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Spatial Organization of Polymer Chains in a Crystallizable Diblock Copolymer of Polyethylene and Polystyrene

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Introduction

A recent publication[1] contained evidence that the crystallizable sequences of a polyethylene-*co*-butylene/polyethylethylene block copolymer (EBEE) organize in the bulk material below the melting point such that the chain direction (*c*-axis) is parallel to the lamellar surface. Because the crystallizable sequences were obtained by hydrogenating polybutadiene precursor blocks which contained about 10% vinyl repeat units, the resulting polyethylene-*co*-butylene contained 2–3 ethyl side branches per 100 carbon atoms. Although arguments were presented[1] to attribute the unusual chain alignment to interface-induced nucleation and crystallization facilitated by the heterogeneous lamellar structure present in the block copolymer melt phase, it remained possible that accommodation of the occasional ethyl branches was in some way responsible for the observed molecular alignment. In the present note we report on our finding regarding the spatial organization of the crystallizable sequences in a specially prepared block copolymer of polyethylene and polystyrene (ES) in which the frequency of ethyl side branches is essentially reduced to zero.

Synthesis and Molecular Characterization

The ES copolymer was synthesized by a transformation reaction in which a living anionic polymer (first block) is used as the alkylating agent in the production of a Ziegler–Natta catalyst which is used to synthesize the second block. Although only about one-third of the first block is expected[2] to be incorporated into the diblock, reasonable amounts of the desired semicrystalline block copolymer can be separated from the reactor products. A detailed description of this methodology has been reported earlier[2] for the case of polybutadiene/isotactic polypropylene diblock copolymers.

The reactor is filled with purified cyclohexane, pressurized to 1.2 atm with purified argon and brought to 50 °C. A calculated amount of *n*-butyllithium in hexane is added, followed by a small portion (5%) of the calculated amount of purified styrene monomer. After about 10 min the remainder of styrene is added. This procedure is employed to minimize molecular weight broadening since no polar modifiers can be used. The conversion of the styrene monomer is estimated from known kinetic expressions as well as followed by GPC. Upon reaching 100% conversion of styrene, a small amount of butadiene monomer is added (4–5 equiv) to the living ends. At this point the reaction is cooled to 0–5 °C, the system is partially evacuated, and a calculated amount of $TiCl_4$ is added to give a Li/Ti molar ratio of 2.25. The system is allowed to "age" at this temperature for 20 min at which time purified ethylene gas is bubbled in to achieve a pressure of 1.2 atm. The reaction is then run at constant pressure for 6 h, terminated by addition of purified, degassed methanol containing 5% HCl by volume. The polystyrene–polyethylene product is insoluble in the reaction medium and is removed by filtration and washed twice with pure cyclohexane in a blender and then twice with 2-propanol before being vacuum dried and subjected to a variety of characterizations. Based on the combined evidence from ambient GPC and high-temperature GPC, IR, DSC and material balances, the ES diblock has the following characteristics: polystyrene block M = 70 000 g/mol; polyethylene block M = 60 000 g/mol; diblock polydispersity, $M_w/M_n = 1.8$; $T_g(S) = 98$ °C and $T_m(E) = 140$ °C; degree of crystallinity of the E block ~85%.

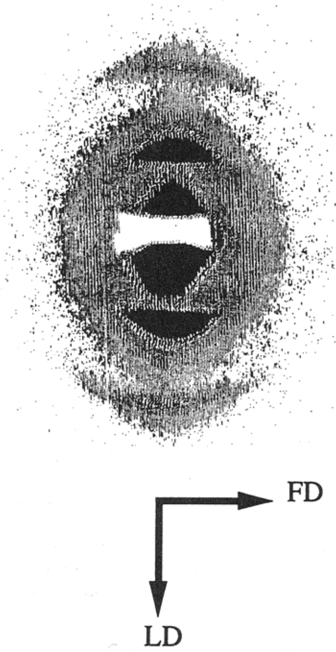

Figure 1. SAXS pattern observed when the compressed and annealed specimen was irradiated along the lateral constraint direction of the channel die. The lamellar repeat spacing is 275 Å. Reference 4 provides details of the SAXS equipment.

Spatial Organization of the E Chains

As in previous work[1] we use a combination of small angle X-ray scattering (SAXS) and wide angle X-ray pole figure analysis (WAXS pole figures) to obtain the orientation of the lamellar long period structure and the orientation of the polyethylene unit cell, all relative to the macroscopic boundaries of our specimens. In the past we have used combinations of high-temperature centrifugal solvent casting and mechanical manipulation to obtain suitable specimens.[1] Here we have employed a thermomechanical processing method, a channel die[3] operation, to produce our specimens. Briefly the temperature controlled channel die provides a state of plane strain compression which orients the heterogeneous lamellar block copolymer melt at 175 °C; the temperature is then lowered through the melting point so that crystallization occurs in the presence of the oriented lamellar structure. Postcrystallization annealing protocols can be carried out if desired while the specimen remains confined in the channel die.

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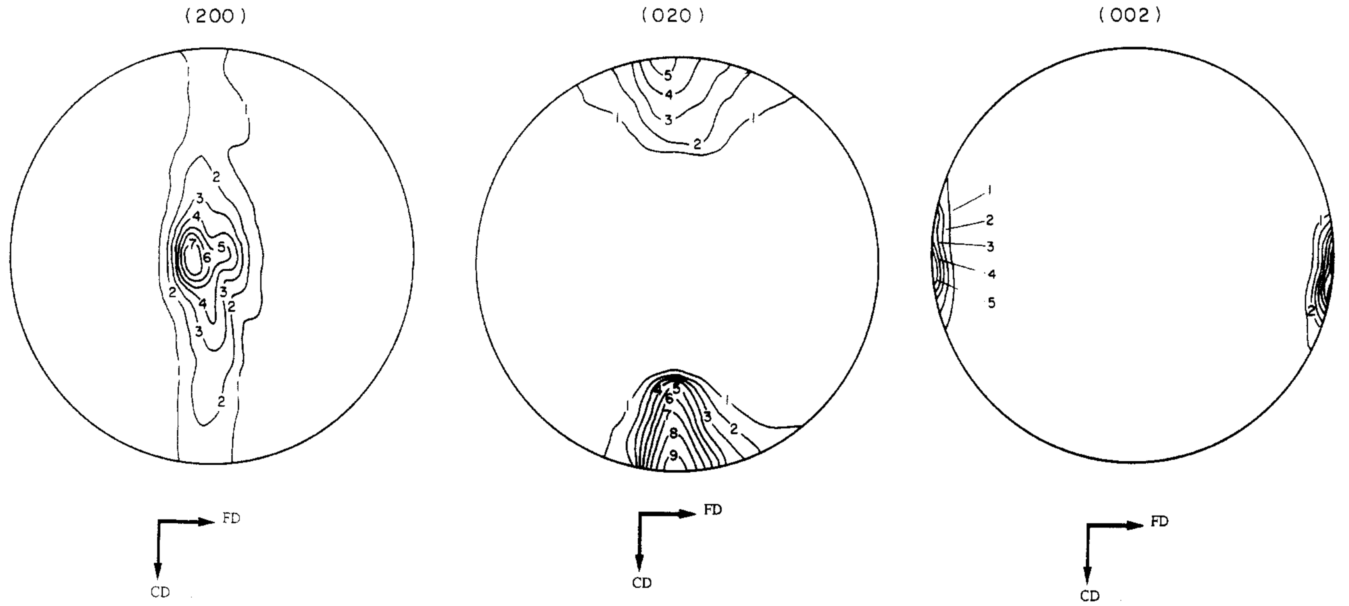

Figure 2. WAXS pole figures of a specimen processed at 175 °C and annealed at 180 °C for 6 h. Directions FD and CD represent the flow and constraint axes of the channel die so that the pole figures are viewed along the direction of compressive load. References 1 and 3 provide details of the WAXS pole figure apparatus.

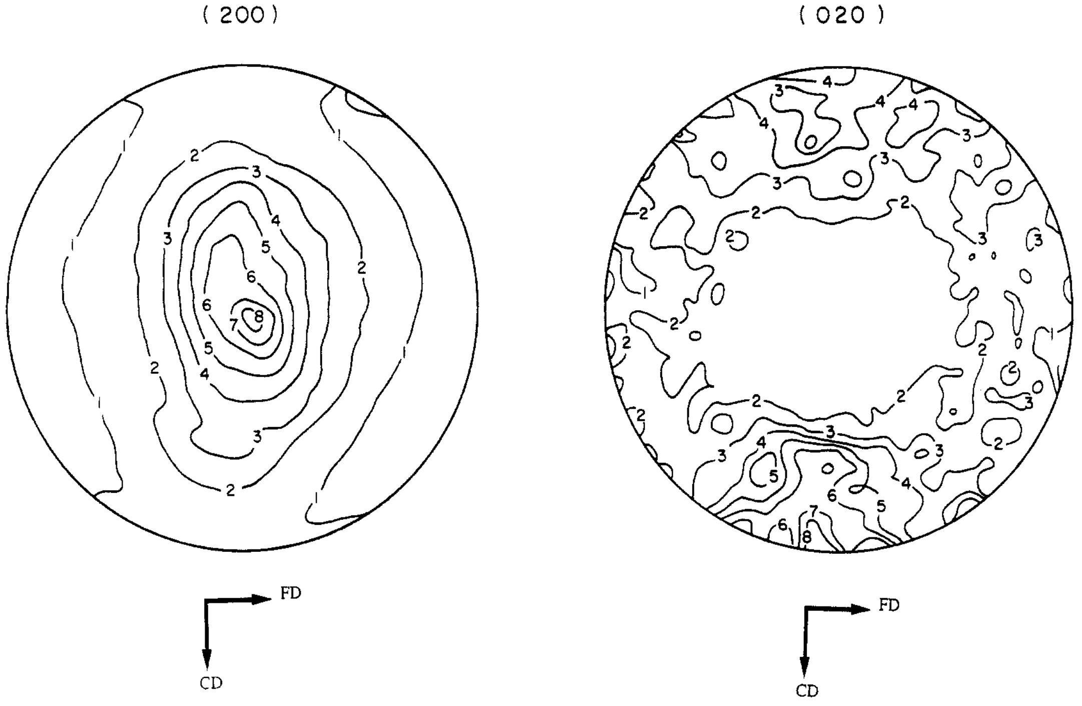

Figure 3. WAXS pole figures for a specimen processed at 175 °C and annealed at 180 °C for 36 h.

Figures 1–3 summarize our findings. The SAXS pattern[4] of Figure 1 was obtained on a channel-die compressed specimen processed at 175 °C and cooled as described above and then annealed in vacuo while under constraint in the channel die at 180 °C for 36 h and cooled over a period of several hours to room temperature. The view shown in Figure 1 is for the case of irradiation perpendicular to the sides of the channel die, i.e. looking along the lateral constraint direction (CD); a similar SAXS pattern is obtained for irradiation in the flow direction (FD). There is no discernible SAXS pattern when the specimen is irradiated in the direction of the compressive load (LD). Thus the lamellar morphology of the block copolymer is oriented such that the lamellar normals are parallel to LD, i.e. the lamellae lie in the FD–CD planes.

Figures 2 and 3 show WAXS pole figures[3] for two different specimens. In Figure 2, the specimen was processed in the channel die and postannealed at 180 °C for 6 h. The specimen for Figure 3 was the same one used for the SAXS analysis discussed above; it was annealed at 180 °C for 36 h. Channel die processed, but otherwise unannealed, specimens exhibited a quasi-single-crystal texture in which the polyethylene (200), (020), and (002) plane normals were tightly aligned with the LD, CD, and FD direction, respectively. Annealing disrupts this quasi-single-crystal crystallographic texture starting (Figure 2) with a noticeable broadening of the b plane pole figure at 6 h of annealing and ending (Figure 3) with a material in while the b axis becomes randomly oriented in the FD-CD plane (which from SAXS is the plane of the lamellae). Figure 3 shows clearly that the *a* axis remains rather well oriented along LD. Thus the *c* axis always lies in the plane of the lamellae. Immediately following channel die processing it is directed along FD and eventually with annealing it becomes randomly oriented around the *a* axis so that it points in all directions in the FD–CD plane with

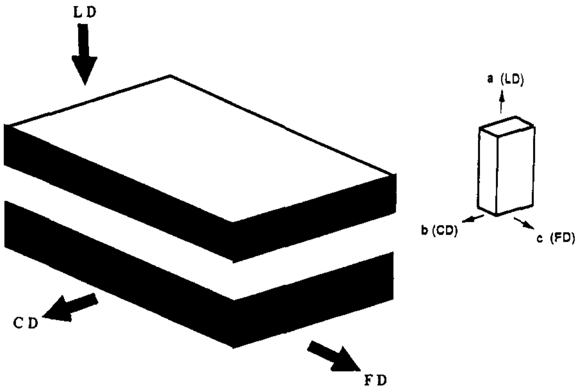

Figure 4. Schematic representation of the morphological and unit cell orientations which are indicated by the SAXS and WAXS results. The unit cell orientation shown (*c*-axis along FD) is observed for specimens taken directly from the channel die. Annealing in the heterogeneous melt and subsequent crystallization leads to a randomization of the direction of the *b* and *c* axes in the LD–CD plane (cf. Figure 3).

essentially equal probability. This structure, the combination of Figures 1 and 3, in which the *a* axis is aligned with the lamellar normals and the *b*, *c* axes lie with random orientation in the plane perpendicular to the lamellar normals, is identical to that found earlier for the EBEE diblock copolymers;[1] a schematic representation is shown in Figure 4.

Conclusion

Channel die compression has been used successfully to orient the lamellar morphology of a polyethylene/polystyrene diblock copolymer. The lamellar orientation is retained when specimens are annealed under constraint at temperatures well above the melting point of the polyethylene crystals. Slow cooling to room temperature then provides a means for crystallizing the polyethylene chains in the presence of a preexisting lamellar morphology.

The SAXS and WAXS results presented here completely corroborate earlier findings[1] which showed that the polyethylene chain direction (*c* axis) is parallel to the lamellae (i.e. perpendicular to the lamellar normals) of the block copolymer morphology. The present results effectively eliminate the occasional occurrence of short-chain branches as the cause of this unusual orientation, and support the conclusion that the interfaces present in the heterogeneous block copolymer melt facilitate the observed chain organization in these materials. We are currently examining block copolymers which contain crystallizable sequences other than polyethylene to determine the extent to which this crystallization behavior is general.

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References and Notes

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