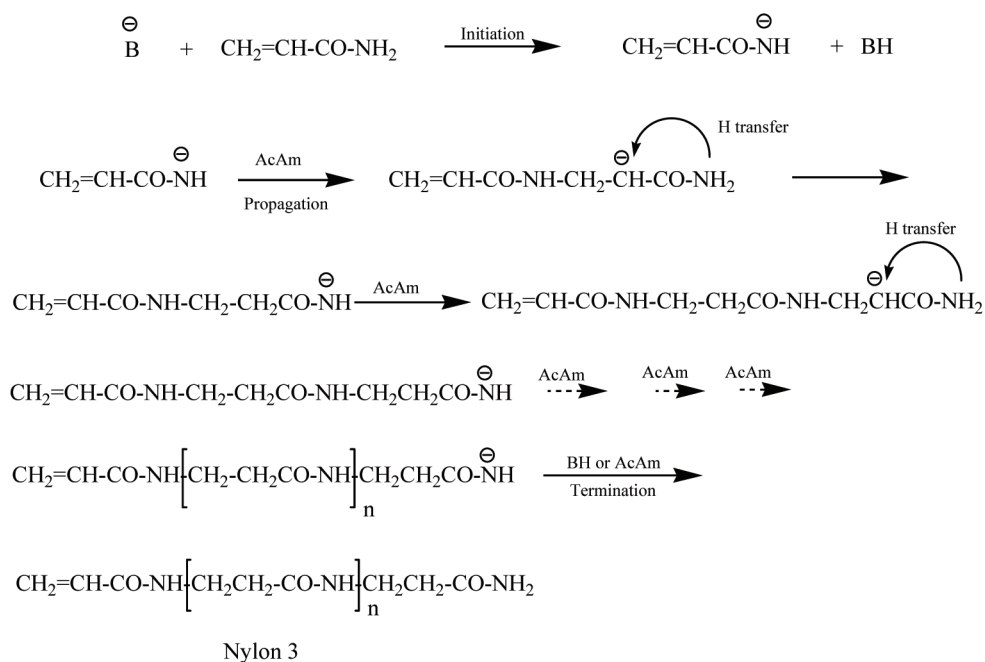
Nylon3 obtained by HTP of acrylamide exhibited high thermal decomposition temperature (above 350 °C) and high crystallinity (about 40%). These properties are important parameters for evaluation of a material as a potential radiation dosimeter application.

## Acknowledgements

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**Scheme 2.** The mechanism proposed for base-catalyzed hydrogen transfer polymerization of acrylamide to yield nylon3

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