Surface Structures of Solvent-Cast Films Prepared from Poly(ethylene oxide)-Segmented Nylons

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ABSTRACT: The surface structures of three kinds of poly-(ethylene oxide)-segmented nylon (PEO–Ny) films prepared by the solvent-cast method were investigated with electron spectroscopy for chemical analysis (ESCA). The PEO–Ny's used were high-crystalline PEO-segmented poly(iminosebacoyliminohexamethylene), low-crystalline PEO-segmented poly(iminosebacoylimino-m-xylene), and amorphous PEO-segmented poly(iminoisophthaloyliminomethylene-1,3-cyclohexylenemethylene), and the PEO contents in the bulk polymers were approximately 10 wt %. The ESCA results showed that the PEO segment was enriched on the top surfaces of all the films, and the degrees of enrichment were different. The mechanism of the PEO enrichment was examined. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 10–16, 2002

Key words: polyether-segmented nylon; solvent-cast film; surface structure; electron spectroscopy for chemical analysis (ESCA)/XPS; segregation; crystallinity

INTRODUCTION

The surface compositions of polymer materials play a very important role in many practical fields. Examples include adhesives, paints, and medical devices because the surface composition will determine the physical and/or chemical properties of the material surface. Therefore, many efforts have been made to clarify and design the surface structures of materials. In particular, the surface structures of block copolymers, graft copolymers, and polymer alloys by using electron spectroscopy for chemical analysis (ESCA), secondary-ion mass spectroscopy (SIMS), infrared spectroscopy, electron microscopy, neutron diffraction, and so on were studied. On the basis of these investigations, it is well known that the segregation of one component to the top surface is occasionally observed, and several mechanisms have been proposed to explain the segregation. One is the minimization of the interfacial free energy between the polymer and the environment, and the component with lower surface free energy segregates to the air surface. The other main factors are the crystallization factor and the entropical factor. The former occurs during the crystallization of one component; the other component is excluded from the crystalline component, resulting in the enrichment of the noncrystallized component at the top surface. The latter occurs when a more flexible segment segregates to the top surface when the difference in the surface energies of the two components is very small.

When a polymer is applied to medical devices coming into contact with blood or tissue, the surface structure is very important in terms of biocompatibility. Therefore, many surfaces have been designed for blood- or tissue-compatible materials. Biomaterials that have been investigated in detail with respect to the surface structures include segmented polyurethane,[1–3] 2-hydroxyethylmethacrylate/styrene block copolymer,[4,5] and poly(propylene oxide)-segmented nylon-610.[6–8]

We have synthesized several kinds of new polyether-segmented nylons (PE–Ny's) and have investigated the possibility of applying them to a hemodialysis membrane in terms of permeability characteristics, membrane morphology, and blood compatibility.[9–16] In previous articles, we reported the surface structures of phase-inversion membranes[16] and molten films[17] made of three kinds of poly(ethylene oxide)-segmented nylons (PEO–Ny's) with different crystallinities: high-crystalline poly(ethylene oxide)-segmented poly(iminosebacoyliminohexamethylene) (PEO–Ny610), low-crystalline PEO-segmented poly(iminosebacoylimino-m-xylene) (PEO–NyM10), and amorphous PEO-segmented poly(iminoisophthaloyliminomethylene-1,3-cyclohexylenemethylene) (PEO–NyBI). For phase-inversion membranes, ESCA analysis revealed that
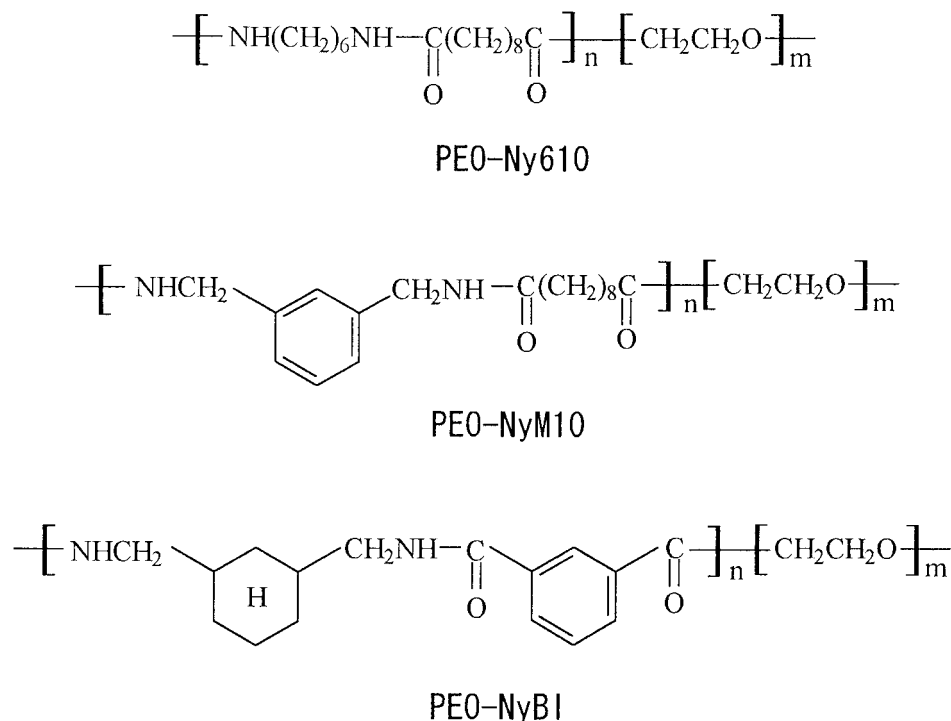
Figure 1 Chemical structures of PEO–Ny.

the enrichment of the PEO segment occurred at the top surfaces of PEO–Ny610 and PEO–NyM10 membranes and that the surface composition of the PEO–NyBI membrane was nearly equal to that of the bulk PEO–NyBI. The difference in the surface compositions in these PEO–Ny membranes was explained by the coagulation mechanism. However, the surfaces of the molten films were enriched with PEO segments for all three samples, and these results were explained by the surface free energy of the homopolymer corresponding to the segment in the melting state. We report here the surface structures of solvent-cast films observed by ESCA that were made of the three PEO–Ny's mentioned previously, and we discuss the segregation mechanism.

EXPERIMENTAL

Materials

The chemical structures of PEO–Ny610, PEO–NyM10, and PEO–NyBI are shown in Figure 1. These PEO–Ny's were prepared via melt polycondensation and were multiblock copolymers. The molecular weights of the PEO segments were 2000 for PEO–Ny610 and PEO–NyM10 and 1000 for PEO–NyBI, and the content of the PEO segment was about 10 wt %. The purification was carried out as follows. A formic acid solution of PEO–Ny was dropped into water. The precipitated PEO–Ny fibril was stirred for 24 h in pure water. This treatment removed the nonreacted PEO from the co-

polymer. The purified polymer was dried in a vacuum oven at 80°C for 24 h. The number-average molecular weights (M_n's) of PEO–Ny's were obtained by the titrations of the end groups, —NH$_2$ and —COOH.[17] The M_n and content of the PEO segment in the copolymer are shown in Table I. PEO–Ny610 is a polymer with high crystallinity [heat of crystalline fusion (ΔH) = 54.6 J/g, melting temperature (T_m) = 222°C], and PEO–NyM10 is a polymer with low crystallinity (ΔH = 30.3 J/g, T_m = 189°C).[11] PEO–NyBI is an amorphous polymer, and its glass-transition temperature (T_g) is 159°C.[15]

Preparation of the samples

The solvent-cast films of the PE–Ny's and corresponding homopolymers were prepared according to the following method. After a hexafluoroisopropanol (HFIP) solution of PEO–Ny (5 wt %) was cast onto a cover glass placed in a petri dish, a top was put on the

TABLE I
Properties of PEO–Ny

Polymer	Content of PEO (by ^{1}H-NMR) (wt %)	M_n of PEO–Ny (by the titration of end groups)
PEO–Ny610	10.6	18,520
PEO–NyM10	10.2	20,830
PEO–NyBI	9.8	21,280

TABLE II
T_m or T_g of homo-Ny and PEO–Ny

Ny610	PEO–Ny610	NyM10	PEO–NyM10	NyBI	PEO–NyBI
226°C (T_m)	222°C (T_m)	192°C (T_m)	189°C (T_m)	180°C (T_g)	159°C (T_g)

dish, and the solvent was evaporated gradually for 1 day at room temperature. The film obtained was dried *in vacuo* at 70 °C for 1 night. The films of PEO and the corresponding homo-Ny were prepared by the same method, except for the drying method of the PEO film (*in vacuo* at room temperature).

Measurement of ESCA

The surface analysis was carried out according to the method described in our previous articles with ESCA (PHI 5600ci, PerkinElmer, CT).[16,17] All the binding energies were referenced by the CH_x peak maximum in the resolved C1s spectra being set to 285.0 eV. The photoelectron take-off angle was 40° for all measurements and corresponded to about a 7-nm sampling depth.

RESULTS AND DISCUSSION

Although the PEO–Ny's used in this work were multiblock copolymers, we found that the T_m or glass transition of the homo-nylon decreased when the PEO segment was incorporated into Ny, which is shown in Table II. In addition, it was observed that PEO–Ny's in the melting state were transparent, and PEO–NyBI and PEO–NyM10 gave transparent films. (PEO–Ny610 gave a white opaque film because of crystalline formation.) These facts imply that the PEO segment and the Ny segment are miscible or partially miscible and do not form clear microphase-separated structures.

A representative survey scan spectrum of ESCA is shown in Figure 2; the sample is a PEO–Ny610 film. Quite similar spectra were obtained for PEO–NyM10 and PEO–NyBI films, except for slightly different peak intensities. These survey scan spectra show that the elements detected are just carbon, oxygen, and nitrogen.

The experimental atomic compositions calculated from the peak intensities in the narrow scans are shown in Table III. These results reveal that a significant increase in oxygen content and a decrease in nitrogen content occur on all the top surfaces of PEO–Ny films. These phenomena are explained by the segregation of the PEO segment to the top surface. Details of the narrow scan spectra of carbon (C1s) and oxygen (O1s) signals are discussed later.

The C1s spectra of PEO–Ny's are shown in Figure 3. In the carbon spectrum, the existence of three peaks
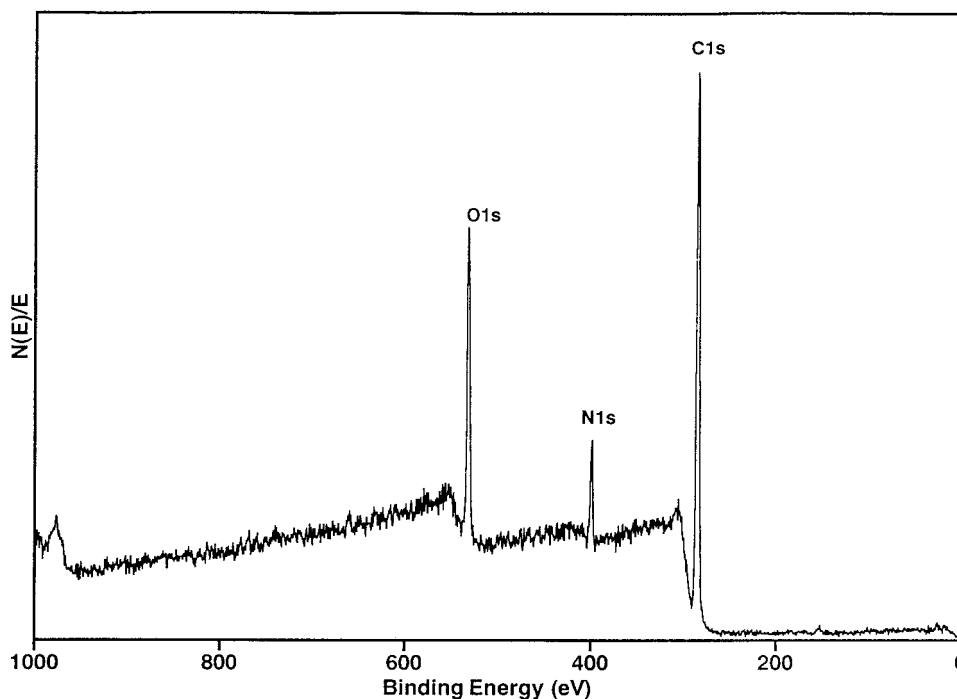

Figure 2   Typical survey scan ESCA spectrum for a PEO–Ny610 solvent-cast film.

Polymer	Stoichiometric atomic ratio (%)			Observed atomic ratio (%)		
	C	N	O	C	N	O
PEO–Ny610	78.6	9.0	12.4	76.6	6.8	16.6
PEO–NyM10	80.4	8.2	11.4	76.9	6.3	16.8
PEO–NyBI	78.9	8.9	12.1	79.0	6.0	15.0
Ny610	80.0	10.0	10.0	80.5	9.5	10.0
NyM10	81.8	9.1	9.1	81.7	9.5	8.8
NyBI	80.0	10.0	10.0	81.9	8.9	9.2

can be predicted from the chemical structure of PEO–Ny, as shown in Figure 1. One is attributed to the carbon atoms that link to carbon (C—C) and/or hy-
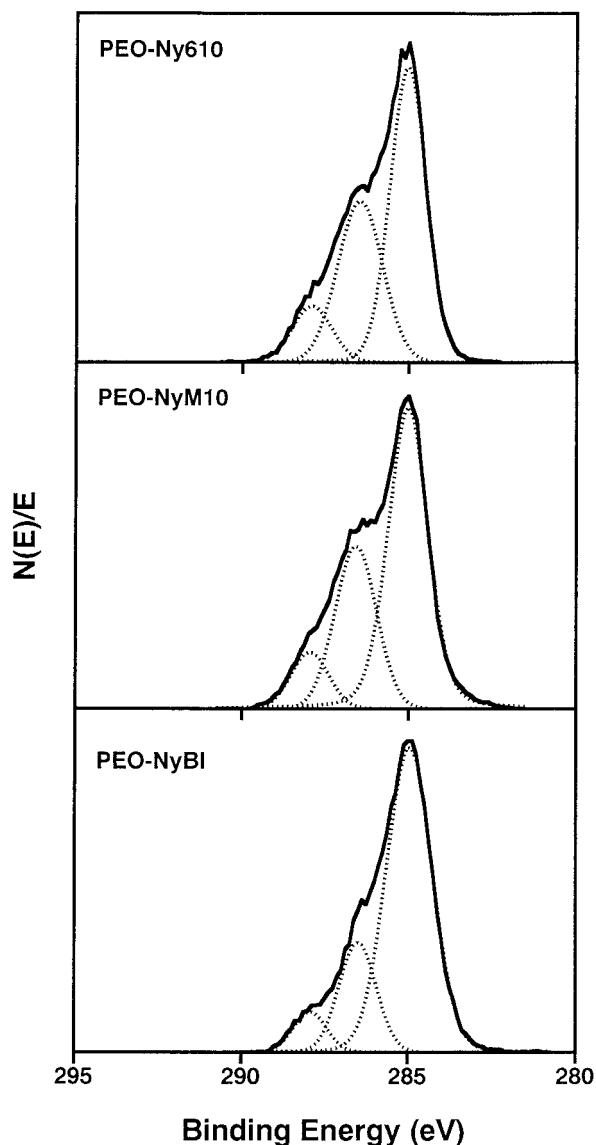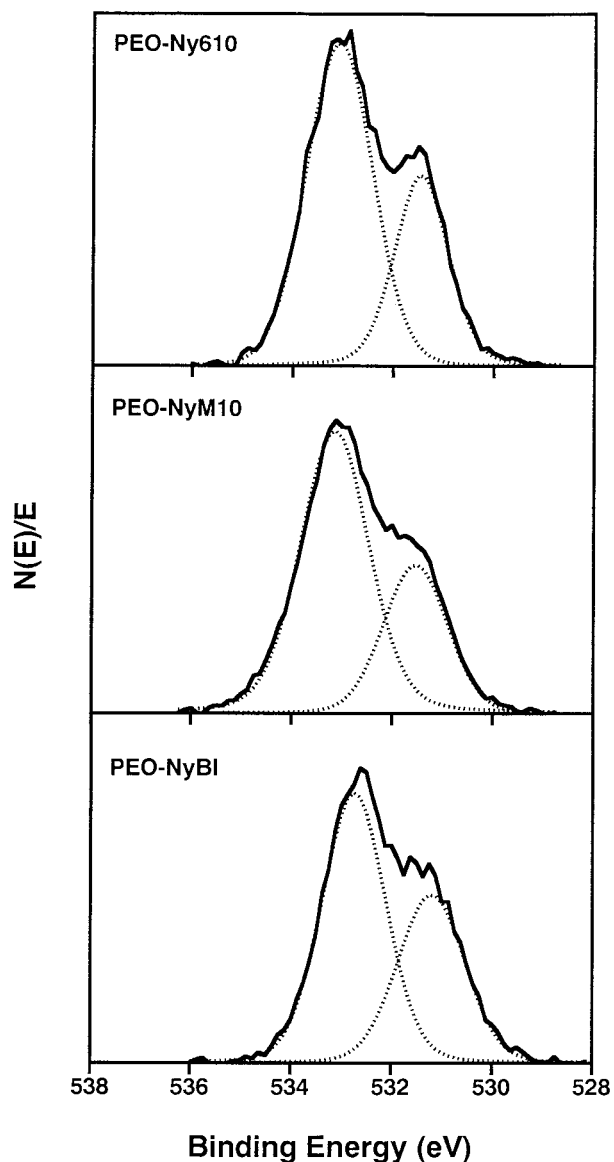

Figure 3 High-resolution ESCA spectra of C1s. The peak at 285.0 eV is assigned to hydrocarbon (C—C/C—H), the peak at 286.6 eV is assigned to carbons linked to ether oxygen (C—O) and/or amide nitrogen (C—NHC═O), and the peak at 288.0 is assigned to amide carbon (NHC═O).

drogen (C—H) atoms, and they appear at 285.0 eV. The second is attributed to the carbons next to the ether oxygen (C—O) derived from the PEO segment and/or those next to the nitrogen of the amide group (C—NHC═O), and they appear at 286.6 eV. The third is attributed to the carbon corresponding to the amide group in the Ny segment (NH—C═O) at 288.0 eV. PEO–Ny610 and PEO–NyM10 have similar shapes for the carbon peak (Fig. 3), and the peak of PEO–NyBI at 286.6 eV is smaller than the peaks of PEO–Ny610 and PEO–NyM10. Consequently, it can be predicted that the segregation of the PEO segment to the surface of PEO–NyBI is small in comparison with that of PEO–NyM10 and PEO–Ny610. When we quantify the chemical composition of the PEO–Ny surface from the carbon peak, we must resolve it into the three peaks mentioned previously. There are many possible ways to curve-fit the peak into three peaks. Moreover, because C—O and C—NHC═O have the same chemical shift, they cannot be divided into each peak. These facts implied that we would obtain a result with a serious error of estimation, and so we did not investigate the carbon peak further to quantify the surface structure.

Next, an analysis of the oxygen (O1s) peak is described. The O1s peak observed at each PEO–Ny film surface is shown in Figure 4. Although it has a broad peak with a shoulder, it can be curve-fitted into just two peaks easily because the chemical structure of PEO–Ny shown in Figure 1 shows that it has only two types of oxygen atoms. The one is solely based on the amide group in the Ny segment, and the other is solely based on the ether group in the PEO segment. The amide oxygen (NHC═O) and ether oxygen (C—O—C) are assigned to the peaks at 531.5 and at 533.1 eV, respectively. Consequently, the curve-fitted peaks will allow discrimination between the Ny and PEO segments. The surface composition calculated from the ratio of the two oxygen peaks is listed in Table IV. The PEO concentration at the top surface of each PEO–Ny is within 31–39 wt % and is significantly higher with respect to the bulk composition of PEO in the PEO–Ny's (ca. 10 wt %). When the attention is focused on the atomic ratios of ether oxygen, it is found that they are within 58–69%, and the ratio at the PEO–NyBI

Figure 4 High-resolution ESCA spectra of O1s. The O1s peak can be resolved into two peaks: amide oxygen (NHC=O) at 531.5 eV and ether oxygen (C—O—C) at 533.1 eV.

surface is the smallest. The difference in the ratio by 10% is significantly large; this agrees with the qualitative result of the PEO enrichment predicted from the C1s peaks.

It is well-known that in block copolymers the segregation of one segment to the free surface is preferentially governed by the interfacial free energy between the polymer and the circumstance. That is, the segment that minimizes the interfacial free energy segregates to the top surface, and there are many reports relevant to this mechanism. However, in almost all the reports, the interfacial free energy is discussed in terms of the relationship between the solid polymer surface and air at room temperature. In a previous article,[17] we reported that in molten PEO–Ny

films, the difference in the interfacial free energy of each segment of PEO–Ny at room temperature did not govern the surface structure. We found that the segregation of the PEO segment could be explained by the difference in the surface free energy in the melting state of the polymers that corresponded to the state forming the surface. There are several examples that cannot be explained by the mechanism mentioned previously. Sangen et al.[18] investigated the surface structure of PEO-segmented poly(ethylene terephthalate) with ESCA and found the enrichment of the PEO segment at the top surface despite the higher surface tension of the PEO segment. They explained the enrichment by the strong crystallization of the polyester segment. During the rapid crystallization of the polyester segment, the PEO segment was extruded from the crystalline region and segregated to the top surface. This explanation is based on Flory's proposal that the crystalline regions in semicrystalline homopolymers exclude the amorphous regions, resulting in well-defined crystal–amorphous interface zones. Brant et al.[19] reported the surface compositions of amorphous and crystallizable polyethylene blends. Their experiments indicated that the component with the lower crystallinity segregated to the free surface, and they concluded that the degree of crystallinity was an important factor for determining the surface structure. In our results, the enrichment of the PEO segment in PEO–Ny610 and PEO–NyM10 films may be brought about by the mechanism mentioned previously because Ny610 and NyM10 are semicrystalline polymers. However, this mechanism cannot be applied to PEO–NyBI because PEO–NyBI is amorphous. Another factor dominating the surface structure is the entropical one, which has been reported by many researchers. One of the works was described by Sikka and coworkers.[20,21] In this mechanism, the flexibility of the segment, or the statistical segment length, plays an important role in the segregation, and the more flexible segment segregates to the surface. The entropical factor, however, should be applied only to the case in which the difference in the surface tensions between the two components is small. Because the difference in the surface tensions of PEO and Ny is not small,[17] it will be hard to explain the exceptional segregation in terms of the entropical factor. It has been

TABLE IV
Surface Composition at PEO–Ny Film Surface

Polymer	Atomic ratio of O1s		PEO content (wt %)
	O—C	O=C	
PEO–Ny610	64.2	35.8	35.9
PEO–NyM10	68.5	31.5	38.8
PEO–NyBI	58.7	41.3	31.5

reported that the nature of the cast solvent plays an important role in the formation of the surface structure. Green et al.[22] reported the effect of a cast solvent on the surface structure of a polystyrene/poly(methyl methacrylate) (PMMA) diblock copolymer with toluene as a solvent. They found that the evaporation rate of the solvent had an effect on the concentration of PMMA at the surface. Deslandes et al.[23] investigated the surface structures of segmented polyurethanes (PUs) containing two different polyethers, poly(tetramethylene oxide) (PTMO) and PEO; the samples were prepared with dimethylacetoamide as a solvent. They concluded that the surfaces of all the samples were completely covered with the PU segment and that the polyether segment could not be detected even by SIMS. Burrell et al.[24] studied the effect of the sample preparation method on the surface structures of the copoly(ether esters) containing mixed polyether blocks, that is, PTMO and PEO, by ESCA and SIMS. The samples were solvent-cast films with HFIP as a solvent and the molded plaque. From ESCA results, they found the enrichment of PTMO relative to the PEO segment at the top surface and little difference in the surface structures between the solvent-cast film and the molded plaque. They explained the reason for the surface free energies of the component; the order was poly(butylene terephthalate) > PEO > PTMO. However, the SIMS result indicated that the solvent-cast film had a higher concentration of PEO at the top surface than the molded samples. They did not, however, clarify the reason for the enrichment of the PEO segment observed in the solvent-cast film. These previously mentioned reports strongly suggest that the solvent used in the preparation of the film or the preparation method affects the formation of the surface structure, and they sometimes bring about different or opposite results. Therefore, the conditions under which the film is prepared from the polymer solution will play an important role. Condition factors include the kind of gas contacting the surface (e.g., air, solvent vapor, or another gas), the solvent vapor pressure, and the interaction of the solvent molecule with the polymer components. We believe that it is important to consider these factors when the surface structure is investigated. If HFIP has a specific interaction with PEO and this causes the enrichment of PEO, it is easy to explain the reason for the enrichment of PEO observed in Burrell's case and our PEO–Ny case. In our experiment, the surface of the PEO–Ny solution was not contacting air but was contacting the HFIP vapor, the pressure of which was nearly equal to the saturated vapor pressure when the surface was formed. Therefore, we can readily predict that the special interaction between each component of PEO–Ny and HFIP vapor affects the formation of the surface, where the word *interaction* includes the minimization of the interfacial free energy between the polymer and the solvent vapor. A further investigation into the interactions between each component and HFIP or the interfacial free energy between them is now in progress.

From the previous discussion, it can be concluded that there will be three main factors affecting the segregation of one component observed on a block copolymer surface. One is the minimization of the interfacial free energy between the polymer and the circumstance, which includes the influence of the solvent vapor. The second is the extrusion effect, which means the extrusion of one segment by the crystallization of the other segment. The third is the entropical factor. The balance of these factors in the formation of the surface determines the surface structures. For PEO–Ny solvent-cast films, the nature of the solvent vapor will preferentially govern the formation of the surface structure. Of course, the extrusion effect and the entropical factor may affect the formation of the surface structure.

CONCLUSIONS

The surface structures of solvent (HFIP)-cast films made of three kinds of PEO–Ny multiblock copolymers with different crystallinities were investigated with ESCA. The PEO–Ny's used were high-crystalline PEO–Ny610, low-crystalline PEO–NyM10, and amorphous PEO–NyBI, and the PEO contents in the bulk polymers were about 10 wt %. The ESCA analysis showed the segregation of the PEO segment to the top surface, and the PEO content at the surface was 31–39 wt %. It can be concluded that the formation of the surface structure in PEO–Ny by the solvent-cast method is strongly affected by the solvent vapor, HFIP.

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