


**Experiment title:**

Crystallization of Molecular Brushes with Block Copolymer Side Chains

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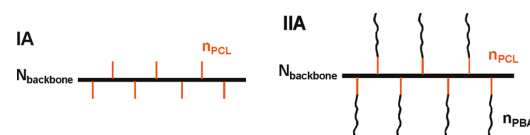
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**Report:**

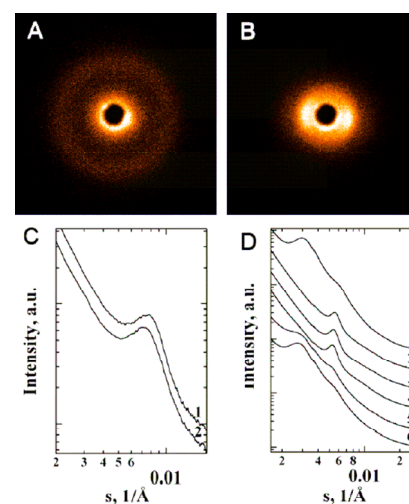
Because of the large size and chainlike nature of polymer molecules, morphology of semicrystalline polymers is kinetically controlled. One of the general strategies to manage the molecular packing is to introduce spatial constraints. A perspective way to confine polymer chains is to exploit the microphase separation of block copolymers,<sup>1</sup> which inherently provides nanometer-sized domains of crystalline blocks imbedded into a matrix of the amorphous block. An interesting example of such phase-separated system is the molecular brushes with diblock copolymer side chains that result in a core-shell molecular structure possessing a crystallizable core and an amorphous corona.<sup>2</sup> In contrast to linear block-copolymers, the brush molecules intrinsically prefer a cylindrical shape stabilized by the steric repulsion between densely-grafted side chains.<sup>3,4</sup> Moreover, the brush-like architecture imposes an additional constraint to the crystalline block due to its covalent linkage to the backbone. In this work, the crystallization behavior of densely-grafted brushes ( $N_{bb}=450$ ) with semicrystalline poly( $\epsilon$ -caprolactone) monoblock (PCL,  $n_{PCL}=48$ ) side chains (sample IA) and with diblock copolymer side chains composed of PCL and an amorphous poly( $n$ -butyl acrylate) (PBA,  $n_{PBA}=110$ ) block (sample IIA) was studied (Figure 1).

The details of the synthesis procedures have been discussed in an earlier publication.<sup>2</sup> For X-ray scattering measurements, oriented fibers of 0.5 mm thickness were prepared by extruding the polymer rapidly cooled from the melt to room temperature using a home-made mini-extruder. SAXS experiments were performed using 2D gas detector with sample-detector distance of 3 m. The sample temperature was controlled with a Linkam heating stage.

A time- and temperature-resolved SAXS technique has been applied to monitor folding of PCL chains during crystallization and orientation of PCL chains. The 2D SAXS



**Fig.1.** Scheme of the brushes chemical structure



**Fig.2.** 2D SAXS patterns corresponding to fibers of IA (A) and IIA (B) measured at 25°C. The fiber axis is vertical. (C) SAXS curves of IA measured at 25°C on an “old fiber” (1) and on a “fresh fiber” (2); (D) SAXS curves of IIA measured at 25°C on an “old fiber” (1), in the melt at 70°C (2) and after different annealing times at 25°C (0min-3, 140 min- 4, 450 min- 5, 1200 min- 6).

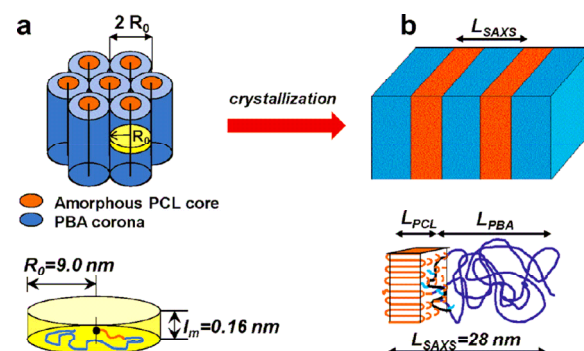
patterns of IA and IIA are presented in Figure 2. In the case of IA, only the peak attributed to the semicrystalline structure of PCL is present at room temperature. This peak vanished upon heating to 70°C but rapidly reappeared upon cooling to room temperature (Figure 2C). The long period (lamellar domain thickness) for IA is determined to be  $L_B=12$  nm, which is significantly shorter than the contour length of the PCL block ( $L_{PCL}=42$  nm). This implies that the PCL side-chains in the fiber are folded upon crystallization. For the IIA fiber, the transformation of the freshly prepared fiber from an initially microphase separated morphology into a morphology controlled by PCL crystallization was observed (Figure 2B, 2D). Immediately after quenching, the freshly-prepared IIA fiber only had a peak with a characteristic spacing (domain size) of  $L_a=19$  nm. Since the quenched sample is purely amorphous, this SAXS peak is attributed to microphase separation of the block copolymer side chains. The copolymer peak broadens and completely vanishes with annealing time at room temperature, and then the second peak at  $L_{SAXS}=28$  nm appears after several hours at room temperature. The development of the second peak at the expense of the first one testifies that the crystallization process disrupts the initial block copolymer morphology.

An important determination from the 2D SAXS patterns in Figure 2B is that the crystalline PCL lamellae are oriented parallel to the fiber axis, i.e. the backbone direction with the PCL chains aligned is perpendicular to the drawing axis. This follows from the relative positions of the SAXS peak of the semicrystalline structure and the strong (110) peak of the PCL lattice on WAXS patterns.<sup>5</sup>

The molecular dimensions obtained from SAXS/WAXS data can be used to calculate molecular packing models for the microphase separated structure and the morphology after PCL crystallization. The molecular packing of IIA prior to PCL crystallization in bulk material can be modeled as a cylinder, composed of microphase separated random coils with a PCL core and a PBA corona (Figure 3A). Each side chain is a disc with radius  $R_0$  in a cylinder with a diameter of  $2R_0$ . The height of each disc equals to the measured length per monomer unit of the brushes in bulk samples,  $l_m=L_n/N_{bb}=0.16\pm0.01$  nm. The volume of each disc is  $V_{SC}=42$  nm<sup>3</sup>. Using this information, the disc diameter is calculated to be  $2R_0=18.2\pm1.0$  nm, which is in agreement with the SAXS characteristic distance of  $L_a=19$  nm for the copolymer structure prior to crystallization.

Crystallization of the PCL block is evidenced by the development of the second peak at  $L_{SAXS}=28$  nm (Fig. 2D). As shown in Figure 3B, this spacing is attributed to the long period of alternating crystalline and amorphous layers. The PCL thickness  $l_{PCL}=5.3$  nm calculated from volume fractions of PCL and PBA blocks is less than the PCL lamella thickness  $l=8$  nm measured for linear PCL chains<sup>6</sup> and suggests that the amorphous PBA block controls folding of the PCL block. As shown in Figure 3B, the crystallinity of PCL in the brush has to be reduced as compared to linear chains due to steric hindrances imposed by the branching points. The PCL sequences close to the main backbone cannot be easily accommodated in the PCL lamellae because of the incommensurability of the distance between the branching points and the length of folds. As for the PBA chains, given that  $l_{PBA}=22.7$  nm, the chains are thought to be coiled and interdigitated with neighboring PBA blocks.

In conclusion, the results of the work show that the specific architecture of the molecular brushes results in crystallization process different from both linear block-copolymers and main-chain columnar liquid crystals. The observed mechanism of the crystallization templating can prove useful information in designing complex nano-structured materials. The recent work was described in details in our publication<sup>5</sup>.



**Fig.3.** Molecular packing in thick films and bulk IIA (A) before and (B) after crystallization of the PCL core.

## References

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