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Crystallization-driven migration of the low surface energy segment of a copolymer to the bulk

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Abstract

$[(\text{BA-C8})_{18}\text{–(6FBA)}]_n$ was synthesized by condensation polymerization of poly(bisphenol A-*co*-octane) containing 18 repeat units with bromine end groups, $(\text{Br–(BA-C8)}_{18}\text{–Br})$, and 4,4′-(hexafluoroisopropylidene)diphenol (6FBA). This copolymer was confirmed to be semicrystalline after a single melting temperature was detected by differential scanning calorimetry. The changes in the surface chemical composition were measured using time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy, the changes in the surface energy were measured using contact angle measurements, and the changes in the surface morphology were detected using atomic force microscopy as the copolymer crystallized. A decrease in the surface fluorine concentration with time was detected because of the movement of the low surface energy units (6FBA) to the bulk during the development of the crystalline phase. This result shows that the decrease in the enthalpy as a result of crystallization overcomes the increase in the surface free energy due to the migration of the low surface energy units to the bulk and the decrease in entropy due to demixing.

Keywords: Crystallization; Copolymer; Surface segregation

1. Introduction

The surface properties of polymers, copolymers and polymer blends are important to numerous industrial applications. Many studies have shown that the surface properties of these polymer systems are related to their morphologies. It is known that a higher concentration of the low surface energy component is usually detected at the surface of copolymers and polymer blends as a result of the minimization of the surface free energy [1–9]. However, the surface properties of blends and copolymers are also found to be dependent on many other factors, including the magnitude of the interaction between the two polymer blend components which determines their degree of miscibility [10–13], the molecular weights of the blend components [10,11,14–17], the length of the segments of the copolymers [18–20], the nature of the end groups [3,7,21] and side groups [22,23], as well as the crystallinity and morphology [24–29]. Clark et al. [25,26] reported that surface and bulk chemical compositions of blends of poly(caprolactone) (PCL) and poly(vinyl chloride) (PVC) were similar when the concentration of PCL was less than 40 wt% because PCL did not crystallize. PCL started to crystallize at concentrations larger than 40 wt%. At these concentrations, the surface was enriched with PCL. This can be easily explained by the fact that the reported surface energy of PCL is lower than that of PVC. However, when the PCL concentration was above 90 wt%, the surface was found to enrich with PVC. It is clear as reported by the authors that crystallinization is one of the driving forces for these observations.

Fluoropolymers are of significant interest in many applications because of their unique surface properties. Fluorinated end groups and chain segments, which tend to segregate to the surface, have been used very often to produce low surface energy surfaces. In a previous publication, the surface chemical composition and morphology of a miscible blend system containing poly(bisphenol A-*co*-octane) (BA-C8), a semicrystalline polymer, and 6FBA-C8, an amorphous polymer obtained by condensation polymerization

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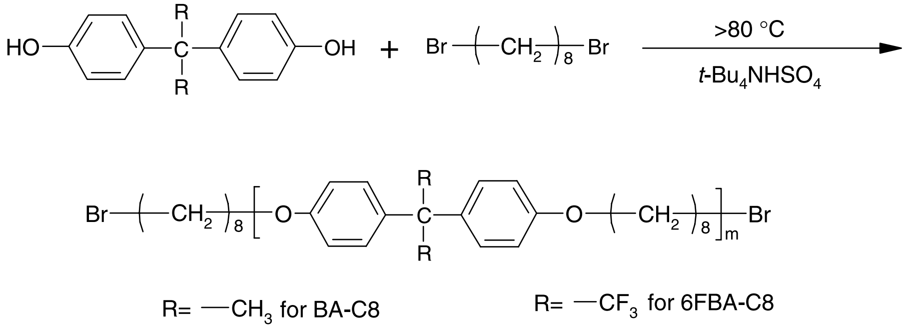


Scheme 1. The synthesis of BA-C8.

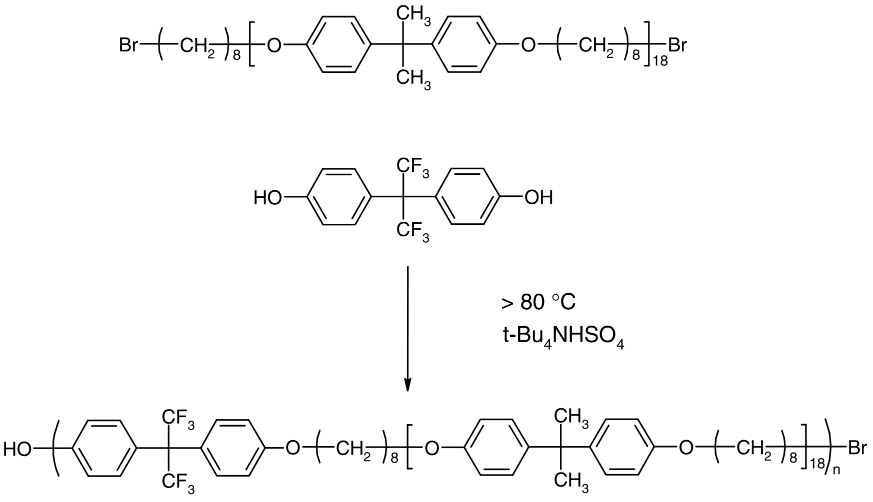
of 1,8-dibromo-octane with 4,4′-(hexafluoroisopropylidene)diphenol(6FBA), were studied [30]. The atomic force microscopy (AFM) results indicated that many small crystalline domains formed and agglomerated to form spherulite-like structures. Together with contact angle measurements, time-of-flight secondary ion mass spectrometry (ToF-SIMS) and XPS provided conclusive evidence that 6FBA, which is the low surface energy component of the blend, segregated to the surface in order to minimize the surface free energy of the system. This result is consistent with the literature.

We synthesized a new copolymer that contains one amorphous 6FBA unit per 18 crystalline BA-C8 units. This new copolymer was found to crystallize slowly at room temperature. Hence, it is an ideal candidate to study the change in surface chemical composition as a function of crystallization time. In the amorphous state, we anticipate that the surface be enriched with the lower surface energy component (6FBA). As the copolymer crystallizes, the surface morphology may change. It is possible that the reduction in the enthalpy will overcome the increase in the surface energy and the decrease in the entropy of system due to the migration of 6FBA units to the bulk. The change in surface chemical composition as the copolymer crystallized was followed using contact angle measurements, ToF-SIMS and XPS and the change in the surface morphology was determined using AFM.

2. Experimental section

The synthesis of BA-C8 was obtained by condensation polymerization of 1,8-dibromo-octane with bisphenol-A as shown in Scheme 1.

The ^{1}H NMR spectrum of the polymer containing Br end-groups (Br–(BA-C8)$_n$–Br) was recorded using $CDCl_3$ as a solvent. The proton NMR signals were analyzed and the results are listed as follows: 7.11(4H, d, *m*-Ar–H), 6.78 (4H, d, O–Ar–H), 3.91 (4H, t, O–CH_2), 3.39 (t, end-group Br–CH_2), 1.71–1.77 (4H, m, –CH_2CH_2–), 1.62 (6H, s, –$C(CH_3)_2$) and 1.36–1.44 (8H, m, –$CH_2CH_2CH_2CH_2$–). By applying the proton NMR integration methodology to the Br-end-group (Br–CH_2) proton signal at 3.39 ppm and the O–CH_2 proton signal at 3.91 ppm, we were able to estimate an approximate number of repeating units, m, to be approximtely 18 for the polymer. The copolymer, [(BA-C8)$_{18}$–(6FBA)]$_n$, was obtained by condensation polymerization of Br–(BA-C8)$_{18}$–Br with 6FBA at a molar ratio of 1:1. The synthesis is described in Scheme 2. The ratio between the 6FBA and BA-C8 units, which was determined using the proton NMR integration of the signals at 7.28 ppm (*m*-6FBA–H) and 7.11 ppm (*m*-Ar–H) (or 6.84 ppm (*o*-6FBA-H) and 6.78 ppm (*o*-Ar–H)), was estimated to be about 1:18.



Scheme 2. The synthesis of $[(BA-C8)_{18}-(6FBA)]_n$.

The weight-average molecular weight ($\bar{M}_w$) of the copolymer and the polydispersity index were measured to be 1.18×10^4 g/mol and 1.6, respectively. Differential scanning calorimetry (DSC) measurements were performed with a TA 2910 calorimeter in a nitrogen atmosphere. The heating rate was 10 °C/min and the temperature ranged from −50 to 200 °C. Two heating and cooling cycles were used. The melting point (T_m) was taken from the first heating cycle, and the glass transition temperature (T_g) was measured from the second heating cycle. The T_m and T_g were measured to be 79 and 16 °C, respectively.

A polymer solution with a concentration of 30 mg/mL was prepared by dissolving the copolymer in chloroform. Film samples were prepared by spin-casting approximately 40 μL of the polymer solution at 3000 rpm on 4-cm^2 silicon wafers. The films were dried in a vacuum oven for 30 min at room temperature. Then they were wrapped in clear aluminum foil and placed in an oven to crystallize at 35 °C. It is important to note the crystallization temperature is above the T_g of the copolymer. The thickness of the film was measured to be about 220 nm using a profilometer.

AFM height and phase images were collected with a NanoScope III™ AFM (Digital Instruments) at room temperature. The exact surface temperature was probably a bit higher than the room temperature due to the heating of the laser. Si tips with a resonance frequency of approximately 300 kHz were used and the scan rate was 0.8 Hz. The set-point amplitude ratio was set at 0.8. For each image, 512 lines were collected.

ToF-SIMS measurements were performed on a Physical Electronics PHI 7200 ToF-SIMS spectrometer. The vacuum was about 1.5×10^{-9} Torr. High-resolution mass spectra were obtained by using a Cs^+ primary ion source operating at 8 keV. The total ion dose was lower than 4×10^{11} ions/cm^2. Positive and negative spectra were taken.

XPS spectra were recorded on a PHI 5600 multi-technique system equipped with an Al monochromatic X-ray source. A pass energy of 58.7 eV was used. The spectra were obtained at take-off angles of 25, 45 and 75°.

Contact angles were measured on a Kruss goniometer at room temperature. The volume of the droplet was approximately 15 μL. Contact angles were measured at different times after the films were prepared. Three measurements were made to obtain the average value for the contact angle. The surface energy was determined by the Owens–Wendt method [31]. According to this method, the relationship between the contact angle, θ, and the surface energy of the liquid, γ_{LV}, can be written as

$$1+\cos\theta = 2\sqrt{\gamma_S^d}\left(\frac{\sqrt{\gamma_L^d}}{\gamma_{LV}}\right)+2\sqrt{\gamma_S^p}\left(\frac{\sqrt{\gamma_L^p}}{\gamma_{LV}}\right), \qquad (1)$$

where γ_S^d and γ_S^p are the dispersion and polar components of the surface energy of the solid, respectively, and γ_L^d and γ_L^p are the dispersion and polar components of the surface energy of the liquid, respectively. The surface energy of the solid is the sum of the dispersion and polar components of the solid. By measuring the contact angles of two different liquids with known surface energies, the surface energy of the solid can be calculated by solving Eq. (1). The value of γ_L^d and γ_L^p for water is 21.8 and 51.0 mJ/m^2, respectively, and the value of γ_L^d and γ_L^p for methylene iodide is 49.5 and 1.3 mJ/m^2, respectively.

3. Results and discussion

The changes in the surface composition of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ with time at 35 °C were measured at room temperature using contact angle measurements, ToF-SIMS and XPS. Fig. 1 shows the surface energy of the $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ as a function of time. Each data point represents the average of three measurements. The surface energy of a freshly prepared sample of this copolymer was measured to be 42.5 mJ/m^2. The surface energy gradually increased and finally reached a steady value of about 49.0 mJ/m^2 after about 300 h. It is known that surface roughness will affect the contact angle and the surface of a semi-crystalline polymer will become rougher as the polymer crystallizes. The root-mean-square roughness of the surface of the copolymer was measured using AFM to be 0.22, 2.02 and 4.77 nm after 1, 23, and 100 h after the sample was prepared. The increase in the surface roughness after crystallization will undoubtedly add some uncertainty in the determination of the surface energy.

In our previous paper [30], we reported the change in the surface energy of a pure BA-C8 sample and a blend containing BA-C8 (80 wt%) and 6FBA-C8 (20 wt%). For the pure BA-C8 sample, the surface energy increased from 46.5 mJ/m^2 to a steady value of about 50.5 mJ/m^2 as BA-C8 crystallized because the surface energy of the crystalline phase is higher than that of the amorphous counterpart. For the blend of BA-C8 with 6FBA-C8, the surface energy decreased from 45.5 mJ/m^2 to a steady value of about 39.5 mJ/m^2, which is very similar to the surface energy of pure 6FBA-C8 (39.4 mJ/m^2) due to surface segregation of the low surface energy component. The change in the surface energy of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ following crystallization is very similar to that of pure

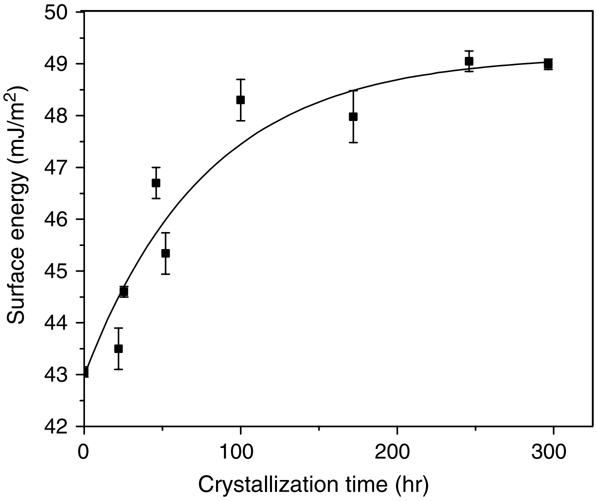


Fig. 1. The surface energy of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ as a function of time.

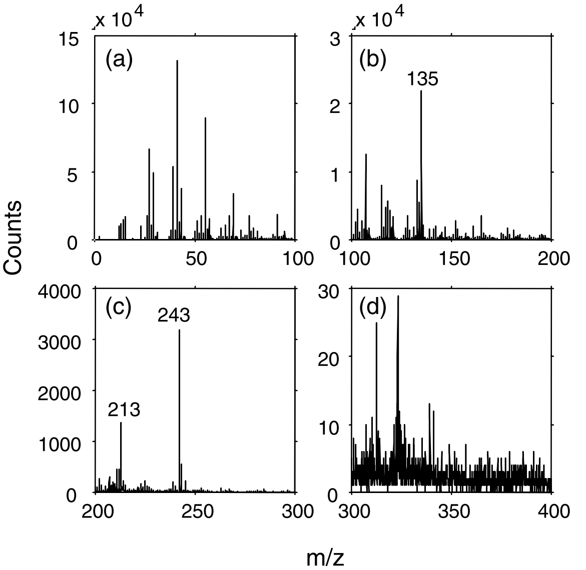
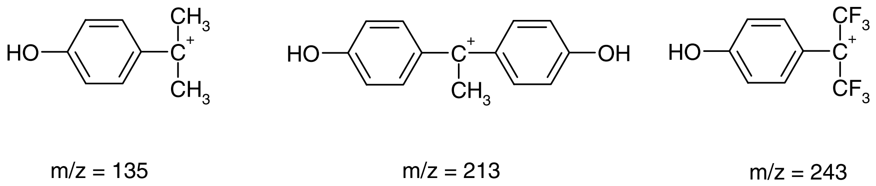


Fig. 2. Positive spectra showing some characteristic ion fragments of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$: (a) 0–100; (b) 100–200; (c) 200–300 and (d) 300–400.

BA-C8. It should be noted that $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ has a structure very similar to that of BA-C8 except that a unit of 6FBA is inserted between every 18 repeat units of BA-C8. The surface energy of the amorphous phase of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$, which was measured to be 42.5 mJ/m^2 is slightly lower than that of the corresponding phase of pure BA-C8 (46.5 mJ/m^2) mainly because of the presence of low surface energy units (6FBA) in the copolymer. As the polymer crystallized, the surface energy increased to about 49 mJ/m^2, which is slightly lower than the steady value (50.5 mJ/m^2) of a BA-C8 sample crystallized for 90 h [30]. In the case of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$, the increase in the surface energy is mostly due to the increase in the crystallinity at the surface and the surface energy of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ is still lower than that of the pure BA-C8 because low surface energy units (6FBA) were still detected at the surface. As shown by both XPS and ToF-SIMS, the fluorine concentration of the copolymer decreased as a function of time and reached a steady value and never disappeared completely due to the fact that the 6FBA units preferentially segregated to the surface of the amorphous regions.

The changes in the surface composition as a function of time at 35 °C were studied using ToF-SIMS. Fig. 2 shows a positive spectrum of a freshly prepared $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ film. The ion fragments at mass-to-charge ratio (m/z) of 135 and 213 are from BA-C8, while the ion fragment at $m/z=243$ is from 6FBA (cf. Scheme 3). The change in the intensity ratio of selected characteristic ion fragments can be used to monitor the change in surface composition of a sample [32–34]. The plots of I_{243}/I_{135} and I_{243}/I_{213} as a function of time, which are shown in Fig. 3(a) and (b), can be used to measure the relative abundance of 6FBA to BA-C8 at the surface of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ as it crystallizes. I_{135} is the intensity of the peak at $m/z=135$. The intensity used is the average of four independent measurements. These two plots show a decrease in the concentration of 6FBA with time.

The fluorine concentration at the surface of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ as a function of time at 35 °C was also measured at room temperature using XPS. The results are shown in Fig. 4. Fig. 4(a) shows the XPS data obtained at the take-off angle of 45°. Each data point is the average of four measured values. It is very clear that the surface fluorine concentration decreases as crystallization proceeds. The fluorine concentration decreases from about 3.1–2.4 at.% after 100 h. These results suggest that



Scheme 3. Proposed molecular structure of some characteristic fragments.

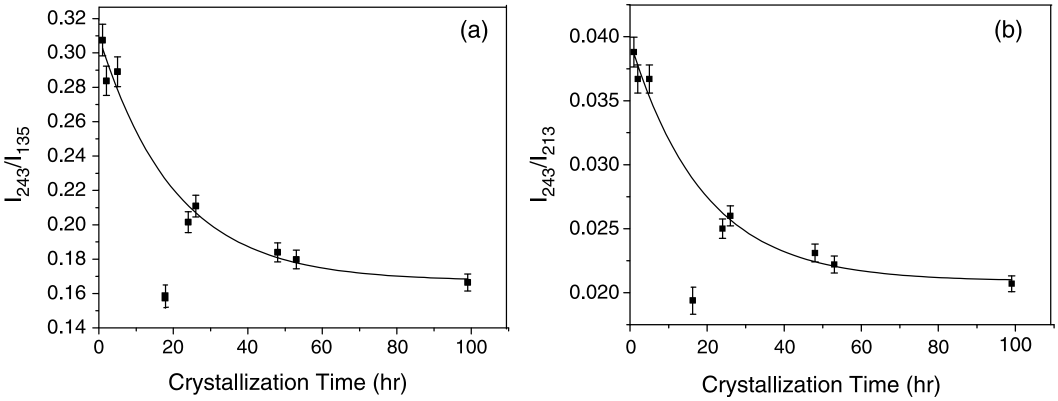


Fig. 3. The change in the surface composition of $[(BA\text{-}C8)_{18}\text{–}(6FBA)]_n$ as indicated by the ion intensity ratios (a) I_{243}/I_{135} and (b) I_{243}/I_{213}.

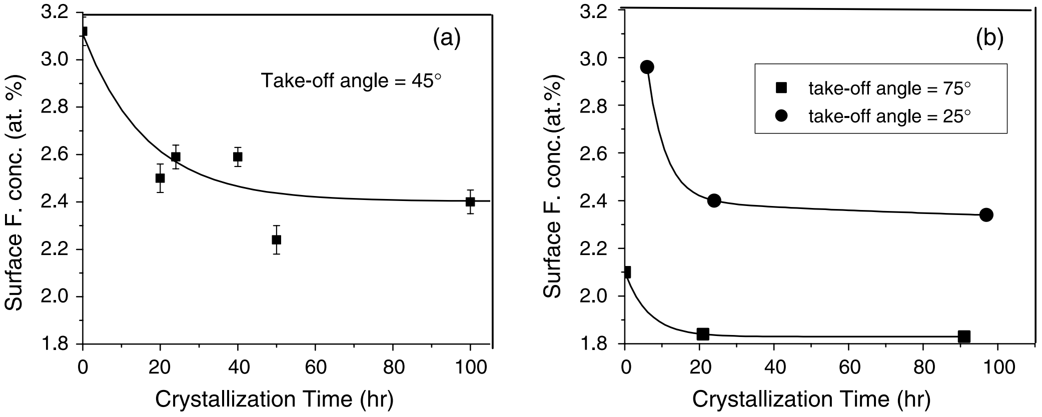


Fig. 4. The surface *F* concentration as a function of time at 35 °C.

there is more fluorine at the surface than in the bulk (calculated bulk value = 1.3 at.%). It is important to note that the sampling depths of ToF-SIMS and XPS are both less than 10 nm, which is much smaller than the film thickness (~220 nm). A sharp decrease in the fluorine concentration is observed as crystallization starts, suggesting the migration of 6FBA units to the bulk. Fig. 4(b) shows the XPS data obtained at the take-off angle of 25 and 75°. The XPS data obtained at take-off angles of 25, 45 and 75°, corresponding to sampling depths of 3.3, 5.5 and 7.5 nm, respectively, assuming the attenuation length of F1s photoelectrons is 2.6 nm (the density of the polymer is assumed to be 1.2 g/cm^3) [35]. These XPS data indicate that the fluorine concentration is higher at the top surface.

It is important to recognize that the sample depths of ToF-SIMS and XPS are not the same. The sample depths of XPS and ToF-SIMS are about 5 nm and less than 2 nm for molecular ions, respectively. Even so, both the ToF-SIMS and XPS results show a decrease in the fluorine concentration with time. However, a 50% reduction in the ion intensity is observed. Only 22.6 and 14.3% decrease in the fluorine concentration are derived from the XPS data obtained at take-off angles of 45 and 75°, respectively. These results suggest that the reduction in the fluorine concentration is most significant at the topmost surface.

It is very common that the low surface energy component of polymer blends or copolymers migrates to the surface. The observation of the reduction in the surface concentration of a low energy component of a polymer blend or copolymer is rather uncommon; however, we believe that the most probable cause for this observation is a change of surface morphology as the polymer chains rearrange themselves from the amorphous to crystalline phases. Fig. 5 shows the phase images of the surface of a copolymer film as a function of time. The surface only shows small edge-on lamellar sheafs in the first 23 h after it was prepared. It is important to point out that edge-on lamellae are usually observed on polymer films that are thicker than 200–300 nm [36] because the surface energy of the flat-on lamellae is 3–6 times higher than that of the edge-on lamellae [37]. As the thickness decreases, the concentration of flat-on lamellae increases. It is reasonable to assume that the influence of the substrate on the morphology and surface chemical composition is small for polymer films with only edge-on lamellae. After 100 h, edge-on lamellae cover most of the surface (cf. Fig. 5(b)). We can thus conclude that for the films used in this work (~220 nm), the influence of the substrate is negligible.

The change in the surface chemical composition is a result of the movement of polymer chains during crystallization. Based on these results, we present schematic drawings showing the polymer chain arrangement in the amorphous (side view) and crystalline states (top view) in Fig. 6(a) and (b), respectively. In the amorphous state, the 6FBA units, which

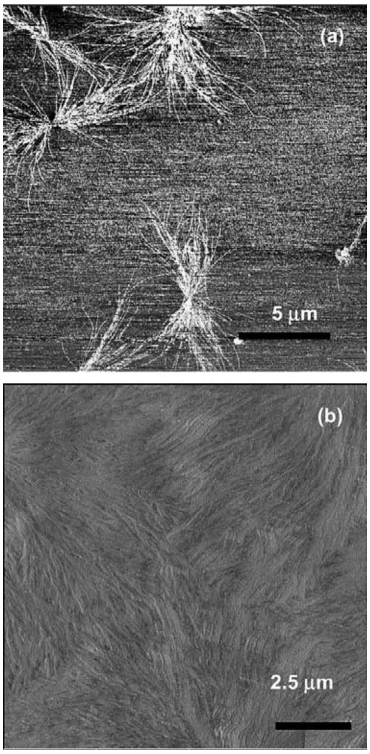
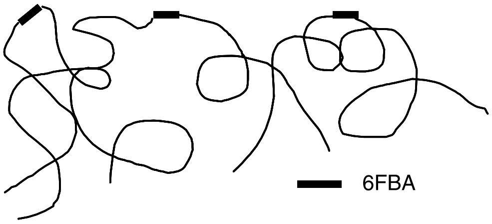
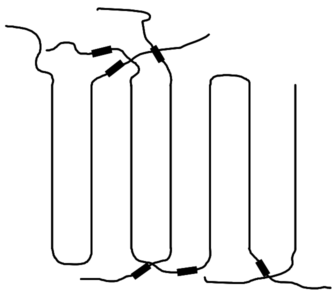


Fig. 5. AFM phase images showing the development of edge-on lamellae after (a) 23 h and (b) 100 h after the film was prepared.



(a) Amorphous phase (side view)



(b) Crystalline phase (top view)

Fig. 6. Schematic drawings of polymer chains arranged in amorphous and crystalline states.

are the lower surface energy components, segregate to the surface of the copolymer to minimize the surface energy, as shown in Fig. 6(a). Consequently, the fluorine surface concentration is much higher than the bulk value. At 35 °C, which is higher than the T_g of the copolymer (16 °C), the polymer chains are very mobile and start to crystallize. As the BA-C8 units crystallize, the reduction in the enthalpy can overcome the increase in the surface energy due to the movement of the 6FBA units to the bulk and the decrease in entropy due to demixing. In the crystalline state, the polymer chains have to assume fixed orientations on the crystallite surface. The 6FBA units, which have segregated at the surface of the copolymer, must move away from the surface and reside at the folding surfaces of the edge-on lamellae, as shown in Fig. 6(b). This can explain why the surface fluorine concentration decreases as the copolymer crystallizes. After 100 h, the edge-on lamellae occupy nearly the whole surface and the surface fluorine concentration reaches a steady-state value. This result indicates that even after the surface reached a steady crystalline state there are still 6FBA units, which segregate at the surface of the amorphous regions.

4. Conclusion

In this work, we have successfully shown the migration of a low surface energy unit (6FBA), which is inserted between 18 units of the high surface energy component (BA-C8), away from the surface as the copolymer crystallizes. In the amorphous state, the surface of the copolymer is enriched with 6FBA units. This phenomenon is commonly observed in many polymer blends or copolymers that contain a low surface energy component. However, in our present case, a reduction in the surface fluorine concentration is observed as the copolymer crystallizes. When the crystalline structure develops, the low surface energy units no longer can freely segregate to the surface. They have to reside at the folding face of the edge-on lamellae. Thus, the concentration of the low surface energy units decreases as the copolymer crystallizes. This result shows that the reduction in the enthalpy of this polymer system due to crystallization plays a dominant role in controlling the surface chemical composition.

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