Crystallization Kinetics of Poly(ε-caprolactone) Blocks Confined in Cylindrical Microdomain Structures: Effects of Confinement Size and Molecular Weight

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1 Introduction

The crystallization of polymer chains confined in various nanodomains has been attracting much attention because they show unique crystallization behaviour and crystal orientation [1,2]. Several experimental studies are reported on the crystallization of confined blocks as a function of nanodomain size d, where changing d requires a change in the molecular weight of crystalline blocks M_n as long as neat diblock copolymers are used. Therefore, the crystallization of confined blocks might be affected by the combined effects of d and M_n. It is an alternative method for changing d to blend a small amount of miscible oligomers into block copolymers.

We investigate here the crystallization rate of block chains with a constant M_n confined in the cylindrical microdomain structure (nanocylinder) as a function of its diameter D, which can be achieved by gradual blending of amorphous oligomers into block copolymers (Figs. 1a and 1b). Next, we examine the crystallization rate of slightly longer blocks confined in nanocylinders using the same method (1c and 1d) to compare the crystallization rate of block chains with different M_n both confined in the nanocylinder with the same D (1a and 1d).

2 Experiment

The crystalline-amorphous diblock copolymers used are

Table Characterization of the samples used in this study.

Sample Code	M_n (g/mol)			M_w/M_n	f_{PCL}	D (nm)
	PCL Block	PS Block	Total			
CS1	13,900	26,200	40,100	1.03	0.345	19.8
CS2	14,100	33,000	47,100	1.03	0.297	19.8
CS3	14,200	46,200	60,400	1.04	0.233	18.6
CS4	15,800	39,900	55,700	1.04	0.282	20.6
PSO	-	1,800	1,800	1.09	-	-

poly(ε-caprolactone)-*block*-polystyrene (PCL-*b*-PS). The volume fraction of PCL blocks f_{PCL} was adjusted so as to form the nanocylinder with the PS matrix. We gradually changed D by adding small amounts of PS oligomers (PSO). Table shows the molecular characterization of PCL-*b*-PS and PSO, where CS1, CS2, and CS3 have PCL blocks with $M_n \sim 14,000$ g/mol, whereas CS4 with $M_n \sim 15,800$ g/mol. The binary PCL-*b*-PS/PSO blends were prepared using a solution-casting method with toluene as a common solvent. PSO is expected to completely mix with PS blocks in the microdomain structure.

The microdomain structures formed in the blend were examined using SR-SAXS at BL-10C. The 2D-SAXS curves were azimuthally averaged to obtain 1D-SAXS curves as a function of wave number s to obtain D.

3 Results and Discussion

3.1. Microdomain Structures. Fig. 2 shows typical 1D-SAXS curves of neat CS1 and CS2 (blue curves) and
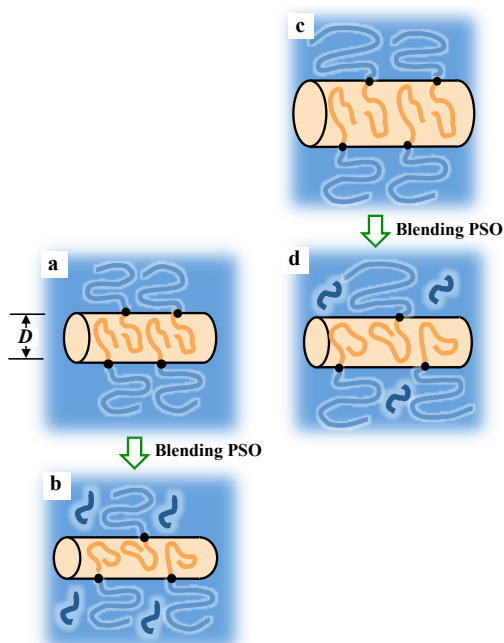
Figure. 1. Schematic illustration showing the strategy to prepare crystalline blocks (orange chains) confined in nanocylinders with different diameters D.
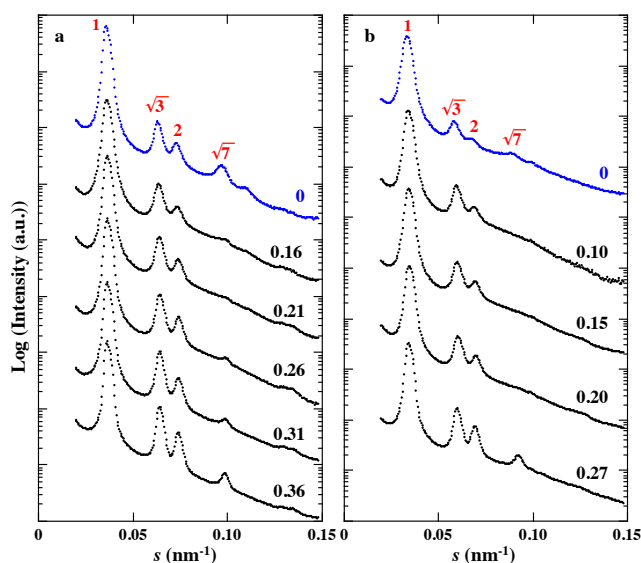
Figure. 2. 1D-SAXS curves from CS1/PSO (a) and CS2/PSO (b) blends. The weight fraction of PSO in the system is indicated on each SAXS curve.

various blends with PSO (black curves). These 1D-SAXS curves have several scattering peaks, the positions of which exactly correspond to a ratio of $1:\sqrt{3}:2:\sqrt{7}$. This fact, together with f_{PCL} in the system, suggests that the cylindrical microdomain structures with the PCL block inside are formed. The primary peak position in 1D-SAXS curves from molten samples was essentially identical to that of crystallized samples, indicating that the microdomain structure existing in the melt is completely preserved after the crystallization of PCL blocks due to the vitrification of PS chains.

The value of D was evaluated from the long period of microdomain structures L and f_{PCL}, and is plotted in Fig. 3 against the weight fraction of PSO in the system w_{PSO}. D decreases linearly with increasing w_{PSO}, and makes individual lines according to D of neat copolymers (Table). Therefore, it is possible to examine the crystallization rate of PCL blocks with $M_{n,} \sim 14{,}000$ or $\sim 15{,}800$ g/mol as a function of D. Furthermore, it is possible to compare the crystallization rate of PCL blocks with different M_n (14,000 or 15,800 g/mol) confined in the nanocylinder with the same D, for example, $D = 18.2$ nm (blue line in Fig. 3). Therefore, we can examine the effects of D and M_n separately on the crystallization rate of PCL blocks confined in nanocylinders.

3.2. Crystallization Behaviour of PCL Blocks. The time evolution of PCL crystallinity shows an abrupt increase at the initial stage of crystallization with no appreciable induction time, followed by an asymptotic increase at the late stage of crystallization. This crystallization behaviour is ascribed to the nucleation-controlled crystallization mechanism of confined chains. That is, once homogeneous nucleation occurs in the isolated nanodomain, the crystal growth finishes instantaneously because of the small size of isolated nanodomains. The crystallization behaviour of PCL blocks can be successfully analysed by assuming that the crystallization rate of PCL blocks at crystallization time $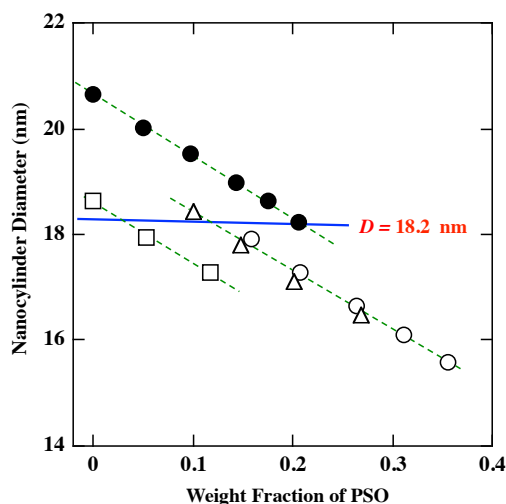t$ is proportional to the volume fraction of un-crystallized PCL blocks existing at t, from which the half-time of crystallization $t_{1/2}$ can be derived.

Figure 4 shows the logarithmic plot of $t_{1/2}$ against D for all the blends investigated, where we find the data points make two separate lines; one consists of three blends including PCL blocks with $M_n \sim 14{,}000$ g/mol (open symbols) and the other CS4/PSO blends with $M_n \sim 15{,}800$ g/mol (closed circles). The former composite line indicates that $t_{1/2}$ depends only on D for PCL blocks with a constant M_n irrespective of w_{PSO}. Furthermore, it is found that the small decrease in D yields an extremely large increase in $t_{1/2}$ during isothermal crystallization at the same T_c (= -42 ℃). That is, $t_{1/2}$ exhibits approximately a 140-fold increase (from 0.48 to 69 min) by a 16 % decrease in D (from 18.6 to 15.6 nm) for the PCL blocks with $M_n \sim 14{,}000$ g/mol and a 260-fold increase (from 0.35 to 94 min) by a 12 % decrease in D (from 20.6 to 18.2 nm) for the PCL blocks with $M_n \sim 15{,}800$ g/mol. Fig. 4 also indicates when we compare $t_{1/2}$ of different PCL blocks at the same D, for example $D = 18.2$ nm (blue line in Fig. 4), $t_{1/2}$ for PCL blocks with $M_n \sim 15{,}800$ g/mol is ca. 90 times larger than that with $M_n \sim 14{,}000$ g/mol. That is, only the small increase in M_n of PCL blocks confined in the nanocylinder with the same D yields an extremely large increase in $t_{1/2}$.

In conclusion, we find from Fig. 4 that D and M_n strongly and comparably affect the crystallization rate of confined PCL blocks.

References

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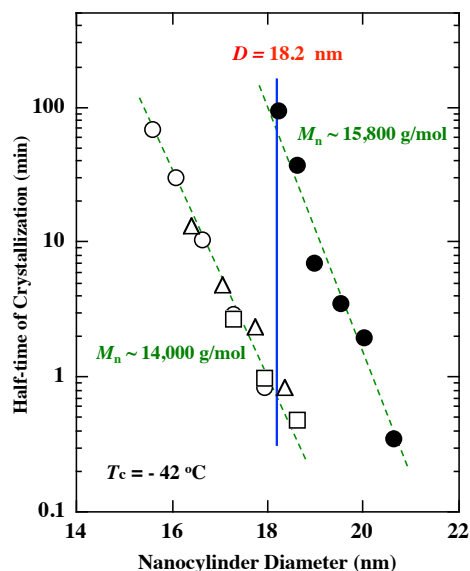
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Figure. 4. Logarithmic plots of $t_{1/2}$ of PCL blocks against D during isothermal crystallization at T_c = -42 ℃ for CS1/PSO (open circles), CS2/PSO (triangles), CS3/PSO (squares), and CS4/PSO (closed circles) blends. The M_n of PCL blocks for open symbols is ca. 14,000 g/mol, and that for closed circles is 15,800 g/mol.

Figure. 3. D plotted against w_{PSO} for CS1/PSO (open circles), CS2/PSO (triangles), CS3/PSO (squares), and CS4/PSO (closed circles) blends.