Morphology of semicrystalline block copolymers: polyethylene-*b*-atactic-polypropylene

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Abstract

Transmission electron microscopy (TEM) and electron diffraction (ED) are used to study the morphology of a semicrystalline polyolefin diblock copolymer polyethylene-*b*-atactic-polypropylene (PE-*b*-aPP) and its blend with polyethylene homopolymer. By using $RuCl_3/NaClO$ as the staining agent, both the contrast between amorphous PP and amorphous PE regions and the contrast between amorphous PE regions and crystalline PE regions can be obtained. As a result, both the larger lamellar structures due to microphase separation and the smaller crystalline PE lamellae can be resolved on TEM micrographs. Electron diffraction coupled with TEM imaging is used to elucidate the orientation of PE crystallites with respect to the interfaces of the microphase separated block copolymer lamellar domains. Fast quenching from a microphase separated melt-state was found to result in confinement of PE crystallization within the microphase separated PE domains of the block copolymer morphology. The orientation of the PE crystallites thus formed was found to be random. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Theoretical predictions on the behavior of semicrystalline diblock copolymers have been developed by Dimarzio et al. [1], Whitmore and Noolandi [2], Vilgis and Halperin [3] assuming that a thermodynamically most stable state can be achieved. The most stable state of symmetrical crystalline/coil diblock copolymers is predicted to be strictly alternating lamella morphology with crystalline chain stems oriented perpendicular to the interface with the amorphous block domains. Experimental investigation of the morphology of semicrystalline diblock copolymers has been carried out by several research groups [4–12]. For many systems studied, the final morphology was found to be path-dependent. When crystallizing the sample from a microphase separated melt-state, one of two results are obtained: (1) The microphase separated morphology is maintained and the crystallizable block crystallizes within the nano scale regions defined by the block copolymer microphase separation. (2) Crystallization destroys the morphology preformed in the melt-state and forms spherulites. The experimental work of Cohen et al. [4], Nojima et al. [10] and Register and co-workers [13] suggest that the final morphology of semicrystalline diblock copolymers is a strong function of: (1) the segregation strength of the copolymers; (2) the mobility of the amorphous block; (3) the crystallization temperature employed.

Most previous results on semicrystalline block copolymers made use of scattering techniques. Transmission Electron Microscopy (TEM) offers the opportunity to directly visualize the morphologies of these materials provided that the problem of achieving adequate contrast between different domains can be solved. TEM contrast between saturated polyolefin blocks is difficult to achieve and this has limited the use of TEM in the study of these materials. Using RuO_4 to stain polyolefins, such as PE and PP, has been reported previously [14–16]. TEM images of LDPE, HDPE, PP, etc. have been obtained by using RuO_4 staining agent. The first report of ruthenium staining of saturated polyolefin diblock copolymers (PE-*b*-PEP and PE-*b*-PEE) was by Khandpur et al. [15]. The contrast produced by using RuO_4 is believed to be, at least in part, a result

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of the differences in transport properties of RuO_4 in the rubbery domains versus the semicrystalline domains. However, based on the difference of mobility of RuO_4 in crystalline and amorphous region, we should also expect contrast between crystalline polyethylene and amorphous polyethylene within microphase separated semicrystalline domains. While good contrast between the amorphous block and semicrystalline PE block was observed by Khandpur et al., the difference between amorphous and crystalline polyethylene was not resolved.

In this report, we use ruthenium trichloride ($RuCl_3$) in sodium hypochlorite (NaClO) to stain the amorphous domains in PE-*b*-aPP, a saturated polyolefin diblock copolymer. The morphological behavior of PE-*b*-aPP diblocks and their blends with aPP have been studied previously by Sakurai et al. [12]. TEM images were obtained for both block copolymers and their blends with aPP without employing any staining agent. Contrast was from differences in density between the two domain materials as well as due to diffraction from the crystalline regions. Although microphase separated morphology could be observed, the difference between crystalline polyethylene and amorphous polyethylene could not be resolved.

The application of $RuCl_3$/NaClO to stain polyolefins has been reported previously by Montezinos et al. [16]. The systems they studied were mainly commercial polyolefins and blends. By using this staining agent for semicrystalline polyolefin diblock copolymers, we now can not only observe the morphology due to microphase separation, but also the crystalline morphology of polyethylene crystallites within polyethylene nanometer scale domains. To the best of our knowledge, this is the first visualization of polymer crystallites within a confined region defined by microphase separation. Electron diffraction patterns were also obtained from local regions of the specimen. Combining TEM imaging and ED, the orientation of the crystalline PE lamella with respect to the interfaces of the PE lamellar domains of the block copolymer morphology can be investigated.

2. Experimental

PE-*b*-aPP used in this research was synthesized via hydrogenation from its precursor, poly(1,4-butadiene)-*b*-poly(1,4-3-methyl-1-pentadiene), which was synthesized via sequential anionic polymerization. PE homopolymer used in this study was also obtained by hydrogenation of anionically synthesized polybutadiene. Detailed information on the synthesis as well as characterization by ^{1}H NMR, ^{13}C NMR and GPC has been presented previously [17,18]. The polyethylene chains in both block copolymers and homopolymers had about 5% ethyl branching due to inevitable 1–2 additions of butadiene. The molecular

weight of the diblock copolymer used was 100,000 g/mol (45,000 g/mol for PE and 55,000 g/mol for aPP) and its polydispersity was 1.06. The molecular weight of the PE homopolymer was 20,400 g/mol, and its polydispersity was 1.03. The melting temperature, T_m, for the crystallites in the polyethylene block was determined by DSC to be 108°C and the T_g for atactic-polypropylene was about −8°C.

Diblock copolymer and PE homopolymer were blended by co-dissolving both polymers in hot xylene. The solvent was slowly evaporated at room temperature over a period of one week. The resulting blend was then completely dried in a vacuum oven. Both the diblock copolymer and its blend with polyethylene homopolymer were shear-aligned in the melt-state by application of an elongational flow field in a channel die, as illustrated in Fig. 1. The channel die and the piston used to compress the polymer were made of aluminum coated with Teflon. The details of this procedure were given previously [12,19]. The samples were then melt annealed at 150°C for one day. After annealing, the samples were quenched in liquid nitrogen.

In order to prepare samples for TEM imaging, the first step was to cut a thick slice about $1 \times 1 \times 5$ mm^3 from the bulk material. This was accomplished with a Reichert Ultracut cryomicrotome using a glass knife at −110°C. The thick section was then stained by exposure to the vapor generated from 1 ml of freshly prepared 2 wt% $RuCl_3$/NaClO in water for 3 h at room temperature. Longer staining provides no advantage as the staining reagent loses it efficiency over time and the heavily stained outer parts of the bulk sample prevent further penetration of the staining reagent. The stained bulk samples became completely black. They were then microtomed with a diamond knife at room temperature in order to obtain ultrathin (about 40 nm) sections for TEM. The microtome cutting speed was about 0.2 mm/s. The sections were collected on 400 mesh copper grids. The initial preparation of a thick microtomed section was
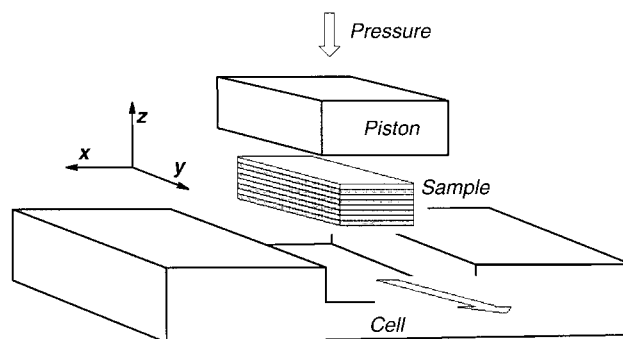

Fig. 1. Schematic of the shear cell used for aligning the block copolymer and its blends with PE homopolymer. Shear is always applied parallel to the *x*-direction and the figure shows the proposed orientation for the lamellae.

necessary since the staining reagent would only penetrate the outer several micrometers. The first few microns of the sample are most effectively stained.

TEM and electron diffraction experiments were conducted on a JEOL 2000 FX-II. The diffraction camera length was calibrated by using an internal gold standard on some of the grids observed. The magnification of TEM imaging was calibrated using etched gratings of standard dimensions. The ruthenium staining agent not only provides TEM imaging contrast to the sample, it also helps to stabilize the PE crystallites in the electron beam of the TEM since the surrounding amorphous regions become heavily crosslinked. This crosslinking around the periphery of the crystallites makes it more difficult for them to melt as they are heated by exposure to the beam. However, the PE crystallites are still beam sensitive and the sharp rings in electron diffraction will disappear in seconds. We offer this as a qualitative observation; no attempt was made to quantitatively measure the increase in beam stability resulting from the ruthenium staining.

3. Results and discussion

Fig. 2 is a TEM micrograph showing the semicrystalline morphology of the pure polyethylene homopolymer. This is the same PE homopolymer used in the blends with the PE-*b*-aPP diblock. It was subjected to the same processing conditions as the diblock copolymer. A loosely developed spherulitic structure is observed in the pure PE with clustering of long PE crystalline lamella which appear ribbon-like in the cross-sectioned image. Clearly the PE lamella are very long (on the order of a micrometer) compared to their thickness (on the order of 100 Å). This estimate of the aspect ratio of the lamella is very rough since the sample is a thin section with a thickness that is much smaller than the lamellar length. What is actually observed is a randomly selected cut through the sample. If anything, however, the actual lamellar lateral dimensions are larger than what is observed in the TEM image.

Fig. 3 shows a TEM micrograph of the PE-*b*-aPP diblock. The sample has a block copolymer microphase separated lamellar morphology with a repeat distance of about 60 nm and is shown to be well aligned. Fast quenching does preserve the morphology formed in the melt-state. The aPP phase appears dark due to preferential staining by the ruthenium reagent. The lighter layers are less heavily stained polyethylene lamellar domains. The moderate amount of variation in aPP domain thickness is unusual when compared to common amorphous–amorphous diblock copolymers such as poly(styrene-*b*-isoprene). Closer examination reveals that the lighter PE layers contain short sections of crystalline lamellae that appear to be randomly oriented. Fig. 4a shows electron diffraction from this material in which the PE 110 and 200 reflections are clearly visible as rings. Fig. 4b shows the region inside the selected area aperture of TEM from which this electron diffraction pattern was taken. Clearly the larger length scale block copolymer lamellar morphology is well aligned over this
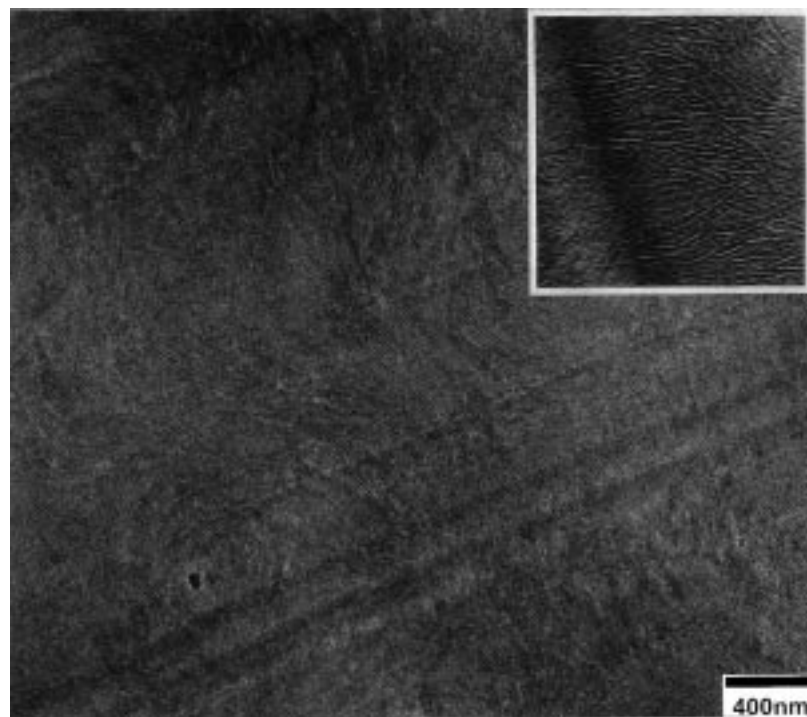

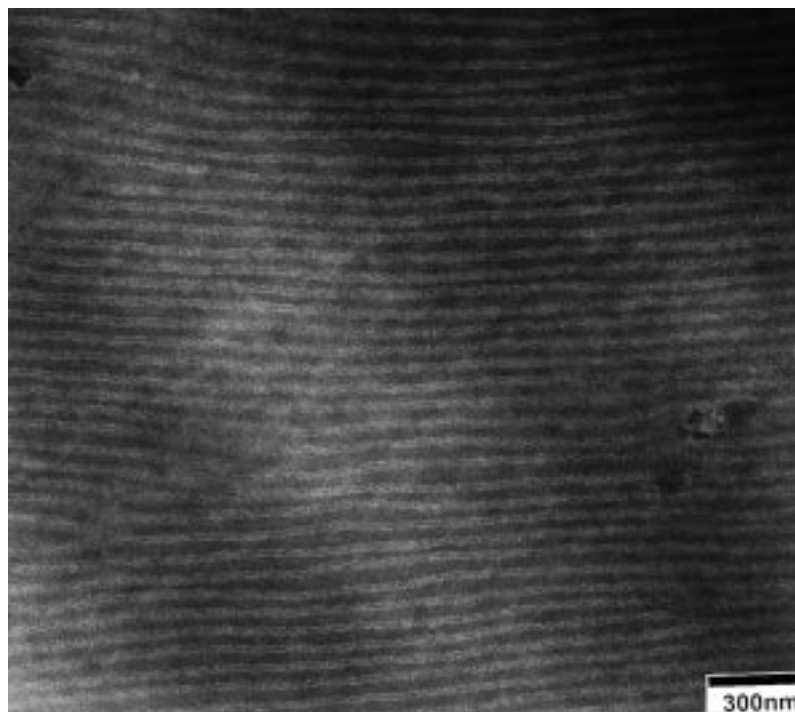Fig. 2. TEM micrograph of PE homopolymer.

Fig. 3. TEM micrograph of PE-*b*-aPP block copolymer.

entire region. Thus the fact that the crystalline PE diffraction produces unoriented rings is an indication that there is no preferential alignment of the PE crystalline lamellae within the PE domains, i.e. the PE–PP interface produces no aligning effect on the crystallites. This random orientation is consistent with previous results from two-dimensional SAXS and WAXS measurements on PE-*b*-aPP blends with aPP homopolymer [12], but different from the results observed in some other systems [5,20]. The morphology of the melt-state can only be maintained if the sample is cooled very fast, otherwise, spherulitic structures grow and in the process break up the block copolymer lamellar organization [12].

Fig. 5 shows TEM micrographs of a blend between PE-*b*-aPP and PE homopolymer with an overall PE volume fraction (including PE blocks of the diblock and PE homopolymer) of 65%. The sample was also shear-aligned and quenched in liquid nitrogen. Fig. 5a and b are images from two microtoming directions (perpendicular to the *x*- and *y*-directions as shown in Fig. 1. The sample was found to be predominantly lamellar, but small regions of co-existing cylinder morphology are visible in Fig. 5a. In these cylinder regions the PE is in the matrix phase, and randomly oriented, crystalline PE lamellae are visible. The darker regions in these two micrographs are heavily stained aPP, while the lighter regions contain both PE blocks from the copolymer and the PE homopolymer. The PE crystallites appear to once again be randomly oriented within the PE domains. This observation is also born out by electron diffraction (not shown) similar to Fig. 4.
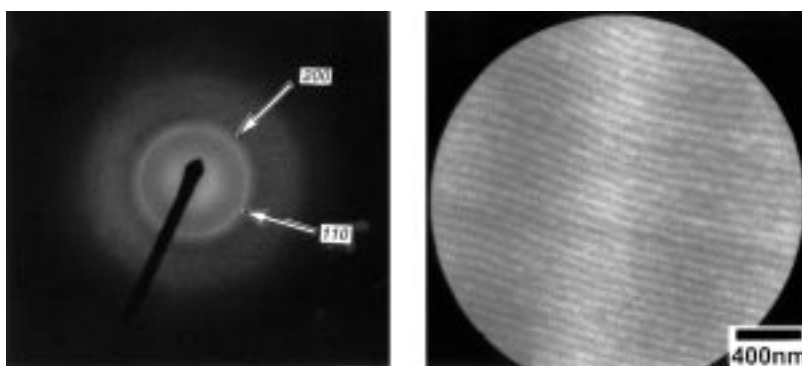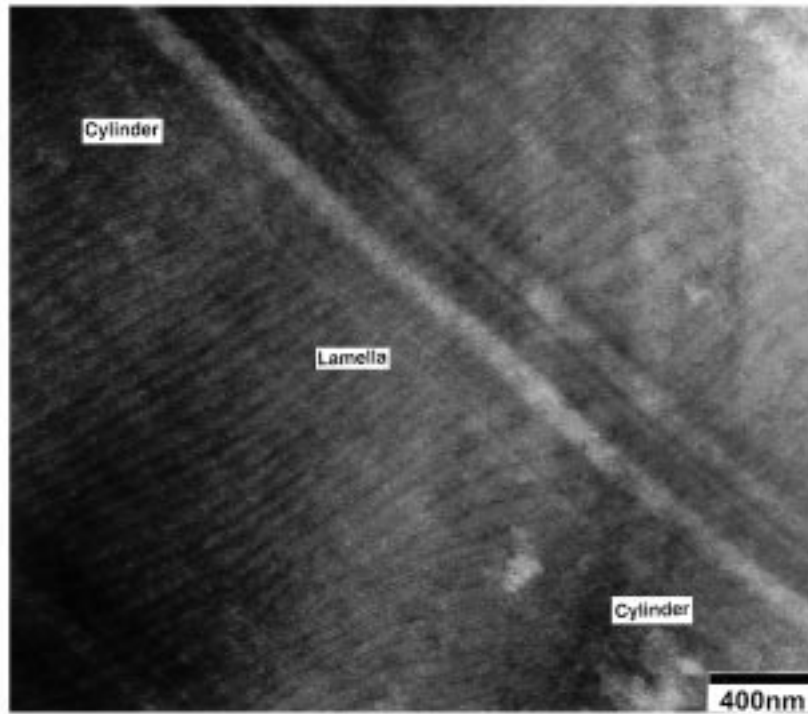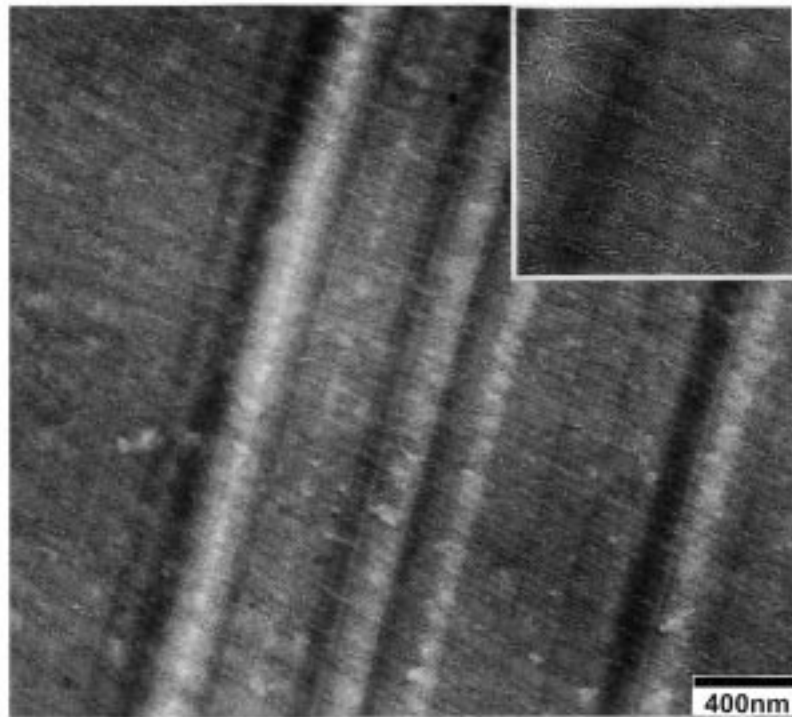

Fig. 4. Determination of the orientation of the PE crystalline chain within the microphase separated domains: (a) electron diffraction pattern of PE-*b*-aPP; (b) TEM micrograph of PE-*b*-aPP in selected area aperture.

(a)

(b)

Fig. 5. TEM micrographs of PE-*b*-aPP and PE homopolymer blend: (a) microtoming direction perpendicular to *y*-axis; (b) microtoming direction perpendicular to *x*-axis. The insets are enlarged regions.

Comparing Fig. 2 with Figs. 3 and 5, the polyethylene crystalline lamellae, as observed in the diblock copolymer and its blends, are much shorter (in dimension perpendicular to polyethylene chain stem) than those observed in homopolymer. This effect is clearly due to confinement of the PE crystallization within the nanometer scale microphase separated PE domains. Since the PE crystallites grow with random orientations, most orientations will allow them only a small amount of lateral growth space before they impinge on the boundaries with the aPP domains.

4. Conclusions

Our results demonstrate that by rapid quenching it is possible to preserve the morphology formed in the microphase separated block copolymer melt-state as the PE block crystallizes. This is the case even for blends with polyethylene as the major component. $RuCl_3$/NaClO provided excellent staining contrast for TEM imaging between aPP and PE microphase separated domains, and between amorphous PE and PE crystalline lamellae within the PE microphase separated domains. The contrast between amorphous PP and amorphous PE region is likely due to a difference in their tendency toward reaction with ruthenium reagent. aPP is more reactive as it has tertiary protons which are more easily abstracted. The contrast between crystalline PE and amorphous PE regions is due to a difference between the rates of transport of the ruthenium stain in amorphous and crystalline regions. Coupling electron diffraction with TEM imaging, it was demonstrated that the PE crystalline lamellae are randomly oriented within the PE microphase separated domains.

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