

Study on the Synthesis of Poly(ether-block-amide) Copolymer Based on Nylon6 and Poly(ethylene oxide) with Various Block Lengths

M. Peyravi,^{1,2} A. A. Babaluo,^{1,3,4} M. Akhfash Ardestani,^{1,2} M. K. Razavi Aghjeh,^{1,3,4}
S.R. Pishghadam,^{1,2} P. Hadi^{2,3}

¹Nanostructure Materials Research Center (NMRC), Sahand University of Technology, Tabriz, I.R. Iran

²Department of Chemical Engineering, Sahand University of Technology, Tabriz, I.R. Iran

³Institute of Polymeric Materials, Sahand University of Technology, Tabriz, I.R. Iran

⁴Department of Polymer Engineering, Sahand University of Technology, Tabriz, I.R. Iran

Received 21 March 2009; accepted 18 February 2010

DOI 10.1002/app.32358

Published online 2 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Various segmented block copolyethers-amides based on nylon6 (N6) and poly(ethylene oxide) (PEO) with different compositions and block length of the hard and soft segments were synthesized. The effect of composition of the hard and soft segments was studied via FTIR spectroscopy based on the characteristic peak of ester group at wave number of 1730 cm^{-1} . The average block length of the hard and soft segments in block copolymers was determined from H-NMR analysis. Differential thermal analysis thermograms confirmed a microphase separated morphology over a broad range of temperature, leading to two separated crystalline

domains. An increase in the interconnectivity of the polyamide segments controlled by chain extension, greatly improved the formation of polyamide lamellae crystals determined by X-ray diffractometry. Atomic force microscopy images indicated different morphologies of dispersed phase in the dominant phase, which plays an important role in their performance for membrane processes. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1211–1218, 2010

Key words: block copolymer; polyamide; poly(ethylene oxide); block length; membrane processes

INTRODUCTION

Incorporation of flexible elastomeric segments in crystallizable polymer chains is one of the methods for overcoming certain disadvantageous properties such as crack propagation and low impact strength and also for optimizing thermal, mechanical, and morphological properties.^{1,2} This can be achieved via polycondensation reactions resulting in polydispersed materials, which show improved elasticity and phase separation and reduced crystallinity compared to the homopolymers.^{3–6} Poly(ether-block-amide) copolymer (PEBA) is a thermoplastic elastomer which consists of linear chain of hard polyamide segments interspaced with soft polyether segments. As the specific properties of a PEBA copolymer are affected by chemical nature and relative content of polyamide and polyether segments, it is possible to design a system for special application by altering the structure and molecular weight of

hard and soft segments.^{5,7} One of the most important applications of these copolymers is the fabrication of polymeric membranes for gas separation processes.^{7–12} Due to polar nature of amide groups in the hard segments and their ability to form hydrogen bonding coupled with strong dipole-dipole interaction, domain segregations can occur in these copolymers.¹³ This trend results in two separated domains: polyamide crystalline domains provide high selectivity according to the abundance of polar groups and polyether amorphous domains offer high permeability due to the high chain mobility of ether linkage.^{9,14}

Technological properties of these block copolymers for the mentioned application can be optimized using different chemical compositions of hard and soft segments. Usually the hard and soft segments are thermodynamically incompatible but under certain conditions, they tend to compatibilize. In this respect, selection of the proper segment length and composition to synthesize segmented block copolymer materials with monodispersed morphology and desirable properties for gas separation processes seems to be a great problem.

In this work, segmented block PEBA copolymer was synthesized based on nylon6 and polyethylene

Correspondence to: A. A. Babaluo (a.babaluo@sut.ac.ir).

Contract grant sponsor: Sahand University of Technology (SUT).

TABLE I
Characteristics of Used Materials

Materials	Function	Molecular formula	Abbreviation	Supplier
Nylon 6	Precursor	$H(NHC_6O)_nOH$	N6	Aldrich ^a
Pole(ethylene oxide)	Precursor	$HO(C_2H_4O)_nH$	PEO	Aldrich ^a
Titanium butoxide	Catalyst	$Ti[O(CH_2)_3CH_3]_4$	Ti(OBu) ₄	Aldrich ^a
Dicholoro methane	Solvent	CH_2Cl_2	–	Merck ^b
Irganox 1010	Thermostabilizer	$C_{30}H_{58}O_4S$	–	CIBA ^c
Hexamethylenediamine	Chain extender	$C_6H_{16}N_2$	HMD	Merck ^b
Adipic acid	Chain extender	$C_6H_{10}O_4$	AA	Merck ^b
Formic acid	Solvent	HCOOH	–	Merck ^b
<i>n</i> -Propanol	Solvent	C_3H_8O	–	Merck ^b
Ethanol	Solvent	C_2H_4O	–	Merck ^b

^a Sigma Aldrich Chemie, D89555 Steinheim, Germany.

^b E. Merck, D6100 Darmstadt, Germany.

^c CIBA Giegy, 225-GR-PP IRGAFOS, Switzerland.

oxide. The main aim of this article was an extension of our studies on the synthesis of PEBA copolymers with various polyamide (PA)-to-polyether (PE) weight ratios. Also, the influence of block length of both hard and soft segments on the properties of the synthesized PEBA copolymers were investigated.

EXPERIMENTAL

Materials

Characteristics of materials used in this work are given in Table I.

The viscosity-averaged molecular weight (M_v) of commercial polymer was determined with proper solvents, via capillary Ubbelohde viscometer at 25°C according to ASTM D2857–87. It is adopted as a measure of molecular weight based on the relationships between intrinsic viscosity and molecular weight of homopolymers reported in the literature.¹⁵ Reliability of the obtained results was confirmed by gel permeation chromatography method (GPC) for PEO.

The intrinsic viscosity and molecular weight of homopolymers were presented in Table II. 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 for PEO revealed that M_n and M_w of this homopolymer are 56,472 and 137,960 g mol⁻¹, respectively (see Table II). As mentioned in the literature,¹⁶ 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.

Synthesis of copolymer

In this study, a batch process was applied for the block copolymerization. The general procedure was accomplished by means of a three-step route as follows:

End-capping of N6

Nylon 6 was mixed with 10 mol % excess amount of adipic acid (AA) in a 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°C ± 5°C and stirred at a rate of 50 rpm for 2 h at argon atmosphere to complete the end capping reaction. The carboxy-terminated nylon6 was solved in formic acid for 24 h and successively was added to ethanol to precipitate. The obtained white precipitate was dried in a vacuum oven for 24 h at 50°C.

Chain extension

In the PA/PE weight ratio of 20/80 which is known as stoichiometric weight ratio no chain extension is required. However, chain extension should be applied for other compositions than the stoichiometric composition. Chain extension of carboxy-terminated N6 and PEO was performed using addition of hexamethylenediamine (HMD) and AA, respectively (see Table III). Stoichiometric weight percent of these chain extenders was determined by Charoters equation.¹⁶ In the case of 10 wt % PA, stoichiometric amount of AA was reacted with PEO at 200°C under 1 bar pressure of argon atmosphere for 2 h in the glass reactor. The resultant material was dissolved in *n*-propanol and then dried at 40°C overnight. But samples containing 40, 60, and 80 wt % PA were chain extended using stoichiometric amount of HMD which was added to carboxy-terminated N6 at 245 ± 5°C under 2 bar pressure of argon atmosphere for 2 h. The increased pressure at the PA chain extension compared to the former one (PEO chain extension) was applied to prevent of HMD evaporation at experimental conditions. The chain extended product was dissolved in 3/2 vol/vol formic acid to *n*-propanol and then was

TABLE II
Intrinsic Viscosity and Molecular Weight of Homopolymers

Homopolymer	Solvent	Intrinsic viscosity ($[\eta]$) (g dL ⁻¹)	Ubbelohde	GPC measurement		Supplier report
			M_v (g mol ⁻¹)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_v (g mol ⁻¹)
Nylon 6	Formic Acid	1.06	29,940	–	–	–
Poly(ethylene oxide)	Benzene	1.13	100,900	56,472	137,960	100,000

precipitated in ethanol. The resultant material was dried at 70°C for 48 h in vacuum oven.

Copolymerization

Constituents used in copolymerization reactions are presented in Table III. The numbers in sample codes denote the weight percent of PA in the component. Stoichiometric amount of these materials were polycondensed in bulk, in the presence of Ti(OBu)₄ as a catalyst (1.5–3 m mol kg⁻¹ based on the amount of reactants) and Irganox 1010 as a thermostabilizer (0.05 to 0.1 wt % based on the total amount of reactants). The reaction was first carried out at 245°C ± 5°C under argon atmosphere for 2 h and then was continued under vacuum (0.3 bar) for 3 h. The product was dissolved in n-propanol and then cooled to room temperature. Subsequently, the synthesized copolymer was dried in high vacuum at 50°C overnight.

Characterization

To confirm the formation of ester groups between amide and ether segments, Fourier transform infrared (FTIR) spectroscopy analysis was carried out in a UNICAM Matson 1000, in the wave number range of 400–4000 cm⁻¹. Composition of the copolymers was calculated using the H-NMR spectra of the samples, which were obtained with a 200 MHz, BRÜKER (Advance DPX) NMR spectrometer. Differential thermal analysis (DTA) was performed for both copolymers and homopolymers by means of a Perkin-Elmer Pyris Diamond TG/DTA analyzer in the temperature range of 30–300°C. The XRD patterns were determined on a TW3710 Philips X'Pert diffractometer using CuK α radiation in the range of 2 Θ = 10–60° with a 2 Θ step of 0.02 for 0.2s per point

($\lambda = 1.54 \text{ \AA}$). Atomic force microscopy (AFM) was utilized to investigate the PA domain size and morphology of the copolymer samples. Free surface of the samples were studied via a digital instruments Dual Scope Tm C-21 scanning probe optical microscope at room temperature.

RESULTS AND DISCUSSION

Synthesis of N6-PEO block copolymers

Copolyetheramides with different chemical compositions and block lengths were prepared from N6, PEO, AA, and HMD following the “three-step route” outlined in Figure 1. In the first step, N6 was reacted with an excess amount of AA to obtain a carboxy-terminated N6. Then the reaction mixture was purified by solvent-nonsolvent method to remove unreacted AA. The excess amount of AA accounts for two facts: (1) to prevent chain extension of end-capped N6 and (2) to verify the completion of the end-capping process which is one of the specifications to approach a narrow molecular weight distribution of the ultimate product. In the second step, chain extension was performed by reacting AA with PEO and HMD with end-capped N6 for samples consisting of lower (<20 wt %) and higher (>20 wt %) amounts of PA, respectively. In the final step, polycondensation was accomplished under vacuum to remove the produced water, supporting the formation of copolymer chains.

Chemical structure

Chemical structure of copolymers was determined from FTIR studies. FTIR spectra of homopolymers and copolymers with various PA/PE weight ratios have been presented in Figure 2. The presence of

TABLE III
Constituents Used for the Copolymerization Reactions

Sample code	Polyamide	Polyether	Chain extension agent
PA-10	Carboxy terminated N6	Chain Extended PEO	AA
PA-20	Carboxy terminated N6	PEO	–
PA-40	Chain extended carboxy terminated N6	PEO	HMD
PA-60	Chain extended carboxy terminated N6	PEO	HMD
PA-80	Chain extended carboxy terminated N6	PEO	HMD

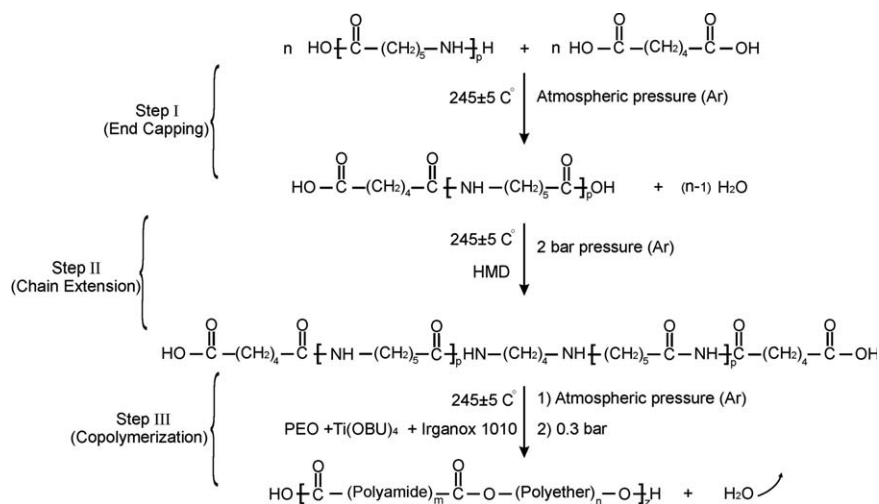


Figure 1 Scheme of the three-step polymerization method used to synthesis of N6-PEO block copolymers.

ester linkage in the samples confirms copolymer formation, which is clearly demonstrated by the appearance of intensive absorption band of ester carbonyl group at 1730 cm^{-1} . In addition, PA content of the synthesized copolymers is evaluated by intensity of the characteristic peak of hydrogen-bonded amide groups at about 1650 cm^{-1} .¹⁷

The intensity of ester (I_E) and amide (I_A) carbonyl absorption bands in FTIR diagrams vary with copolymer composition. As shown in Figure 3, the esterification ratio (I_E/I_A) decreases with increasing PA content. The reason underlying such a behavior is as follows. As mentioned earlier, in samples containing less than 20 wt % PA, PEO must be chain extended resulting in an increase of ester functional groups, but when the PA content exceeds 20 wt %, the ester functional groups decrease due to the chain extension of N6. The ultimate result is the increase in the intensity of amide band and decrease in the intensity of ester band by increasing PA content, which leads to a considerable decrease in esterification ratio.

The chemical structures of the synthesized copolymers can be specified more quantitatively by H-NMR analysis. Figure 4 shows H-NMR spectra of the synthesized N6-PEO block copolymers. The five methylene groups in the repeating unit of N6 have the respective different positions in NMR spectrum depending on the degree of protecting of the proton attached to each methylene group. On the other hand, the NMR spectrum of the block copolymer displays a sharp additional peak at 3.6 ppm, which is attributed to the protons of CH_2O group of PEO. This peak becomes stronger by increasing PE content.

Compositions of the copolymers were determined from the corresponding H-NMR spectra. Hence, the average degree of chain extension and weight

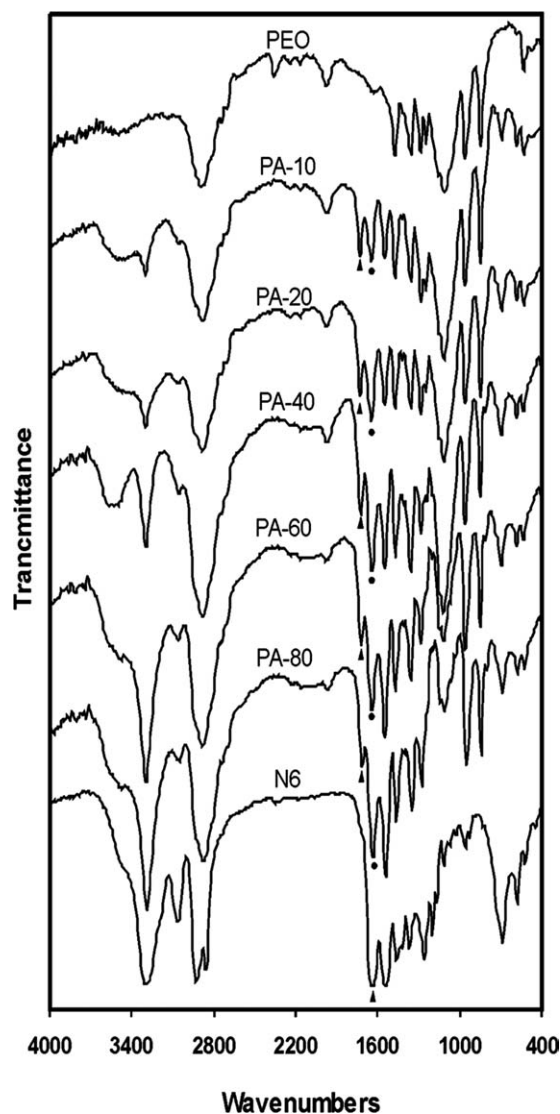


Figure 2 FTIR spectra of homopolymers and copolymers with various PA/PE weight ratios (▲: $\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$ ester and ●: $\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}$ amide groups).

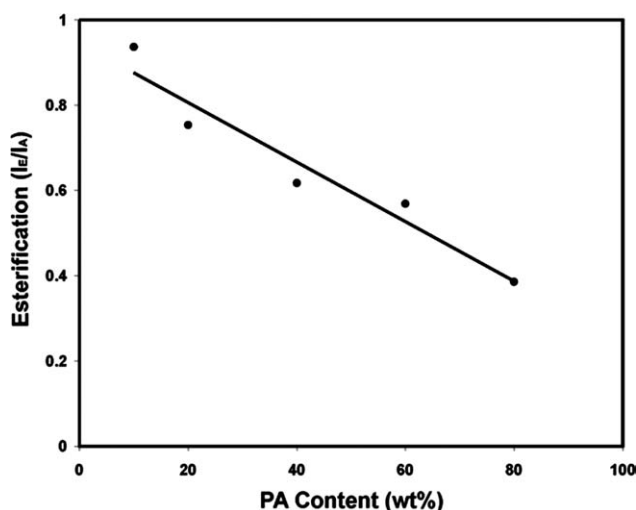


Figure 3 Esterification ratio of the synthesized copolymers with different PA contents.

fraction of N6 and PEO in the copolymer chains were determined from the integrated intensities of CH_2CO (2.4 δ) and CH_2O (3.6 δ) protons, respectively. As the wt % of PE is very low in PA-10 diagram, no peak is observed in 2.4 δ position and the intensity of CH_2NH (3.4 δ) was calculated, instead. The compositions of copolymers calculated from H-NMR spectra are listed in Table IV, which are in good agreements with theoretical data.

Crystalline structure

The crystalline structure of copolymers and homopolymers was characterized by X-ray diffraction (XRD) method. Figure 5 shows two distinct crystalline phases of PA and PE in the crystalline structure of the synthesized copolymers. The presence of two peaks at about 19° and 23° at lower PA contents is attributed to the PE phase as a dominant phase in copolymer structure. The diffraction peaks at about 20° and 24° for the samples with higher PA contents, demonstrate the existence of α -phase of PA

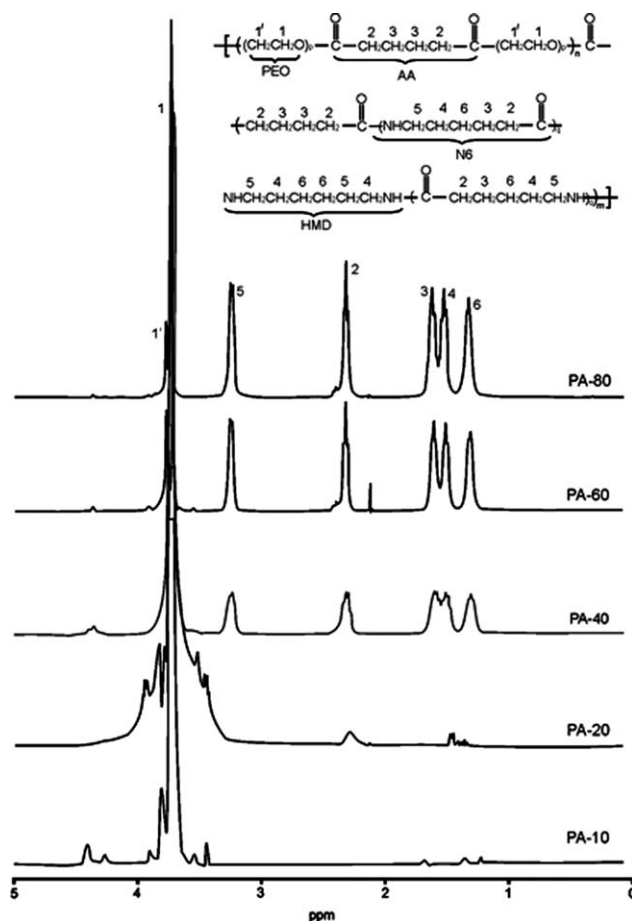


Figure 4 H-NMR spectra of samples with various PA/PE weight ratios [resonance assignment: (1') near end CH_2O , (1) CH_2O , (2) CH_2CO , (3) $\text{CH}_2\text{CH}_2\text{CO}$, (4) $\text{CH}_2\text{CH}_2\text{NH}$, (5) CH_2NH , (6) $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$].

with different thicknesses, which is the most stable crystalline structure of N6 thermodynamically.¹⁸

As mentioned in literature,¹⁹ the diffraction peaks at 2θ of 20° and 24° are attributed to the (002+202) plane and (200) plane of α -crystals of PA, respectively. Intensity ratio of the α -crystal, $I_{(002+202)}/I_{(200)}$, has been known as a measure of PA chains rotation. Figure 6 shows that the intensity ratio increases by increasing PA content in copolymer composition.

TABLE IV
Average Degree of Chain Extension and Composition of Copolymers Determined from H-NMR Spectra and Theoretically

Sample designation	Composition (from H-NMR spectra)				Composition (theoretically)				Average degree of chain extension	
	wt %		mol %		wt %		mol %		PA (m)	PE (n)
	PA	PE	PA	PE	PA	PE	PA	PE		
PA-10	9.2	90.8	25.3	74.6	10	90	27.3	72.7	1	2.94
PA-20	26	74	54	46	22.8	77.2	50	50	1	1.2
PA-40	36.2	63.8	65.6	34.4	40	60	69.2	30.8	1.91	1
PA-60	61.6	38.4	84.4	15.6	60	40	83.5	16.5	5.4	1
PA-80	80.5	19.5	93.3	6.7	80	20	93.1	6.9	13.8	1

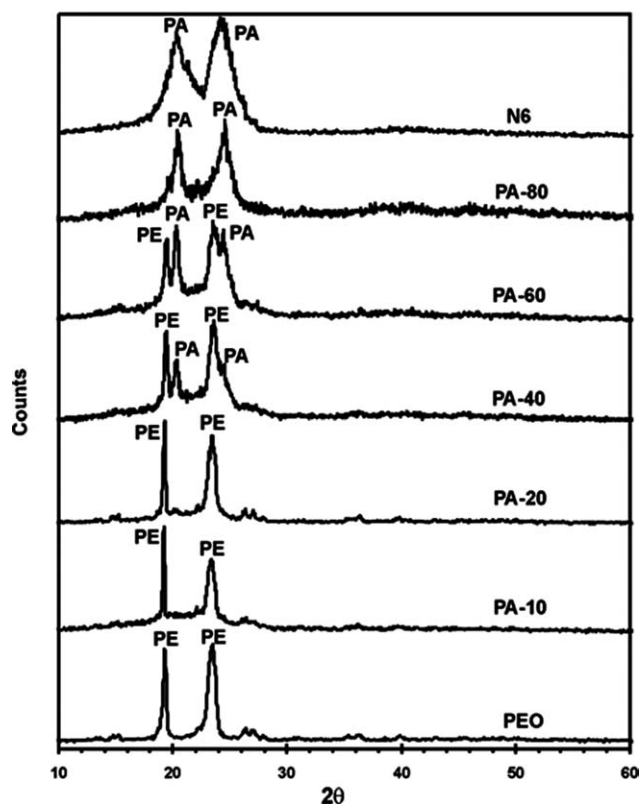


Figure 5 XRD patterns of PEO-N6 copolymers and starting homopolymers.

The observed trend can be explained by this fact that the introduction of the long PEO units into the N6 backbone may cause crystalline defects and statistical disorder, giving rise to the rotation of the polymer chain.

Thermal behavior

DTA was carried out to investigate the effect of composition on the crystalline structure of N6-PEO copolymer. Figure 7(a) shows the cooling scan of the homopolymers and copolymers. Two observed crys-

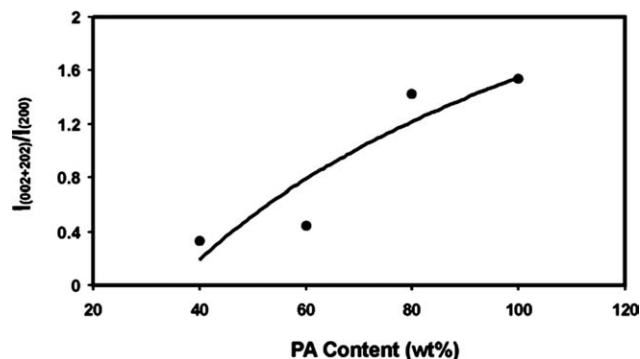


Figure 6 Intensity ratio of the α -crystal vs. PA content.

talline peaks in PEBA copolymers are indicative of existence of two different crystalline phases, as expected. The peak in lower temperature is the characteristic of PE phase, while the peak in higher temperature is indicative of the existence of PA phase. The highest crystallinity of PE phase can be observed in PA-10 copolymer, however it decreases by increasing PA content, so that it vanishes in PA-80 sample. It is notable that an opposite trend can be observed for the crystallinity of PA phase. Figure 7(b) illustrates the second heating scans, demonstrating the melting points of the crystalline regions. The same behavior can be observed for PA and PE melting peaks intensity with increasing PA content. On the other hand, existence of two distinct peaks validates the microphase separation of PEBA

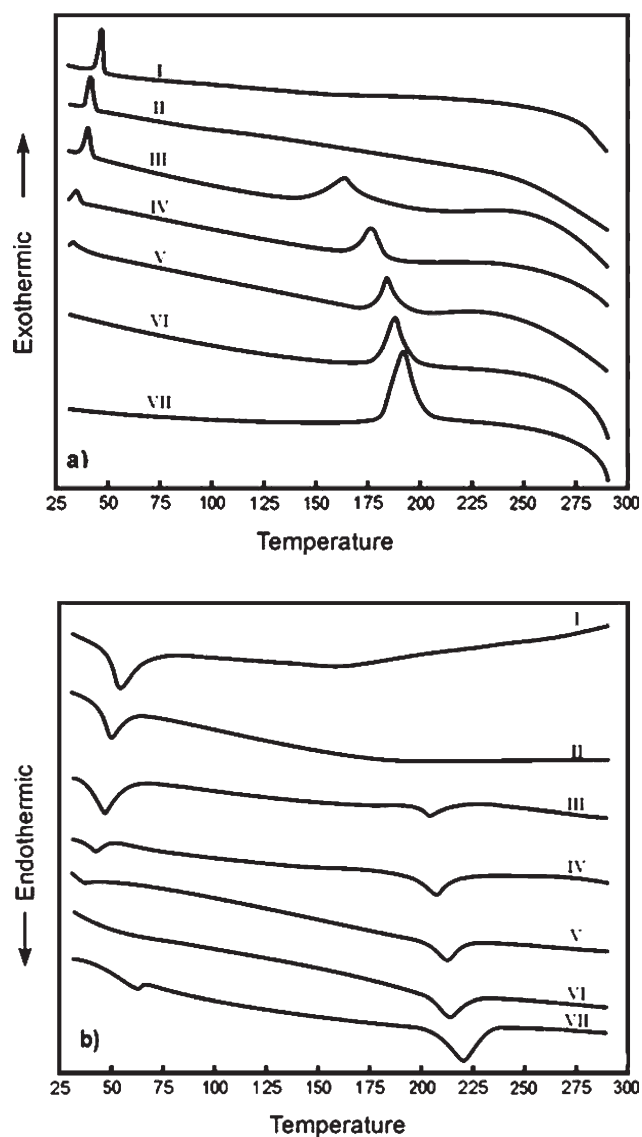


Figure 7 DTA thermograms of the PEO-N6 copolymers and starting homopolymers: (a) cooling thermal scans and (b) the second heating thermal scans (I: PEO, II: PA-10, III: PA-20, IV: PA-40, V: PA-60, VI: PA-80, VII: N6).

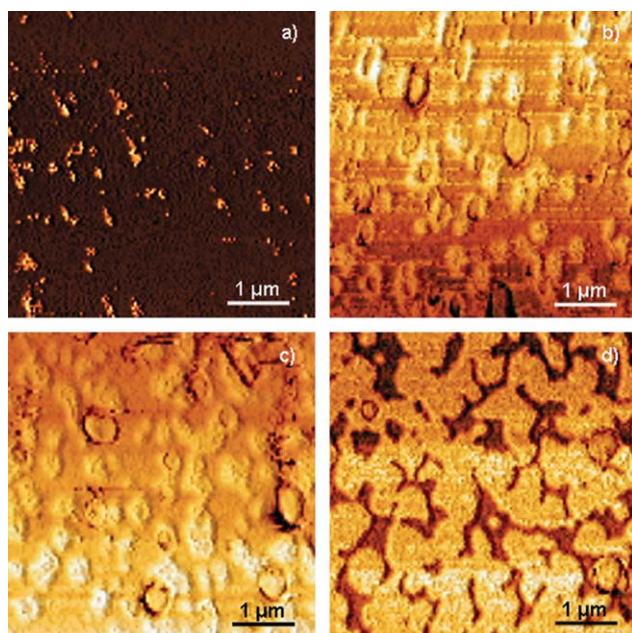


Figure 8 AFM phase images of copolymers (a) PA-20, (b) PA-40, (c) PA-60, and (d) PA-80. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolymers leading to two separated domains: 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.

It is interesting to note that the onset of crystallization for N6 distinctly shifts to lower temperatures by increasing PE content, which arises from two facts:

1. PE chains are incorporated into PA crystalline domains, resulting in deformation of PA chains and thus decreasing of their crystallinity.
2. By decreasing PA content, the chain length of N6 compared to PEO are reduced, leading to lower probability for chain folding and consequently the crystallinity of the PA domains decreases. This trend confirms the obtained results of the intensity ratio of PA α -crystal by XRD.

Morphology

Morphology of the synthesized copolymers were investigated by AFM. In the case of PEBA copolymers, light regions are corresponding to PA stiff phase and the PE low-stiff phase is displayed as dark regions (Fig. 8). Microphase separation has been observed in the PA-20 sample as demonstrated in Figure 8(a) where the hard PA phase is uniformly distributed in the soft PE matrix phase. As the PA

content increases (PA-40 and PA-60 samples), it becomes more difficult to distinguish the matrix phase from the dispersed phase [Figs. 8(b) and (c)]. By further increasing of PA content (PA-80), phase inversion occurred and PA formed the matrix as a dominant phase. In addition, independent domains were not formed by the PE phase due to incapability of this homopolymer to form physical crosslinks between polyether chains [see Fig. 8 (d)].

CONCLUSION

A series of copolyetheramides (PEBA) with different PA/PE weight ratios were synthesized in a three-step route. The effect of block length variation in the hard and soft segments on the final product properties was investigated. The results of FTIR and H-NMR spectra suggested the reaction product to be a multiblock copolymer. Esterification ratio decreased by increasing of PA content, which was in good agreement with the calculated average degree of chain extension from H-NMR analysis. XRD patterns showed four peaks at about 19° and 23° in lower PA contents and 20° and 24° for the samples with higher PA contents, which are corresponding to two distinct crystalline phases of PE and PA in the synthesized copolymers, respectively. In DTA measurements, as a result of two crystalline phase structure of the copolymers, two distinct sharp melting points one at higher and another at lower temperatures were observed related to polyamide and polyether blocks, respectively. AFM phase images revealed microphase separation in PA-20 sample. However, this form of morphological and separated domains was diminished in samples with higher content of the PA hard segments. On the basis of these conclusions, process guidelines can be established for fabricating polymeric PEBA membranes with high performance in the separation processes.

The authors thank Sahand University of Technology (SUT) for the financial support of this work. They also thank the co-workers and technical staff in the Chemical and Polymer Engineering Departments, Institute of Polymeric Materials and Nanostructure Materials Research Center of SUT for their help during various stages of this work.

References

1. Fakirov, S.; Gornanov, K.; Bosvelieva, E.; Chesne, A. *Macromol Chem* 1992, 193, 2391.
2. Niesten, M. J.; Feijen, J.; Gaymans, R. J. *Polymer* 2000, 41, 8487.
3. Candia, F.; Petrocelli, V.; Russo, R. *Polymer* 1986, 27, 797.
4. Hutten, P. F.; Walch, E.; Veecken, A. H. M.; Gaymans, R. J. *Polymer* 1990, 31, 524.
5. Boulares, A.; Tessier, M.; Marechal, E. *Polymer* 2000, 41, 3561.

6. Gaymans, R. J.; Schwering, P.; Haan, J. L. *Polymer* 1989, 30, 974.
7. Yeong, C. Y.; Won, H. J. *J Appl Polym Sci* 1994, 54, 585.
8. Yeong, C. Y.; Won, H. J. *J Appl Polym Sci* 1995, 56, 895.
9. Liu, L.; Chakma, A.; Feng, X. *J Membr Sci* 2004, 235, 43.
10. Liu, L.; Chakma, A.; Feng, X. *Chem Eng Sci* 2006, 61, 6142.
11. Gugliuzza, A.; Drioli, E. *Polymer* 2003, 44, 2149.
12. Sridhar, S.; Suryamurali, R.; Smitha, B.; Aminabhavi, T. M. *Colloids Surf A* 2007, 297, 267.
13. Ghosh, S.; Khatgir, D.; Bhowmick, K. *Polymer* 1998, 39, 3967.
14. Chatterjee, G.; Houde, A. A.; Stern, S. A. *J Membr Sci* 1997, 135, 99.
15. Sobhanmanesh, K.; Hajizadeh, A. *Iran Polym J* 2005, 14, 15.
16. Odian, G. *Principle of Polymerization*; Wiley: New York, 1991.
17. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy, A Guide for Students of Organic Chemistry*; Washington University Bellingham: Washington, 1996.
18. Hatfield, G. R.; Yihong, G.; Killinger, W. E.; Andrejak, R. A.; Roubicek, M. *Macromolecules* 1993, 26, 6350.
19. Yeong, C. Y.; Won, H. J. *J Appl Polym Sci* 1995, 56, 595.