The Influence of Melt Processing on the Spatial Organization of Polymer Chains in a Crystallizable Diblock Copolymer of Nylon 6 and PDMS

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ABSTRACT: Crystallized chains of nylon 6 lie parallel to the interfaces of the microphase-separated morphology of a nylon 6/PDMS diblock copolymer. Orienting the morphology in the melt using plane strain compression enabled the nylon chain direction to be determined through a combination of transmission electron microscopy, small-angle X-ray scattering and wide-angle X-ray scattering pole figure analysis. Processing at temperatures above the nylon 6 melting point serves to orient the microphase-separated morphology of the melt; the nylon 6 chain orientations are then largely dictated by thermodynamic considerations that apply to chains crystallizing within the confines of a microphase separated melt. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1985–1990, 1998

Key words: nylon 6; melt processing; polymer chain orientation

INTRODUCTION

There has been considerable interest in the variety of morphological arrangements that can result from the processing of microphase-separated block copolymer melts in various flow patterns. Winey and coworkers have discussed the parallel, perpendicular, and other more complex orientations that are achievable for the case of lamellar systems.¹ For cases in which the constituent blocks are amorphous, the main focus has been on process-induced orientation of the microphaseseparated morphology, with some attention given to amorphous orientation of the copolymer chains.² We have demonstrated in the past that postprocessing crystallization of one of the blocks can facilitate inquiry into the nature of chain organization within the oriented microphase-separated morphologies.³ We have been successful in demonstrating⁴ that a part of the observed chain orientation in these systems is induced by the melt flow process, and that this kinetically controlled orientation can be eliminated, for example, by appropriate annealing protocols; certain equilibrium constraints on chain organization also exist, and these appear to be imposed by the existence of the stable, oriented microphase-separated morphology itself.

Block copolymers with at least one crystallizable moiety have been known and studied since

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the 1960s.⁵ In the 1980s several theories were proposed to describe the essential features of the expected equilibrium morphologies of semicrystalline diblocks.^{6,7} In these theories, an underlying premise is that the crystallizable chains are expected to fold at the block copolymer interfaces, leaving the chain axes essentially perpendicular to these interfaces. The major predictions of these theories are scaling laws for the morphological periodicity in terms of the chain length of the crystallizable and amorphous blocks of the copolymers. Although small-angle X-ray scattering observations in the early 1990s in our laboratory⁸ clearly verified the essential features of these scaling laws, wide-angle X-ray pole figures indicated equally clearly that the chain orientation of the semicrystalline block was entirely opposite to expectation. The chains crystallize in a way that leaves the chain axes parallel to the block copolymer interfaces when crystallization occurs after microphase separation.^{4,9} Findings in other groups^{10,11} have verified our early observations regarding the unexpected parallel chain orientation.

We attributed⁹ the occurrence of the parallel chain orientation to the presence of the preexisting interfaces and the very small lamellar thicknesses that are present in the ordered block copolymer melt above T_m . This reasoning is consistent with recent work of Pickett and Balazs,¹² who calculate a reduction in free energy when block copolymer chains are stretched out along an impenetrable neutral surface. Accordingly, a crystallizable homopolymer would also be expected to exhibit unusual parallel chain orientation if crystallization were confined to ultrathin layers approaching the dimensions of block copolymer domains; this observation has been recently documented in our laboratory for the case of a polyamide homopolymer crystallized between rubbery confining plates¹³ and for polyethylene crystallized against various rubbery and inorganic substrates.¹⁴ Crystallization of a block copolymer from a homogeneous melt or crystallization of a block copolymer for which spherulite nucleation and growth govern the final morphology should lead to the more conventional perpendicular chain orientation. These situations have also been documented in the literature.^{15,16}

In the present article we report our findings concerning the orientation of nylon 6 chains relative to the microphase separated morphology of a nylon 6/polydimethylsiloxane diblock copolymer. The copolymer was processed as a mi-

CHANNEL DIE COMPRESSION

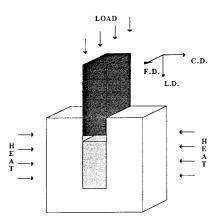


Figure 1 Schematic of the channel die used to process the copolymer melt in plane strain compression.¹⁹

crophase-separated melt¹⁷ at temperatures above the nylon 6 melting point, and its morphological and molecular organization was characterized at room temperature following crystallization of the nylon chains.

EXPERIMENTAL

The nylon 6/PDMS diblock copolymer was synthesized, purified, and characterized according to procedures reported previously.^{17,18} The block molecular weights were 15.2 kg/mol for PDMS and 39.1 for nylon 6, leading to a volume percentage of about 36% PDMS. Differential scanning calorimetry revealed a nylon 6 melting point near 220°C, a suggestion of a PDMS T_g below -100°C, and two thermal history-dependent melting transitions for PDMS near -50 and -40°C.¹⁷

The block copolymer was melt processed in plane strain compression to produce an oriented heterogeneous morphology within which the nylon crystallization could take place. This step was accomplished by compressing a premolded billet of the material in a heated channel die device, described in detail in earlier publications from our laboratory¹⁹ and shown schematically in Figure 1. The compression ratio of 6 was imposed at 265°C, and then the entire assembly was cooled slowly to room temperature over a period of several hours, while maintaining the geometric constraints on the specimen.

Transmission electron microscopy of ultramicrotomed specimens was carried out on a Jeol

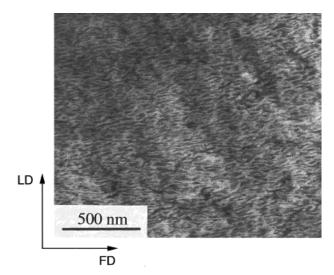


Figure 2 Transmission electron micrograph showing the block copolymer morphology viewed along the lateral constraint direction of the channel die. Dark regions are PDMS.²⁰

200CX microscope using procedures similar to those followed in previous work²⁰ on the nylon 6/PDMS system. Small-angle X-ray scattering measurements were conducted using a Siemens 2-D detector, and WAXS pole figures were generated using a Rigaku rotating anode point source instrument operating at 50 kV and 60 mA. More experimental details can be obtained elsewhere.^{17,19}

RESULTS AND DISCUSSION

Solution-cast films of nylon/PDMS diblock copolymers present a variety of morphologies, depending on the solvent and thermal history used in the casting procedures.^{17,20} The compression-molded/ channel die-compressed specimens examined in the present study showed the oriented morphology of Figure 2. Based on a set of micrographs taken from views along the lateral constraint direction of the channel die and along the flow direction, the best description of the morphology is a collection of flattened platelets (interrupted lamellae) of PDMS of about 100–200 Å thick, with top and bottom surfaces perpendicular to the loading direction (LD) of the channel die process. These PDMS platelets are intermittently interrupted by regions of nylon along the flow direction (FD), as seen in Figure 2, and along the lateral constraint direction (CD). Along the loading direction there is a clearly recognizable regular layerlike alternation of nylon and PDMS with a long period of about 300 Å, as seen in Figure 2.

Small-angle X-ray scattering analysis supports the above interpretation of the block copolymer morphology and provides some information on the semicrystalline organization of the nylon portion of the material. Figure 3 is a two-dimensional SAXS scattering pattern obtained when the incident X-rays are directed along the constraint direction (CD). In Figure 3 there are two distinct spots above and below the beam stop, along the loading direction; these diffraction maxima correspond to a long-period spacing of about 550 Å. larger than but consistent with the morphological periodicity revealed in the micrograph of Figure 2. As expected, the overall layered morphology of the block copolymer is also revealed in SAXS data obtained with the X-ray beam directed along the flow direction. Figure 4 shows the two spots above and below the beam stop, here corresponding to a spacing of about 600 Å. We are accustomed to observing larger characteristic dimensions in SAXS than in TEM, particularly when there is a broad distribution of morphological spacings such as observed in Figure 2. SAXS is known to report a higher moment of the distribution of distances,

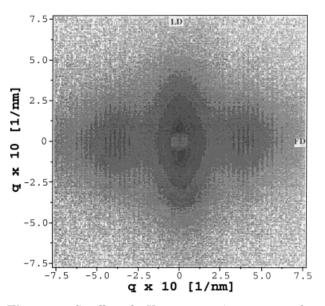


Figure 3 Small-angle X-ray scattering pattern obtained when the incident beam is directed along CD. The spots above and below the beamstop correspond to the morphological periodicity seen in the TEM of Figure 1, while the spots left and right provide information on the (smaller) Nylon 6 semicrystalline lamellar periodicity not observable in the TEM.

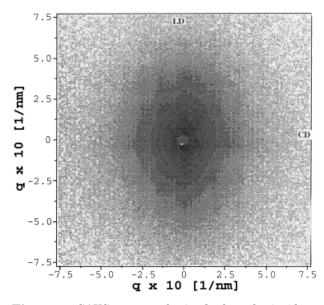


Figure 4 SAXS pattern obtained when the incident beam is directed along FD. Here only the morphological periodicity is observed in the two spots above and below the beam stop.

thereby accounting for the larger value of a single reported length scale in the SAXS measurement.

The two maxima located left and right of the beam stop in Figure 3 correspond to a characteristic spacing of about 150 Å along the flow direction. This same set of spots, along FD, is also observed when the specimen is illuminated with the X-ray beam parallel to the loading direction. This 150 Å spacing is associated with the crystalline/amorphous long period of the nylon region of the block copolymer. Thus, the nylon regions of the crystallized block copolymer contain a much smaller repeating long period compared to the length scale of the microphase-separated morphology in which the crystallization takes place. This semicrystalline periodic structure is oriented orthogonal to the larger periodic structure associated with microphase separation.

TEM and SAXS results indicate that the plane strain compression of the nylon/PDMS block copolymer melt produces an ordered morphology in which the nylon crystallization takes place. To understand how the nylon chains organize when crystallization occurs within this preexisting block copolymer morphology, we carried out wideangle X-ray scattering pole figure analysis of the crystallized material. Figure 5 is a pole figure of the (002) plane, of the monoclinic unit cell characteristic of the alpha form of the nylon 6 crystal.

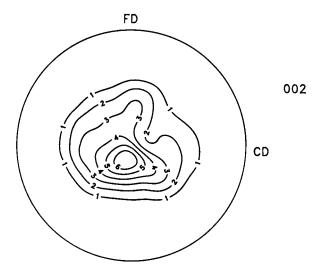


Figure 5 Pole figure of the (002) plane normals of the monoclinic alpha phase nylon 6 unit cell. The (002) poles are well oriented along LD, indicating that the (002) plane lies in the FD-CD plane of the channel die-processed sample.

Poles of the (002) plane are well oriented along the loading direction, indicating that the (002) planes lie in to the FD-CD plane of the specimen, perpendicular to the loading direction. The (002) plane of nylon 6 is known to contain the nylon chains, hydrogen bonded into well-organized sheets. Thus, Figure 5, along with the morpholog-

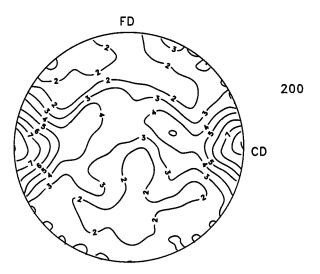


Figure 6 Pole figure of the (200) plane normals for nylon 6, showing a preference for the (200) planes to lie with their normals oriented toward CD. The 22.5° tilt of the (200) plane relative to the FD-CD plane accounts for some of the breadth of orientation seen in the pole figure.

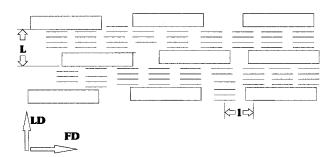


Figure 7 Schematic representation of the morphological and molecular level organization in the channel die-processed nylon 6/PDMS diblock copolymer. L represents the 300–600 Å length scale of the block copolymer morphology and 1 indicates the 150 Å lamellar repeat spacing in the semicrystalline nylon 6 regions. The crystallized chains lie parallel to the major surfaces of the flat, interrupted lamellar regions of PDMS. Amorphous nylon and PDMS chain segments are not represented.

ical information presented above, is sufficient to demonstrate that the nylon chains lie parallel to the top and bottom surfaces of the PDMS domains. The (200) pole figure of Figure 6 reveals a preferred orientation of the (200) plane normals toward the constraint direction (CD) and clearly away from the flow direction (FD). Figures 5 and 6 taken together indicate that the chain direction is parallel to FD, i.e., along the direction of flow out of the channel die.

A cartoon depicting a constraint-direction view of the elucidated structure of the nylon/PDMS block copolymer is presented in Figure 7. The PDMS domains are aligned by the melt processing in the channel die, and during cooling the nylon chains crystallize with their axes lying parallel to the PDMS surfaces. In the course of this crystallization, amorphous regions of nylon 6 are generated; this crystalline/amorphous periodicity was readily seen in the CD view (Fig. 3) and LD view SAXS patterns. The crystalline/amorphous periodicity (1) lies orthogonal to the morphological long period (L), which repeats along the loading direction. The crystallized chains in this nylon 6/PDMS copolymer sample lie parallel to the PDMS surfaces and perpendicular to the crystalline/amorphous interfaces contained within the nylon 6 region of the copolymer. In this sense, the ordered melt morphology of the copolymer serves as a directional template for conventional crystallization of the nylon 6 chains. An unanswered question concerns the preference for the semicrystalline periodicity of the nylon 6 to repeat selectively along FD, rather than with planar isotropy within the CD-FD plane, as observed in previous studies of polyethylene-containing diblocks.^{4,9} Significant differences from polyethylene arise in the monoclinic nature of the nylon unit cell and the tendency to form hydrogen bonded sheets within its crystal structure. These two structural features may account for the resistance to inplane randomization upon slow cooling or annealing for the case of the nylon 6/PDMS diblock copolymer examined here.

CONCLUSION

The parallel orientation (chains lying parallel to block copolymer interfaces) of crystallized chains was observed in a nylon 6/PDMS block copolymer, which had been subjected to plane strain compression orientation in the melt. This result serves to generalize this unusual spatial organization of crystallized chains in block copolymers to systems beyond those containing polyethylene as the crystallizable block. In addition to the morphological long period, SAXS results revealed a crystalline/amorphous spacing oriented perpendicular to the copolymer morphology.

The parallel orientation of crystallized chains in semicrystalline block copolymers is an important consideration in the mechanical performance of these materials. For example, the mechanism of chain slip on the (002) plane will be facilitated by any mechanical loading pattern that tends to shear the block copolymer structure. The (002) chain slip mechanism has a plastic resistance which is about 35% smaller²¹ than any other crystalline deformation mode in nylon 6. Similar considerations of facilitated shear associated with preferred chain slip apply to the case of the polyethylene containing block copolymers studied earlier.^{3,4,8,9}

An essential consideration is the fact that semicrystalline block copolymers that crystallize from a heterogeneous melt must be viewed as a material with a preferred crystallographic texture. This texture is intimately connected to the orientation of the ordered block copolymer morphology. This complex interplay between copolymer morphology and crystallographic order should be considered carefully when attempts are made to interpret and exploit properties and processing characteristics of semicrystalline block copolymers. This research was supported in part by the National Science Foundation, Division of Materials MRSEC Program through the MIT Center for Materials Science and Engineering (DMR 94-00334).

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