

SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED-SEGMENTED BLOCK COPOLYETHERAMIDE BASED ON NYLON6 AND POLY(ETHYLENE OXIDE)

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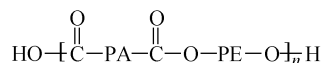
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Abstract Segmented block copolymer based on nylon6 (N6) and polyethylene oxide (PEO) with stoichiometric ratio was synthesized *via* a two-step process. The first step represents end capping of N6 in the presence of adipic acid leading to carboxy terminated N6, and the second one is polycondensation of the latter product with PEO in the presence of catalyst and thermostabilizer to form a high molecular weight multi-block copolymer. Several methods were applied to characterize the synthesized copolymer such as Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, differential thermal analysis, differential scanning calorimetry, X-ray diffraction and atomic force microscopy. The obtained results confirmed the multi-block structure for copolymer with a very high degree of micro-phase separation. Atomic force microscopy micrographs indicated that the morphology was the dispersion of high stiffness nanostructured polyamide (PA) domains in the amorphous region of PEO matrix, which can be very important in their performance for membrane processes.

Keywords: Copolyetheramide; Segmented block; Nylon6; Poly(ethylene oxide); Nanomaterial.

INTRODUCTION

Thermoplastic elastomers have many advantages such as good solvent resistance, good mechanical properties, wide application temperature range, ease of processing and potential for recycling. Poly(ether-*block*-amide) (PEBA) copolymers are a relatively new family of thermoplastic elastomers (TPE) with unique physical and processing properties^[1–5]. The unique nature of these materials has been attributed to their structures which conceptually consist of alternating polyamide as hard segments and polyether as soft segments. The general structural formula of these block copolymers is as follow^[6, 7]:



The hard segments crystallize in lamellae and form physical crosslinks for the amorphous (soft) segments^[8]. The high polarity difference between hard and soft segments and the likely development of a three-dimensional

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hydrogen-bonding network between the amide units lead to a micro-phase separated morphology^[6, 9]. But, the covalent links between the two blocks prevents macro-phase separation^[10–12].

Micro-phase separated morphology, crystallinity of each phase and properties of the resulting multi-block copolymers depend on the nature and length of the hard and soft blocks^[13–15]. Hence, by altering the structure and molecular weight of hard and soft segments, it is possible to design a system for a special application.

Block copolymers are widely used for different purposes including breathable coatings^[16, 17], barrier materials^[17, 18], electrochemical^[19], biomaterials^[20, 21] and polymeric membranes^[22, 23]. Membranes made from certain grades of PEBA copolymers exhibits good permselectivity as well as excellent chemical separation and pervaporation applications, because hard phase provides high selectivity and soft phase offers high permeability due to the high chain mobility of the ether linkage^[24, 25]. Block copolymers containing PEO segments have been extensively investigated for CO₂ removal from light gases. Ether oxygens in ethylene oxide (EO) units appear to be the most useful groups for achieving high CO₂ permeability and high CO₂/light gas selectivity. The approach of harnessing specific interactions of polar groups in polymers with CO₂ is an interesting route for improving membranes for CO₂/light gas separations^[26–28].

PEBA copolymers have usually been synthesized *via* polycondensation of amide monomer or oligoamide with various polyethers. For this mean, amide monomer (caprolactam) is polymerized in the presence of distilled water as ring opening catalyst and then end capping and polycondensation are accomplished in the presence of adipic acid and polyethers, respectively^[1–6, 13–15, 29, 30]. Although, a considerable number of research works have been published in the synthesis of PEBA copolymer membranes^[22–25, 29–31], but a few studies have been done on the synthesis of these kinds of membranes with emphasis on the investigation of morphology and dispersion of crystalline phase in the amorphous matrix. Therefore, synthesis of segmented block PEBA copolymers with uniform dispersion of the nanostructured high stiffness PA phase in the PEO matrix is necessary to obtain high performance membranes in the separation processes.

In this work, a high molecular weight PEBA copolymer was synthesized based on commercial homopolymers *via* polycondensation of carboxy terminated nylon6 and poly(ethylene oxide) which resulted in a high degree micro-phase separation in the final product. Several methods; Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (¹H-NMR), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were utilized to specify the synthesized copolymer characteristics. Also, copolymer morphology and distribution of high stiffness PA domains in PEO matrix phase were investigated by atomic force microscopy (AFM) micrographs with high magnifications for the first time.

EXPERIMENTAL

Materials

The copolymer was synthesized using commercial-grade starting materials without any purification. Nylon6 (N6) and poly(ethylene oxide) (PEO, $M_v = 100000$) were purchased from Sigma-Aldrich Co. The 5 wt% titanium butoxide (Ti(OBu)₄) solution in dichloromethane (CH₂Cl₂) as a catalyst, was obtained from Sigma-Aldrich and Merck. Adipic acid (AA) for carboxy end capping of Nylon6 was purchased from Merck. Formic acid, benzene and *n*-propanol as solvents for end capped N6, PEO and copolymer respectively, were purchased from Merck. Ethanol as a non-solvent for end capped N6 was purchased from Merck. Irganox 1010 was used as an antioxidant obtained from Ciba Geigy Co.

Synthesis of Copolymer

The general procedure for the synthesis of copolymer is described as follows: a mixture of AA and N6 (AA with excess amount of 10 mol% referred to the composition theoretically needed to obtain hard segment blocks of distinct length) was placed in 50 mL glass reactor equipped with an argon inlet and outlet and a central mechanical stirrer. The reactor was placed in a temperature controlled oil bath. The reaction mixture was heated up to (245 ± 5)°C and stirred with 50 r/min for 2 h to complete the end capping reaction. The carboxy

terminated nylon6 was dissolved in formic acid for 24 h and consequently added to ethanol to precipitate end capped nylon6. Finally, the white obtained precipitate was dried in a vacuum oven for 24 h at 50°C.

The carboxy terminated nylon6 and a stoichiometric amount of PEO were polycondensed in bulk, in the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ ($1.5\text{--}3\text{ mmol kg}^{-1}$ based on the amount of reactants) and a thermostabilizer (0.05 wt% to 0.1 wt% based on the total amount of reagents). The reaction was first carried out at $(245 \pm 5)^\circ\text{C}$ under argon atmosphere for 2 h, and then the process was conducted under vacuum ($3 \times 10^4\text{ Pa}$) for 3 h. The product was dissolved in *n*-propanol and cooled to room temperature. The synthesized copolymers were dried in high vacuum at 50°C overnight.

Characterization

Viscometry

The intrinsic viscosity ($[\eta]$) is adopted as a measure of molecular weight, and some relationships between intrinsic viscosity and molecular weight of homopolymers have been reported in the literature^[32]. The intrinsic viscosity of the base polymers and the synthesized copolymer was determined with proper solvents, using capillary Ubbelohde viscometer at 25°C according to ASTM D2857–87. Reliability of the obtained results was confirmed by gel permeation chromatography method (GPC) for PEO. The obtained intrinsic viscosity values and viscosity-averaged molecular weight of homopolymers (M_v) are presented in Table 1.

Table 1. Intrinsic viscosity and molecular weight of homopolymers and copolymer

Sample	Solvent	Intrinsic viscosity ($[\eta]$) (g dL^{-1})	Ubbelohde M_v	GPC measurement		Supplier report M_v
				M_n	M_w	
Nylon 6	Formic Acid	1.06	29940	—	—	—
Poly(ethylene oxide)	Benzene	1.13	100900	56472	137960	100000
Copolymer	<i>n</i> -Propanol	2.24	—	173197	250511	—

The calculated M_v of commercial PEO homopolymer is in good agreement with data reported by supplier. Also, molecular weight distribution curve obtained from GPC analysis of PEO is shown in Fig. 1. M_n and M_w of this homopolymer are reported as 56472 and 137960, respectively (see Table 1).

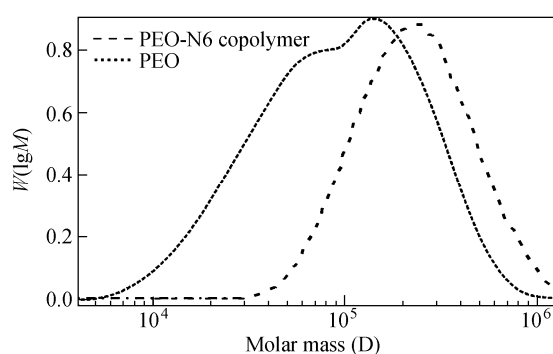


Fig. 1 Molecular weight distribution curves obtained from GPC analyses of PEO and PEO-N6 copolymer

As mentioned in the literature, M_v value of polymers is commonly placed between M_n and M_w ($M_n < M_v < M_w$). This trend also confirms the obtained result by viscometry method.

Fourier transform infrared spectroscopy (FT-IR)

The specimens for FT-IR analysis were fabricated in a pellet form in KBr. FT-IR spectra were obtained by using of an FTIR-1000 Unicam Mattson, England, in the range of $400\text{--}4000\text{ cm}^{-1}$.

Proton nuclear resonance spectroscopy ($^1\text{H-NMR}$)

$^1\text{H-NMR}$ analysis was carried out on a Bruker 200 MHz spectrometer. The synthesized PEO-N6 copolymer was dissolved in CDCl_3 as solvent and TMS was used as an internal reference. The areas of characteristic peaks were used to determine weight fraction constituent of copolymers. By way of example, the weight fraction of PEO was calculated from the integral intensities (B) and (D) corresponding to CH_2O and CH_2CO resonances, respectively as Eq. (1)^[33]:

$$\text{PEO (wt\%)} = \frac{44(B/4)}{44(B/4) + 113(D/2)} \quad (1)$$

where 44 and 113 are the molecular weight of the polyether and polyamide chain repeat unites, respectively.

Differential thermal analysis (DTA)

DTA measurements were carried out on a Perkin Elmer Pyris Diamond TG/DTA analyzer under nitrogen atmosphere. The samples (*ca.* 10 mg) were placed in sealed aluminum pans and heated up to the adjusted temperature. The usual procedure for the synthesized copolymer was as follows:

- (i) First heating run with 20 K min^{-1} rate up to 20 K above the melting temperature of PA.
- (ii) Equilibrium for 5 min at the latter temperature.
- (iii) Cooling run with 20 K min^{-1} rate down to room temperature.
- (iv) Second heating run with 20 K min^{-1} rate up to 20 K above the melting temperature of PA.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a Netzsch DSC analyzer model DSC 200 at heating rate of 5 K/min. The samples (*ca.* 15 mg) were placed in sealed aluminum pans and heated up to 250°C under N_2 atmosphere in two consecutive scans intercalated with a cooling stage at 5 K/min. The second heating run was used to quote the thermal events. Modulation was carried out with amplitude of $\pm 0.1^\circ\text{C}$ and period of 6 s.

X-ray diffraction (XRD)

The synthesized PEO-N6 copolymer was grinded and then dried at room temperature under vacuum for several days before XRD analysis. The XRD pattern of the copolymer was determined on a TW3710 Philips X'Pert diffractometer using $\text{CuK}\alpha$ as radiation ($\lambda = 0.154 \text{ nm}$). Data were collected in the range of $5 \leq 2\theta^\circ \leq 50$ with a 0.03° 2θ -step and 2 s per step (40 kV and 30 mA).

Atomic force microscopy (AFM)

AFM was utilized to study the morphology of the copolymer sample. PEO-N6 copolymer sample was finely grinded and dried at room temperature under vacuum for several days before AFM studies. Free surface of sample was studied *via* a digital instruments Dual Scope Tm C-21 scanning probe optical microscope at room temperature.

RESULTS AND DISCUSSION

The preparation of PEBA was accomplished by means of a two-step method: end capping and copolymerization. In the first step, amino end groups of N6 were converted into carboxy groups by the reaction with an excess amount of AA at $(245 \pm 5)^\circ\text{C}$ under argon atmosphere (see Fig. 2). Chain extension is not expected in this step owing to the 10 mol% excess of AA. The reaction mixture was purified by solvent-nonsolvent method for removing of unreacted AA. Subsequently, the synthesized carboxy terminated N6 was used at a high temperature polycondensation step with the stoichiometric amount of PEO under vacuum in order to remove the produced water to prevent the decrease of copolymer chains.

Contamination of the synthesized copolymers by unreacted PEO could be excluded on the basis of benzene extraction of the crude products. According to ASTM D2765–95, a certain amount of the final product was weighted and then immersed in the extracting solvent (benzene) at 150°C for 12 h. After the extraction, samples were removed, dried and reweighed as directed. The extracted amount of PEO obtained was about 4 wt%, confirming a high conversion for this copolymerization. As presented in Table 1, it is obvious that the

viscosity of copolymer is higher than that of both homopolymers, confirming the higher molecular weight of the synthesized copolymer in comparison with homopolymers. Molecular weight distribution curve obtained from GPC analysis of the synthesized PEO-N6 copolymer is also shown in Fig. 1. As presented in Table 1, M_n and M_w of this copolymer are reported as 173197 and 250511 respectively, which confirm the obtained result by viscometry method.

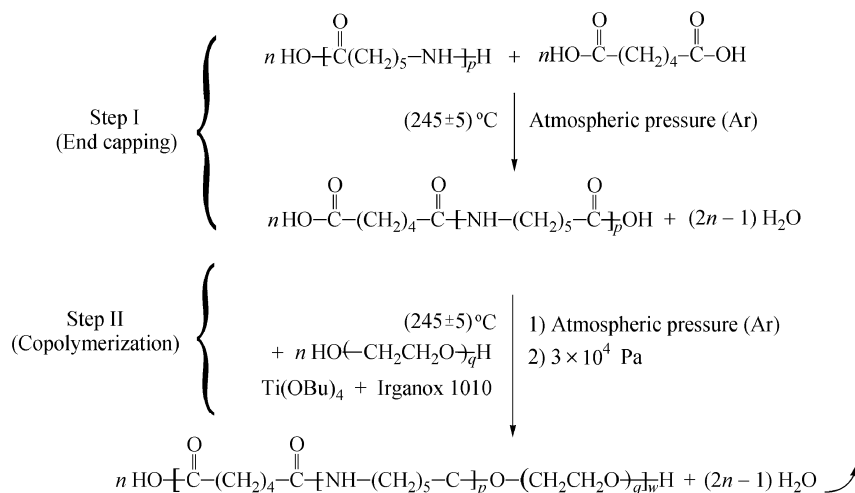


Fig. 2 Schematic of N6 and PEO copolymerization

As shown in Fig. 2, the hard and soft blocks are linked together by ester groups. In order to check the presence of such groups, FT-IR measurements were carried out to justify the formation of block copolymer rather than a polymer blend. In Fig. 3(a) the FT-IR spectrum of PEO-N6 copolymer shows characteristic absorption of hydrogen-bonded amide groups at 3300, 1646, 1542 and 1284 cm^{-1} (Fig. 3a, A, B, C, D)^[34]. Also, the band centered around 1100 cm^{-1} can be attributed to the ether C—O—C asymmetric stretch (E). Furthermore, appearance of a band at 1730 cm^{-1} attributed to the C=O stretching of ester groups, confirms the formation of the ester linkage in the copolymer macro-chains.

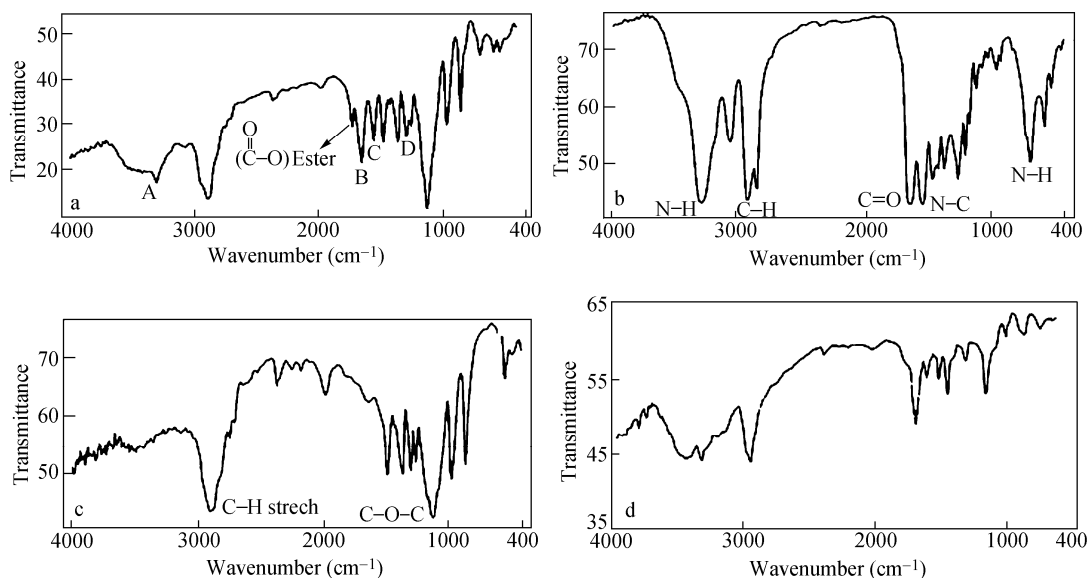


Fig. 3 FT-IR spectra of (a) PEO-N6 copolymer, (b) N6 and (c) PEO homopolymers and (d) homopolymers mixture

As shown in Figs. 3(b) and 3(c) the similarity of these bands and the bands in the FT-IR spectra of N6 and PEO suggests a block structure of hard N6 linked by soft PEO on the basis of reaction mechanism presented in the second step of reaction (Fig. 2) can be expected. These results are in good agreement with the literature^[12, 33].

To verify N6 linked by PEO well, the FT-IR spectrum of N6 and PEO homopolymers mixture is directly provided in Fig. 3(d). As can be seen, the C=O stretching of ester groups at 1730 cm⁻¹ wavenumber is not observed in the FT-IR spectrum of homopolymers mixture.

As shown in Fig. 4, ¹H-NMR spectrum of PEO-N6 copolymer indicates hydrogen resonance of CH₂O at δ = 3.6 and CH₂CO at δ = 2.4 which are attributed to PEO and N6 segments, respectively.

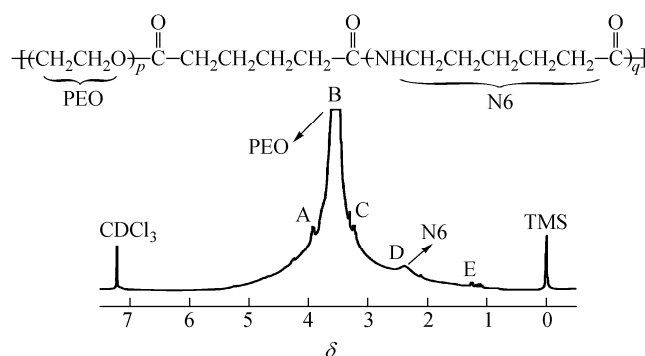
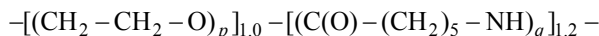


Fig. 4 ¹H-NMR spectrum of the PEO-N6 copolymer in CDCl₃, resonance assignment: (A) CH₂OCO, (B) CH₂O, (C) CH₂NHCO, (D) CH₂CO, (E) CH₂CH₂CO

The chemical structure of the copolymer can be derived from the mole fraction of copolymer constituents as follow:



The chemical composition values obtained using ¹H-NMR spectroscopy are in good agreement with those obtained by theoretical values (Table 2).

Table 2. Composition of the synthesized copolymer determined by ¹H-NMR spectroscopy and calculated theoretically

Copolymer	Polyamide		Polyether	
	mol%	wt%	mol%	wt%
Theoretical values	50	22.8	50	77.2
¹ H-NMR values	54	26	46	74

The thermal properties and phase separation behavior for the synthesized copolymer compared to homopolymers were obtained using differential thermal analysis and are shown in Fig. 5. This copolymer shows a first-order endotherm transition at 204°C having a depression relative to N6 melting temperature (220°C). Moreover, first-order endotherm transition could be observed in the melting temperature range of the PEO at 54°C which is attributed to PEO crystalline phase.

The results of the conducted characterization suggest that the obtained PEBA consist of two distinct crystalline phases: a rich crystalline phase of N6 and a crystalline phase of PEO which can be dispersed in amorphous phase of PEO as well some amount of noncrystallized hard segment. In other words, the crystalline hard domain exists as a discrete phase in an amorphous matrix such as a plasticized thermoplastic which results in micro-phase separated morphology. The depression of the melting temperature of the crystalline phase in the final product relative to homopolymers, confirms the formation of copolymer structure which is in good agreement with FT-IR results. The observed trend also indicates that the degree of crystal perfection is lower which is probably attributed to the incorporation of PEO chains into PA crystalline domains as an impurity^[1, 35].

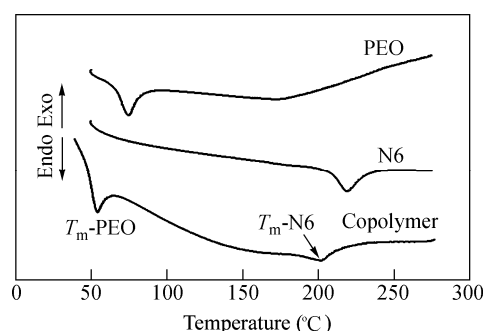


Fig. 5 DTA thermograms of N6 and PEO homopolymers and PEO-N6 copolymer with heating rate of 20 K/min

To understand bulk and surface structures of the copolymer, differential scanning analyses were done on the N6 and PEO homopolymers and the synthesized copolymer. DSC curves for pure PEO and N6 and PEO-N6 copolymer are presented in Fig. 6. Table 3 shows the melting temperature and enthalpy experimental values. Furthermore, melting enthalpy (ΔH_m) was calculated for the synthesized copolymer taking into account the PEO and N6 homopolymers contents and the ΔH_m for 100%-crystalline PEO and N6 fractions. The reported ΔH_m of PEO and N6 crystals in 100%-crystalline samples are 196.8 J/g and 230 J/g, respectively^[36]. The experimental values show degrees of crystallinity of 76% for pure PEO and 25% for pure N6 as characterized in the DSC experiment second heating scanning (Table 3). PEO-N6 copolymer with crystallisable components usually show a considerable decrease in experimental melting points and degrees of crystallinity compared to the pure polymers, because the interaction of the two polymers reduces crystallite size. This trend is in good agreement with differential thermal analyses results.

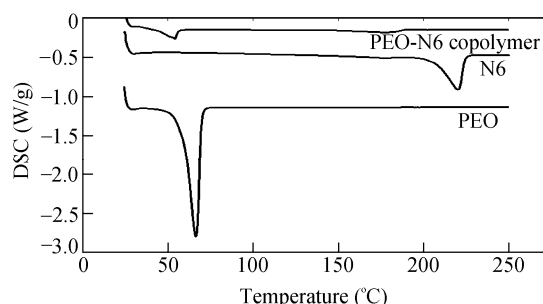


Fig. 6 DSC curves of N6 and PEO homopolymers and PEO-N6 copolymer with heating rate of 5 K/min

Table 3. DSC results: melting temperature, enthalpy for PEO and N6 homopolymers and PEO-N6 copolymer and calculated values and crystallinity percents

		T_m peak (°C)	ΔH_m^{exp} (J·g ⁻¹)	$\Delta H_m^{\text{calc.}}$ * (J·g ⁻¹)	$\Delta H_m^{\text{exp. calc.}}$ ** (J·g ⁻¹)	Crystallinity (%)
Homopolymers	PEO	66.6	150.1	196.8	—	76.27
	N6	220.1	58.23	230.1	—	25.31
Copolymer	PEO	54.2	13.52	157.4	120.1	8.59
	N6	177	9.675	46.02	11.65	21.02

* Assuming a completely crystalline PEO and/or N6 content in the synthesized copolymer;

** Assuming a similar crystalline PEO and/or N6 content in the synthesized copolymer and pure homopolymers

The XRD pattern of PEO-N6 copolymer shows a partially crystalline polymer with a narrow diffraction peak at $2\theta = 19^\circ$ and also peaks 14° , 23° and 27° (2θ) (Fig. 7). These results are in good agreement with the literature^[25].

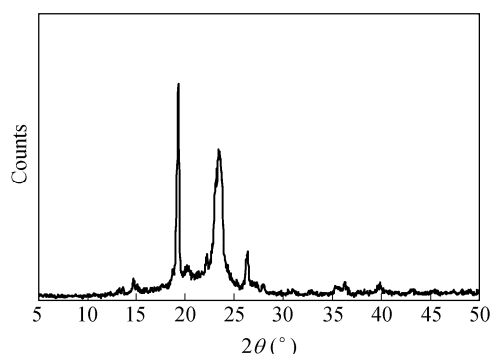


Fig. 7 XRD pattern of the PEO-N6 copolymer

Surface morphology and micro-phase separation behavior of the synthesized copolymer was investigated by atomic force microscopy with different magnifications. AFM micrographs of this sample Figs. 8(a), 8(b) show a monodispersed morphology of high stiffness PA phase in a soft rubbery PEO matrix phase. The obtained morphology for the synthesized copolymer reveals micro-phase separation of PA (hard segments) and PEO (soft segments) phases which is in good agreement with DTA and DSC results.

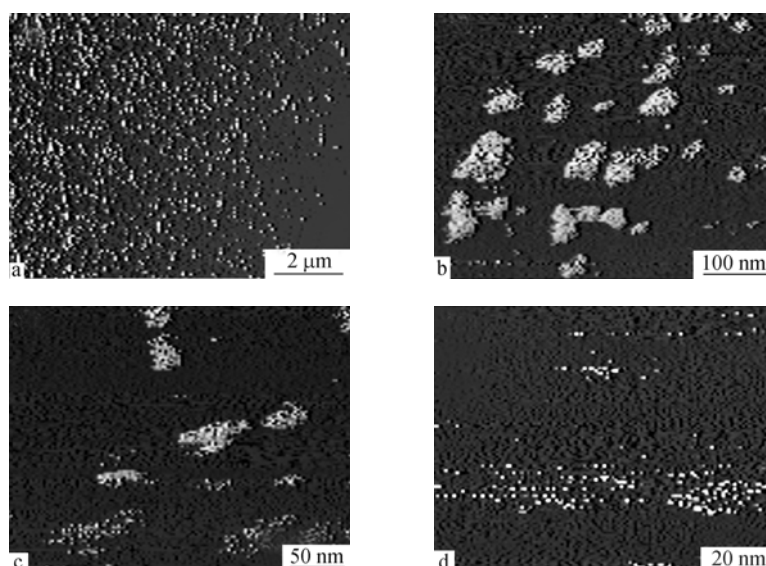


Fig. 8 AFM phase micrographs of the free surface of PEO-N6 copolymer at different magnifications

As shown in Figs. 8(c), 8(d), AFM micrographs with high magnification reveal that the high stiffness PA domains have nanometric structures which can be desirable in manufacturing of polymeric membranes with high performance in separation processes. More detailed studies on performance of this membrane are under investigating.

CONCLUSIONS

In this work poly(ether-block-amide) copolymer was successfully synthesized based on N6 and PEO. Several methods were applied to characterize the synthesized copolymer. The obtained results can be concluded as follows:

- (i) FT-IR spectra revealed the formation of ester linkage in the copolymer chains.
- (ii) H-NMR spectrum of PEO-N6 copolymer suggested a multi-block structure for the final product.

- (iii) DTA results confirmed the synthesis of copolymer with high degree of micro-phase separation and the low degree of crystal perfection which was verified by DSC results.
- (iv) AFM micrographs showed monodispersion of nanostructured PA phase in the soft rubbery PEO matrix phase.

On the bases of these conclusions, process guidelines can be established for fabricating polymeric membrane with high performance in separation processes.

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