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Morphology of Block Polymers near a Free Surface

The microphase transition and morphology of block polymers have been the subject of extensive studies in recent years.[1-11] These studies have been concerned with the morphology of the microdomains in solutions[8,10,11] and solids[1-7,9] as a function of molecular parameters (such as molecular weight and chemical composition), polymer concentration, and temperature and also with microphase transitions (i.e., formation and dissolution of the microdomains) caused by changing temperature[7-9,12] and concentration.[8,10,11] Except for a few studies,[13,14] most of this work has been devoted to study the structure of block polymers in bulk but not near a free surface or interfaces with other materials.

In this report we present the morphology of the microdomains of an AB diblock polymer formed as a consequence of liquid–liquid microphase separation of the constituent polymer A and B at or near the air surface in contrast to the morphology in bulk. The morphology at the surface will be dramatically affected by the surface free energy (an additional physical factor which does not affect the morphology in bulk) and therefore be different from the morphology in bulk. It may be unnecessary to say that studies of the surface morphology of block polymers are of academic and practical importance in connection with biomedical science and applications such as in thromboresistance[15] and cell separation.[16]

A polystyrene–polyisoprene diblock polymer designated HY-12 was synthesized by living anionic polymerization at −78 °C using *sec*-butyllithium as the initiator and tetrahydrofuran as the solvent. The number-average molecular weight of the block polymer determined by osmometry was 5.24×10^5 and the weight fraction of the polystyrene component determined by elemental analysis was 52%. The film used in this study was prepared by casting a ca. 10 wt % solution of the block polymer in toluene in a petri dish and evaporating the solvent very gradually at 30 °C for a few days. After further drying under vacuum for several days, a film of 0.35-mm thickness was obtained. Test specimens 1 cm × 1 mm were cut from the film and stained overnight with osmium tetraoxide vapor. This process was necessary before embedding the specimens. Otherwise, the block polymer film would have been swollen by epoxy resin during the embedding process and the original structure would have been destroyed. The effectiveness of the structural fixation by osmium tetraoxide to prevent the swelling by epoxy resin was rigorously examined. Then the test specimens were embedded in epoxy resin.

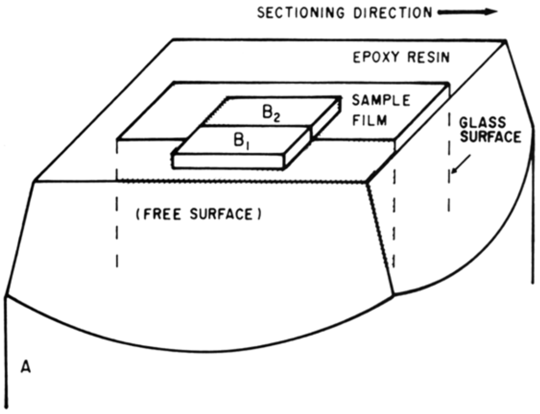

Figure 1. Schematic diagram representing the trimming method of specimen embedded in epoxy resin blocks.

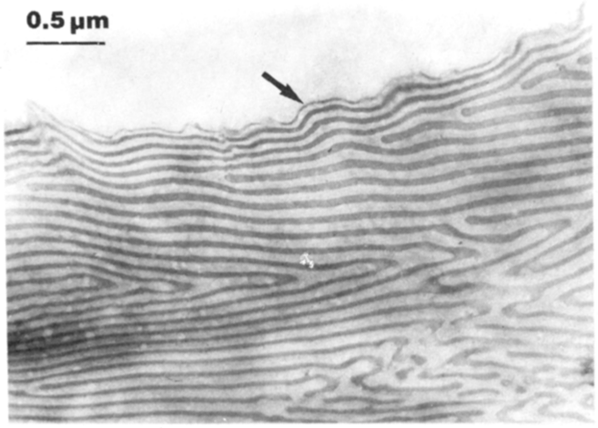

Figure 2. Electron micrograph showing a typical microdomain structure at the free surface of the HY-12 film. The lamellae are parallel to the surface. The arrow indicates the free surface.

Special care was taken to distinguish the two sample surfaces, i.e., the surfaces which contact air and glass. For this purpose, the solidified epoxy resin blocks A were trimmed into small blocks B composed of B_1 (solidified epoxy resin) and B_2 (block polymer specimen) in the way shown in Figure 1. The morphology of the specimen at a free surface can be studied by examining the morphology at and near the interface between B_1 and B_2. Other surfaces of the block B are nothing other than those of bulk epoxy resin and bulk specimen. In this way the free surface of the specimen can be definitely distinguished from the interface with the glass.

Ultrathin sections sliced normal to the film surface and of ca. 50-nm thickness were obtained from the trimmed blocks B using an LKB 4800A ultrotome. Transmission electron micrographs of the ultrathin sections were obtained with a Hitachi H-600S electron microscope. The free surface of the block polymer film was easily distinguished in the micrographs, because the thin sections are attached by the structureless epoxy resin. In this way one can investigate the morphology of the microdomains as a function of depth from the free surface in the plane normal to the film surface.

Figure 2 shows a typical cross section of the HY-12 film at and near the free surface. The top bright part of the micrograph without structure corresponds to that of epoxy resin and the bottom part with periodic dark and bright microdomains corresponds to that of HY-12. The alternating lamellar structures of polyisoprene (dark domains) and polystyrene microphases (bright domains) are more or less aligned with their interfaces parallel to the free surface of the film. In this micrograph the free surface, i.e., the interface between the specimen and air, is observed between the dark, thin polyisoprene layer (which is indicated by an arrow) and epoxy resin. In general, lamellar

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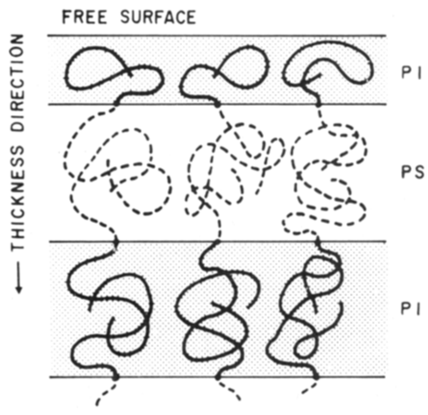

Figure 3. Schematic representation of placement of block polymer chains in the microdomains at the free surface of the film.

microdomains in polystyrene–polyisoprene block polymer film cast from solutions tend to align with their interfaces parallel to the film surfaces.[1] Small-angle X-ray scattering investigation of the HY-12 film, which will be described elsewhere,[17] revealed the same tendency. The electron micrographs of the HY-12 film showed that in most areas at the free surface the lamellae were parallel to the free surface of the film although the free surface of the film appeared somewhat rough. The free surface of the film is always covered with the dark polyisoprene layer, which is usually thinner than the corresponding inner polyisoprene domains, and there was no evidence for the existence of an additional polystyrene layer on the outermost polyisoprene layer. This may be explained by the schematic representation in Figure 3. The outermost layer must consist of a single layer of polyisoprene block chains since the polyisoprene chain ends represented by the chemical junctions to polystyrene chains cannot emerge from the air interface, while the inner layers are composed of bimolecular layers since the block chains can emerge from the two opposing interfaces of the domains. Therefore the thickness of the outermost layer will be approximately half that of the inner domains if the density of the layer and the domains and the average distances between adjacent chemical junctions along the interfaces remain unaffected. The conformation of the polyisoprene block chains in the outermost layer should be considerably perturbed in comparison with that of the polyisoprene block chains in the polyisoprene microphases far from the interface because of the effect of surface tension.

In some areas at the free surface of the HY-12 film lamellae with their interfaces normal to the free surface were occasionally observed (Figure 4). Even in such a case, the free surface was covered with the polyisoprene layer and the exposure of alternating polyisoprene and polystyrene microphases to the free surface was never observed. Again the thickness of the outermost polyisoprene layer is approximately half that of the corresponding inner microdomains. Thus the electron microscopic investigation of the free surface of the polystyrene–polyisoprene block polymer revealed that the free surface is preferentially covered with the polyisoprene phase regardless of the orientation of the microdomains. This is quite reasonable because it conforms to the thermodynamical requirement of lowest surface free energy. The reported values[18] of critical surface tension for polyisoprene, 30–32 (mN m^{-1}), are smaller than those typical for polystyrene, 33–36 (mN m^{-1}), although smaller values also have been reported for the latter. Therefore the free energy of the free surface composed of polyisoprene must be smaller than that composed of polystyrene.

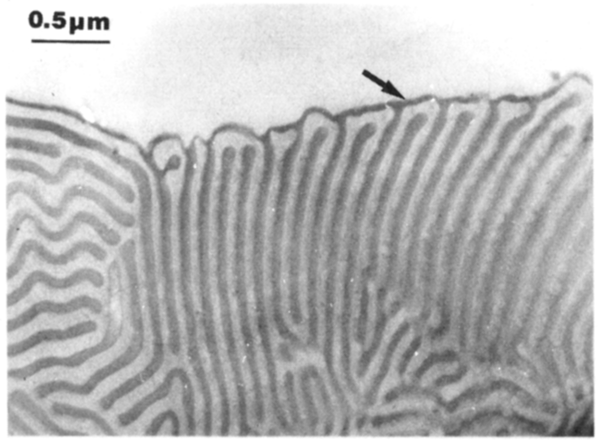

Figure 4. Electron micrograph of the lamellae with their interfaces normal to the free surface of the film. The arrow indicates the free surface.

We have obtained similar results for polystyrene–polyisoprene block polymers of morphologies other than lamellar microdomains. Even for block polymers with spherical polyisoprene domains in a polystyrene matrix, the free surfaces of the films are covered with a polyisoprene layer. A paper on the detailed analysis of the surface morphology of the block polymers is in preparation. Surface morphology analysis of other types of block and graft polymers and polymer blends, including those for biomedical use, is also going on in our laboratory.

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