

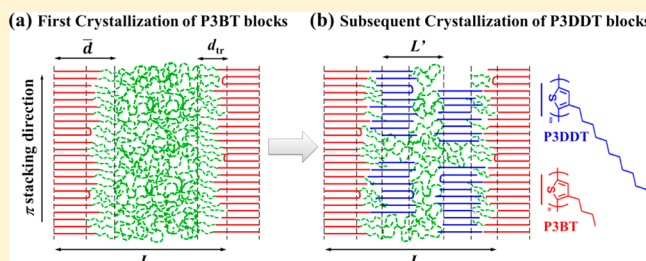
Microphase Separation and Crystallization in All-Conjugated Poly(3-alkylthiophene) Diblock Copolymers

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Supporting Information

ABSTRACT: The microphase separation and crystallization of all-conjugated poly(3-butylthiophene)-*b*-poly(3-dodecylthiophene) (P3BDDT) diblock copolymers were systematically investigated by temperature-resolved wide-angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR), and synchrotron small-angle X-ray scattering (SAXS) in a step-by-step cooling process. The WAXD, FTIR, and SAXS results revealed that the crystallization of poly(3-butylthiophene) (P3BT) blocks with shorter alkyl side-chains in high temperature region led to the formation of microphase-separated lamellar structure consisting of P3BT crystalline domains and P3BT/poly(3-dodecylthiophene) (P3DDT) amorphous domains, followed by a rapid crystallization of P3DDT blocks in relatively low temperature region, which occurred in the amorphous domains between P3BT crystalline domains. Analysis of the one-dimensional (1D) correlation function derived from SAXS data suggested that the previously crystallized P3BT segments could confine the size of P3DDT crystalline subdomains and possibly contribute to the rapid increase in the P3DDT crystallinity.



1. INTRODUCTION

Crystallization in block copolymers has attracted considerable attention over the past few decades,^{1–3} since the crystallization process has a profound effect on the solid-state structure and morphology in block copolymers. It is well-known that block copolymers can self-assemble into microphase-separated structures driven by the thermodynamic incompatibility between its different blocks.^{4,5} When one or more blocks in the block copolymer can crystallize, a competition between phase separation and crystallization can result in major changes in structure and morphology. These have been demonstrated in detail, particularly for the case of diblock copolymers with only one crystalline block, which is the simplest case of crystallizable block copolymers. The crystallization in crystalline–amorphous block copolymers can drive structure formation, or it can be confined within the phase-separated microdomains, depending on the relative location of the order–disorder transition temperature (T_{ODT}) of the diblock copolymer, the crystallization temperature (T_c) of the crystalline block, and the glass transition temperature (T_g) of the amorphous block. All possible cases in crystalline–amorphous block copolymer systems resulted from the various relative locations of these important transition temperatures have been recently reviewed.³

The crystallization in double-crystalline diblock copolymers can be even more complicated, since the crystallization of one block may affect the crystallization and morphology of the second block.⁶ In this situation, the interplay between two blocks during crystallization process also need be considered in

great detail. When the melting temperatures of the two blocks, T_{m1} and T_{m2} , are close enough, a coincident crystallization phenomenon of the two blocks can be obtained. In the contrary, when the melting temperature of one block is far from the other (i.e., $T_{m1} \gg T_{m2}$), the first block to crystallize (i.e., block 1 with higher melting temperature) can result in a specific structure, which may or may not be changed by the crystallization of the other block. The crystallization behaviors and morphologies have been extensively studied in several different double-crystalline diblock copolymers, including poly(ethylene oxide)-*b*-poly(ϵ -caprolactone) (PEO-*b*-PCL),⁷ poly(L-lactide)-*b*-poly(ϵ -caprolactone) (PLLA-*b*-PCL),^{8,9} and poly(L-lactide)-*b*-poly(ethylene oxide) (PLLA-*b*-PEO)^{10,11} etc. These double-crystalline diblock copolymers belong to coil–coil type diblock copolymers, which are comprised of two flexible, chemically incompatible and dissimilar blocks. Besides this kind of double-crystalline diblock copolymers, rod–rod type diblock copolymers, consisting of two different rigid blocks (such as polypeptide, DNA, and conjugated polymers, etc.), are the other important category of double-crystalline diblock copolymers, since these rigid blocks have high tendency to aggregate into (liquid)crystalline domains. On the basis of the rigid-rod structure of such rod-like building blocks, rod–rod diblock copolymers were reported to preferably show low-curvature vesicular (dilute solution) or lamellar (concentrated

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solution, solid state) nanostructures independent from their specific chemical structure and composition,¹² which is quite different from the situation in coil–coil double-crystalline diblock copolymers. Although the nanostructures of rod–rod diblock copolymers have been widely studied, there is still lack of knowledge about the detailed microphase separation and crystallization behaviors of this kind of double-crystalline diblock copolymers.

Among the rod–rod diblock copolymers, the research into all-conjugated diblock copolymers have been strongly intensified, driven by their potential applications in the next generation of functional polymer materials for photovoltaic devices or sensors, due to their fantastic combination of remarkable electronic activity and well-controlled nanoscale morphology.¹³ In principle, the final nanoscale morphologies and the resulting semiconducting properties of all-conjugated block copolymers are determined by both the microphase separation and the crystallization behaviors of P3AT blocks.^{14–16} Different thin film morphologies have been observed in all-conjugated poly(2,5-dihexyloxy-*p*-phenylene)-*b*-poly(3-hexylthiophene) (PPP-*b*-P3HT) diblock copolymers by changing block ratios and annealing processes, which can tune the competition between the microphase separation and crystallization.¹⁷ Besides, we have recently reported an effective method, i.e., the “two-step” thermal annealing treatment, to tune the relationship between the microphase separation and crystallization in all-conjugated poly(3-butylthiophene)-*b*-poly(3-dodecylthiophene) (P3BDDT) diblock copolymers, resulting in the significantly enhanced crystallinity compared to their homopolymer counterparts.¹⁸ However, the exact interplay between microphase separation and crystallization and the interplay between two blocks during crystallization of all-conjugated double-crystalline diblock copolymers remain to be understood.

Herein, we take the typical family of all-conjugated double-crystalline diblock copolymers, P3BDDTs, as the research objects, systematically explore their microphase separation and crystallization by temperature-resolved WAXD, FTIR, and synchrotron SAXS during a stepwise cooling process, and reveal the interplay between microphase separation and crystallization and the interplay between the two blocks during crystallization of P3BDDTs. Our results demonstrate that initially the crystallization of P3BT blocks with shorter alkyl side-chains in the high temperature region drives P3BDDTs to form a microphase-separated lamellar structure consisting of P3BT crystalline domains and P3BT/P3DDT amorphous domains; and then, the crystallization of P3DDT blocks in the relatively low temperature region proceeds rapidly in the amorphous domains between the P3BT crystalline domains. Through the analysis of the one-dimensional (1D) correlation function derived from SAXS data, we conclude that the previously crystallized P3BT segments could confine the size of P3DDT crystalline subdomains, and possibly contribute to the rapid increase in the P3DDT crystallinity.

2. EXPERIMENTAL SECTION

Materials. The P3BDDT diblock copolymers were synthesized by quasi-living modified GRIM polymerization. The detailed synthesis method can be found in our previous work.¹⁸ The molecular characteristics of P3BDDT diblock copolymers are list in Table 1. The molecular weights and polydispersity indices (PDIs) of P3BDDT diblock copolymers were measured by gel permeation chromatography (GPC), using a Agilent 1100 system equipped with a UV detector

Table 1. Molecular Characteristics of Poly(3-butylthiophene)-*b*-Poly(3-dodecylthiophene) (P3BDDT) diblock copolymers

denotation of P3BDDTs ^a	$\bar{M}_n^b$	PDI ^b	<i>n</i> / <i>m</i> (%) ^c	melting temperature ^d (°C)	
				P3BT	P3DDT
B34DD66	27700	1.11	34:66	228	167
B46DD54	18500	1.07	46:54	229	179
B63DD37	9800	1.03	63:37	231	164

^aDenoted according to the varied block ratios. ^bDetermined by GPC.

^cDetermined by ¹H NMR. *n*, *m*: the molar amount of P3BT block and P3DDT block, respectively. ^dObtained by DSC.

(eluent: THF; calibration: polystyrene standards). The compositions of P3BDDT diblock copolymers were derived from ¹H NMR spectra, which were collected on a DMX 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and using CDCl₃ as the solvent. The melting temperature of each block was measured by Differential scanning calorimetry (DSC), using TA DSC Q2000 at a heating rate of 10 °C/min under N₂ flow.

Characterizations. *In situ* temperature-resolved wide-angle X-ray diffraction (WAXD) experiments were performed on Rigaku SmartLab X-ray diffractometer equipped with the Anton Paar DHS 900 hot stage, using Cu Kα radiation ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectra were collected using Nicolet 6700 spectrometer equipped with a hot stage. The spectra were obtained by averaging 16 scans at a resolution of 4 cm^{−1}. *In situ* temperature-resolved synchrotron small-angle X-ray scattering (SAXS) experiments were performed at BL16B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). Two-dimensional (2D) SAXS scattering patterns were collected on a charge coupled device camera. The one-dimensional (1D) correlation function ($G(r)$) can be described as¹⁹

$$G(r) = \int_0^\infty I(q) q \frac{\sin qr}{r} dq \quad (1)$$

where $I(q)$ is the scattering intensity, q is the scattering vector defined as $q = (4\pi \sin \theta)/\lambda$ (2θ is the scattering angle), and r is the direction along the lamellar stack. Since the experimental SAXS data were measured in the finite q range, extrapolation of the 1D SAXS data to both $q = 0$ and $q \rightarrow \infty$ is necessary for the Fourier transformation. Extension to low q was performed using an intensity profiles based on Guinier's law,²⁰ and continuation to large q can be achieved by using the Porod–Ruland model.²¹

We also calculated the deviation of $G(r)$ (ΔG) based on the measurement error introduced by SAXS curves. During the data collection of SAXS measurements, the values of $I(q)$ were a constant in the region of $q - q + \Delta q$, where Δq is the step length of data collection. Thereby, ΔG can be calculated as

$$\Delta G = \int_0^\infty I(q) \left[(q + \Delta q) \frac{\sin(q + \Delta q)r}{r} - q \frac{\sin qr}{r} \right] dq \quad (2)$$

Since $(\sin(q + \Delta q)r/r) = (q + \Delta q)r/r - (q + \Delta q)^3 r^3/(3!r) \approx (q + \Delta q)r/r = q + \Delta q$, eq 2 can be deduced to

$$\Delta G \approx \int_0^\infty I(q) [(q + \Delta q)^2 - q^2] dq = 2\Delta q \int_0^\infty I(q) q dq \quad (3)$$

We note that ΔG has no relationship with r , which is reasonable that ΔG is introduced by SAXS measurement error.

3. RESULTS AND DISCUSSION

Temperature-Resolved WAXD of P3BDDT Crystallization. To investigate the crystallization behavior of P3BDDT diblock copolymers, we employed *in situ* temperature-resolved WAXD measurements. All samples were heated to their

melting temperature to eliminate the thermal history, followed by the stepwise cooling at the rate of $-10\text{ }^{\circ}\text{C}$ per 15 min. Figure 1a shows WAXD profiles of B34DD66 during the

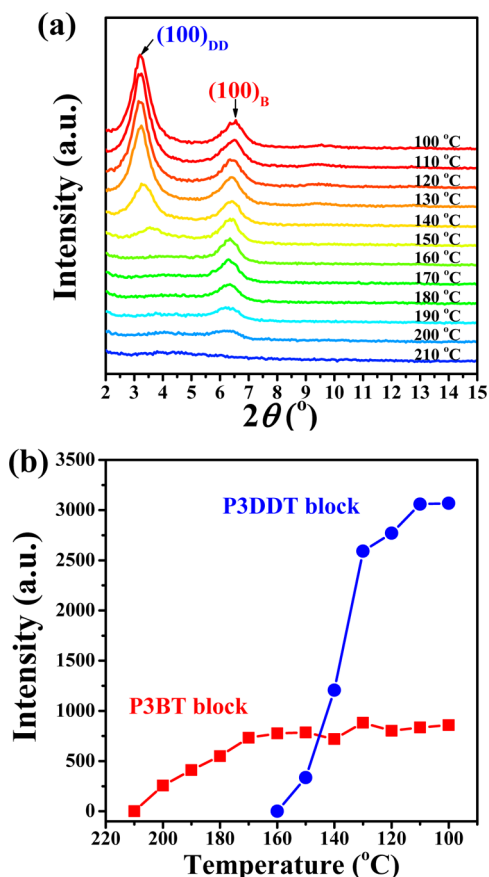


Figure 1. (a) Temperature dependence of WAXD profiles for B34DD66 during the stepwise cooling process, and (b) the (100) peak intensity of P3BT blocks and P3DDT blocks dependence on temperature.

stepwise cooling process. When the temperature was decreased to 200 $^{\circ}\text{C}$, a recognizable diffraction peak appeared at 2θ angle of $\sim 6.4^{\circ}$, corresponding to a spacing distance of 13.8 $\text{\AA}$. This peak can be assigned to the first-order reflection from crystallographic (100) plane of P3BT crystals (denoted as $(100)_{\text{B}}$), indicating that P3BT blocks crystallize into π - π stacking lamellar layer structure, which is similar to their homopolymer counterpart.²² The intensity of $(100)_{\text{B}}$ peak increased as the temperature decreased. When the temperature was reduced to 150 $^{\circ}\text{C}$, another diffraction peak emerged at 2θ angle of $\sim 3.3^{\circ}$, corresponding to a spacing distance of 26.7 $\text{\AA}$. This peak could be associated with the first-order reflection from crystallographic (100) plane of P3DDT crystals (denoted as $(100)_{\text{DD}}$), suggesting the subsequent crystallization of P3DDT blocks. The intensity of $(100)_{\text{DD}}$ peak also increased as the temperature decreased.

As the temperature-resolved WAXD profiles are *in situ* characterized, the intensity of (100) peak is proportional to the crystallinity of P3BDDT films.²³ Hence, to quantitatively analyze the growth of P3BT and P3DDT crystalline domains, the peak intensities of $(100)_{\text{B}}$ and $(100)_{\text{DD}}$ of B34DD66 are summarized in Figure 1b. The result shows that when the temperature was decreased from the melting temperature of B34DD66 (i.e., 228 $^{\circ}\text{C}$) at the rate of $-10\text{ }^{\circ}\text{C}$ per 15 min,

P3BT blocks started to crystallize first at $\sim 210\text{ }^{\circ}\text{C}$, the crystallinity of which increased with the temperature falling and reached a plateau at $\sim 170\text{ }^{\circ}\text{C}$; while P3DDT blocks began to crystallize subsequently at $\sim 160\text{ }^{\circ}\text{C}$, followed by a rapid increase in the crystallinity. It is noteworthy that the rapid increase of the P3DDT crystallinity is not usually observed in P3DDT homopolymer, as the long dodecyl side chains may suppress the ordered packing of thienyl backbones.²⁴ The crystallization behaviors of B46DD54 and B63DD37 are similar to that of B34DD66, and their WAXD profiles collected during a stepwise cooling process are shown in Figure S1, Supporting Information.

FTIR Spectra of P3BDDT Crystallization. FTIR spectroscopy can provide a lot of information on local molecular structures of polymers, due to its sensitive characterizing specificity to different molecular groups and segmental constituents, which thus has been extensively applied in studying the crystallization of P3AT homopolymers.^{25–27} The typical FTIR spectrum of P3AT includes three regions: the wavenumber region of 3100–2800 cm^{-1} , corresponding to C–H stretching ($\nu(\text{C–H})$); the wavenumber region of 1530–1300 cm^{-1} , corresponding to C=C stretching, CH_2 bending and wagging, and CH_3 bending and wagging; the wavenumber region of 900–700 cm^{-1} , corresponding to methyl rocking, C_{β} –H out-of-plane bending ($\delta(\text{C}_{\beta}\text{–H})$), and $(\text{CH}_2)_n$ in-phase rocking ($\gamma(\text{CH}_2)_n$). Figure S2 shows the full-scale temperature-resolved FTIR spectra of P3BDDTs with block ratios of 34:66, 46:54, and 63:37 during stepwise cooling from the melting state. All the spectra have been normalized by methyl bending mode at 1378 cm^{-1} , which is often used as the internal standard because the frequency and intensity of this vibration mode are not sensitive to structural changes.²⁸ As shown in Figure S2, the FTIR characteristic bands of P3BDDTs (listed in Table S1) can be determined according to those of P3AT homopolymers.^{25–27}

The C_{β} –H out-of-plane bending ($\delta(\text{C}_{\beta}\text{–H})$) bands in the region of 850–800 cm^{-1} are related to the π - π stacking of thiophene backbones,²⁹ which can be used to identify the crystallization of P3BDDTs. The temperature-resolved FTIR spectra changes of B34DD66 in the wavenumber region of 890–760 cm^{-1} are shown in Figure 2a. The band at 836 cm^{-1} should be assigned to the C_{β} –H out-of-plane bending of B34DD66 in the amorphous state (as list in Table S1) due to its dominance at 230 $^{\circ}\text{C}$, in which B34DD66 is in the molten state. The band at 820 cm^{-1} , which appeared with cooling and dominated at the end of cooling process (i.e., 105 $^{\circ}\text{C}$), should be assigned to the C_{β} –H out-of-plane bending of B34DD66 in the form I crystal modification (i.e., side chains are tilted and little overlapped) of each block in B34DD66 (as list in Table S1).³⁰ The intensity changes of these two bands as a function of temperature are shown in Figure 2b. A two-step crystallization process can be clearly observed: the first step in the temperature range of 220–160 $^{\circ}\text{C}$ is related to the crystallization of P3BT blocks; while the second step in the temperature range of 150–105 $^{\circ}\text{C}$ is correlated with the crystallization of P3DDT blocks, which corresponds well with the WAXD results. We note that the temperature of 220 and 150 $^{\circ}\text{C}$ are slightly lower than the melting temperatures of P3BT blocks (i.e., 228 $^{\circ}\text{C}$) and P3DDT blocks (i.e., 167 $^{\circ}\text{C}$ as shown in Table 1).

The WAXD and FTIR results revealed that P3BDDTs behave in a two-step crystallization manner with cooling, in which P3BT blocks with short side chains crystallized at the

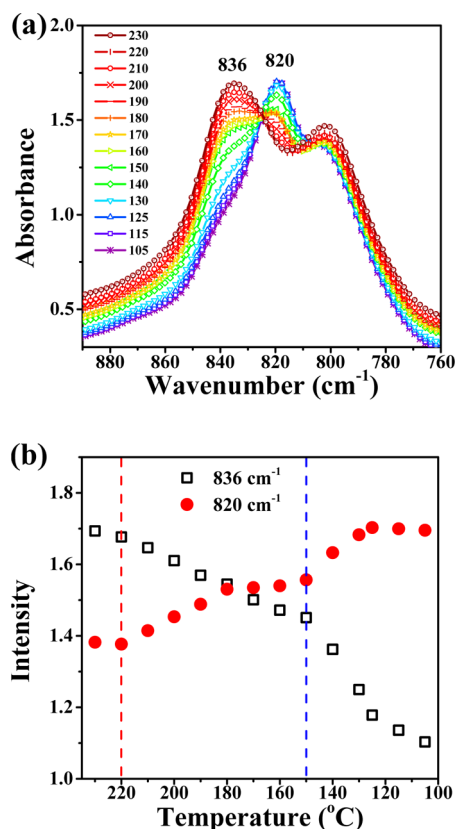


Figure 2. (a) Temperature-resolved FTIR spectra of B34DD66 in the region of 890–760 cm^{-1} during the stepwise cooling from melting state. (b) Intensity changes of the bands at 836 and 820 cm^{-1} as a function of temperature for the $\text{C}_\beta\text{--H}$ out-of-plane deformation mode in B34DD66.

first step, followed by the rapid crystallization of P3DDT blocks in relatively low temperature region. The exact interaction between the stepwise crystallizations of the two blocks will be discussed afterward.

SAXS Analysis of P3BDDT Microstructure. To further investigate the microstructure of P3BDDT diblock copolymers in the two-step crystallization, *in situ* temperature-resolved synchrotron SAXS measurements were performed. Figure 3a shows the Lorentz-corrected 1D SAXS curves of B34DDT66 when it was cooled from 300 °C at the rate of -5 °C per 15 min. No scattering peak appeared at 300 °C, indicating that B34DD66 was in a miscible molten state. The SAXS profiles remained featureless until the temperature was cooled to 200 °C, then a scattering peak was identified at the scattering vector of ~ 0.027 $\text{\AA}^{-1}$, suggesting the emergence of microphase separation with a long-period domain spacing (L_B) of ~ 233 $\text{\AA}$, calculated based on Bragg's law. As P3BT blocks started to crystallize at ~ 220 °C (revealed by WAXD and FTIR results), it can be inferred that the microphase separation of B34DD66 at ~ 200 °C was probably driven by the crystallization of P3BT blocks. Considering the highly rigid-rod-like nature of crystalline P3BT segments, the $\pi\text{--}\pi$ stacking structure of P3BT crystals, and previously reported lamellar-like nanostructure in P3BDDT thin films after thermal annealing,¹⁸ the most likely microphase-separated structure of B34DD66 was lamellar structure, similar to that of poly(3-butylthiophene)-*b*-poly(3-octylthiophene) (P3BOT) reported by Wu and co-workers.³¹

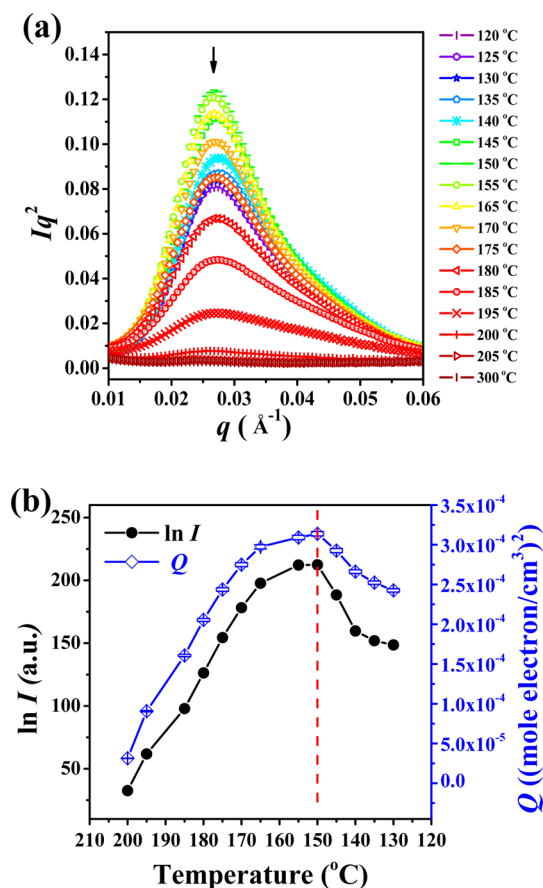


Figure 3. (a) Lorentz-corrected 1D SAXS profiles of B34DD66 collected during stepwise cooling from 300 °C. (b) Intensity of the scattering peak in SAXS profiles and invariant Q of B34DD66 as a function of temperature during the stepwise cooling. The red vertical line separates the two regions with different temperature dependences of the intensity and invariant. The deviations of the invariant Q are derived from the measurement errors in SAXS curves.

The SAXS peak intensities of B34DD66 diblock copolymer as a function of temperature are shown in Figure 3b. The peak intensities increased with the decrease of temperature in the range of 200–150 °C, and in turn decreased in the range of 150–130 °C. According to the WAXD and FTIR results, the temperature range of 200–150 °C is related to the crystallizing temperature of P3BT blocks, while the temperature range of 150–130 °C is correlated with the crystallizing temperature of P3DDT blocks. The scattering intensity is proportional to the electron density difference between the microphase-separated domains.³² The crystallization of P3BT blocks in the high temperature region produced P3BT crystalline domains and P3BT/P3DDT amorphous domains, the electron density difference of which is reflected on the increased SAXS peak intensity when the temperature is decreased. The subsequent crystallization of P3DDT blocks in the relatively low temperature region from 150 to 130 °C led to the formation of P3DDT crystalline subdomains in the previous amorphous domains, partially reduced the electron density difference, and thus resulted in the decrease of SAXS peak intensity when the temperature was decreased from 150 to 130 °C. In the crystallization process of P3BT blocks, the melting P3DDT blocks and the amorphous P3BT segments should be pushed aside by P3BT crystalline domains, resulting in the trapped P3BT/P3DDT amorphous domains between P3BT crystalline

domains. And the subsequent crystallization of P3DDT blocks proceeded in the amorphous domain between P3BT crystalline domains instead of breaking through P3BT crystalline domains, as indicated by the phenomenon that the SAXS peak remained at $\sim 0.027 \text{ \AA}^{-1}$ in the temperature region of P3DDT blocks' crystallization (shown in Figure 3a). *In situ* temperature-resolved synchrotron SAXS measurements were also performed on B46DD54 and B63DD37 during the stepwise cooling process, and the changes of their scattering peak intensities as a function of temperature showed similar variation trend to B34DD66 (shown in Figure S3).

The 1D correlation function derived from SAXS data can provide the structural parameters of lamellar systems, which allows us to further investigate the interplay of the microphase separation and crystallization and the interplay of the two blocks of P3BDDT diblock copolymers in the two-step crystallization process. A typical 1D correlation function obtained for B34DD66 at 155 °C is shown in Figure 4,

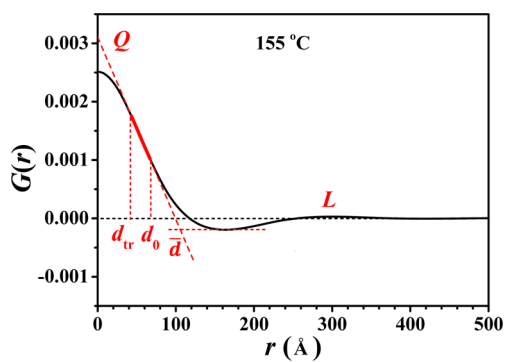


Figure 4. Typical 1D correlation function obtained for B34DD66 at 155 °C. The red solid line represents the straight line part in this correlation function curve. And the scattering invariant (Q), transition zone thickness (d_{tr}), the core thickness of the thinnest lamella (d_0), number-averaged lamellar thickness ($\bar{d}$), and long period domain spacing (L) are marked here.

where all the structural parameters are marked clearly. For ideal situations, the beginning part of 1D correlation function is a straight line; while for certain practical situations, only part of the straight line may be kept, given that the thickness of the transition zone is smaller than the core thickness of the thinnest lamella.¹⁹ For B34DD66, the straight line part in the correlation function curve exists and is represented by the red solid line in Figure 4. The r axis value of the start point of the straight line corresponds to the transition zone thickness d_{tr} value; the r axis value of the end point of straight line relates to the core thickness of the thinnest lamella d_0 value; the intersection of the extrapolation of this line and baseline gives the number-averaged lamellar thickness $\bar{d}$, and the intercept of extrapolation of this line on G axis yields the scattering invariant Q in the system.¹⁹ In order to obtain more precise values of these structural parameters (i.e., d_{tr} , d_0 , $\bar{d}$, and Q), we have calculated their deviations based on three 1D correlation functions, $G(r)$, $G(r) + \Delta G$, and $G(r) - \Delta G$, where ΔG is derived from SAXS measurement errors (see the Characterizations). The invariant Q is proportional to the electron density difference between the crystalline phase and amorphous phase.³³ The invariant Q of B34DD66 as a function of temperature is presented in the same chart as SAXS peak intensities, i.e., Figure 3b. Both Q and peak intensities show an unambiguous synchronized change with temperature, further confirming our conclusion on the

interaction between crystallization and microphase separation of P3BDDTs.

Figure 5a shows the number-averaged lamellar thickness ($\bar{d}$) of B34DD66 as a function of temperature. The values of $\bar{d}$

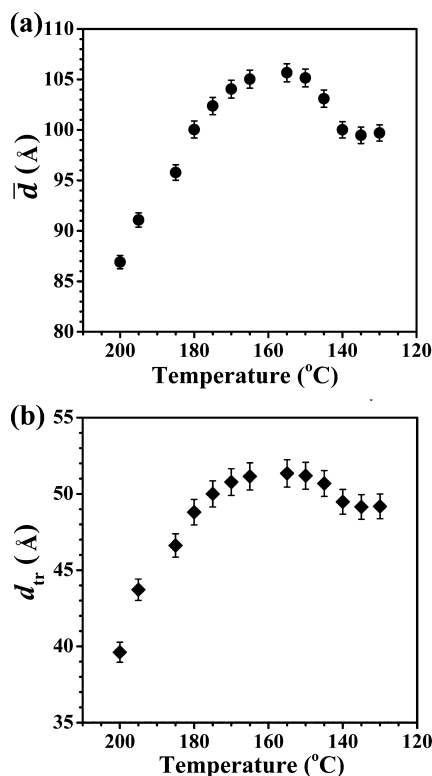
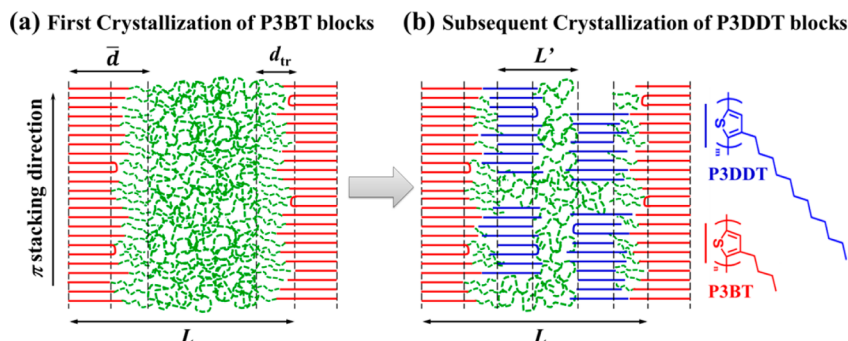


Figure 5. (a) Number-averaged lamellar thickness ($\bar{d}$) and (b) the thickness of the transition zone (d_{tr}) of B34DD66 as a function of temperature during the stepwise cooling. The deviations of these values are derived from the measurement errors introduced by SAXS curves.

increased with the crystallization of P3BT blocks in the temperature region of 200–150 °C, confirming that one of the microphase-separated domains was composed by crystallized P3BT segments. However, $\bar{d}$ values decreased with the crystallization of P3DDT blocks in the temperature region of 150–130 °C. The $\bar{d}$ value is defined as the number-averaged thickness of all the lamella; hence, $\bar{d}$ values in the temperature region of 150–130 °C reflect not only the number-averaged lamellar thickness of P3BT crystalline domains but also that of P3DDT crystalline subdomains. The reduction of $\bar{d}$ values in the P3DDT-crystallizing temperature region indicates that the number-averaged thickness of P3DDT crystalline subdomains is smaller than that of the previously formed P3BT crystalline domains, despite of the relatively high volume fraction of P3DDT blocks in B34DD66, probably due to the confined crystallization nature of P3DDT blocks.

The transition zone thickness d_{tr} of B34DD66 as a function of temperature is shown in Figure 5b. The d_{tr} values increased when the temperature was decreased from 200 to 150 °C, corresponding to the crystallization process of P3BT blocks, indicating that the transition zones between P3BT crystalline domains and amorphous domains become thicker when the crystallinity of P3BT blocks increases. Considering the previous conclusion that the crystallization of P3BT blocks set up the microphase-separated structure, i.e., P3BT blocks crystallize

Scheme 1. Sketch of the Microscopic Structure for B34DD66 after (a) First Crystallization of P3BT Blocks in the High Temperature Region and (b) Subsequent Crystallization of P3DDT Blocks in the Relatively Low Temperature region, Respectively^a



^a L , $\bar{d}$, d_{tr} , and L' are long period domain spacing, average lamellar thickness of P3BT crystalline domains, thickness of transition zone between the P3BT crystalline domains and P3BT/P3DDT amorphous domains, and inter-domain repeated spacing of the subdomains in the amorphous domains, respectively. The red rod, blue rod, and green coil represent the crystalline P3BT, crystalline P3DDT, and amorphous P3BT/P3DDT segments, respectively.

spontaneously with little impact from microphase separation or other external factors, P3BT blocks are most likely to crystallize into bigger crystalline domains with rougher surfaces as the temperature decreased, which reasonably accounts for the increase of transition zone thickness in the temperature region of 200–150 °C. On the other hand, the d_{tr} values decreased with the increased crystallinity of P3DDT blocks in the temperature region of 150–130 °C, indicating that the transition zone became thinner with the increased crystallinity of P3DDT blocks from the perspective of overall average. This phenomenon suggests that the P3DDT-block crystallization was possibly initiated by the ordered P3BT segments on the edges of the P3BT crystalline domains due to the covalent linkage between P3DDT and P3BT blocks, and thus, such initiated crystallization of P3DDT blocks led to the formation of small P3DDT crystalline subdomains with fine surfaces, which contributed to the decrease of the overall-averaged value of transition zone thickness. The initiated crystallization nature of P3DDT blocks may be the reason for the rapid increase of the P3DDT crystallinity after P3DDT blocks started to crystallize, which was revealed by the WAXD results. Besides, the initiated crystallization nature of P3DDT blocks could also account for why the depression behavior of the crystallization temperature and melting points of P3DDT blocks as a function of the block ratio was not observed (such nondepression behavior was also observed previously by our DSC measurements¹⁸). We note that the speculation of the initiated crystallization nature of P3DDT blocks needs to be verified by more direct evidence, for example, the comparison between the nucleation rate of P3DDT blocks in P3BDDTs and that of P3DDT homopolymer.

Microphase Separation and Crystallization in P3BDDT. On the basis of the detailed crystallization and microphase separation information from WAXD, FTIR, and synchrotron SAXS, it is now possible to depict the interplay of crystallization and microphase separation and the interplay of the two blocks of P3BDDTs (exemplified by B34DD66) in the two-step crystallization process. For the first step in the high temperature region, P3BT blocks with short side chains crystallize and thus reject the amorphous segments from the front of P3BT crystals to result in the formation of microphase-separated lamellar structure consisting of P3BT crystalline

domains and P3BT/P3DDT amorphous domains, as shown Scheme 1a, where the long period domain spacing L of the microphase-separated structure, the number-averaged lamellar thickness $\bar{d}$ of P3BT crystalline domains, and the transition zone thickness d_{tr} between P3BT crystalline domains and P3BT/P3DDT amorphous domains are labeled, respectively. After the crystallization of P3BT blocks, the structural parameters of the microphase-separated morphology in B34DD66 can be calculated from the 1D correlation function of B34DD66 at 155 °C (shown in Figure 4), those are the transition zone thickness d_{tr} is 51.4 ± 0.9 Å; the core thickness of the thinnest lamella d_0 is 56.6 ± 0.9 Å; the number-averaged lamellar thickness $\bar{d}$ of P3BT crystalline domains is 106.7 ± 0.9 Å; the long period domain spacing L is ~ 297.8 Å (listed in Table 2). Using the same method, the structural parameters of

Table 2. Structure Parameters of P3BDDT diblock copolymers after the first step crystallization of P3BT blocks

	transition zone thickness d_{tr} (Å)	core thickness of the thinnest lamella d_0 (Å)	number-average lamellar thickness $\bar{d}$ (Å)	long period domain spacing L (Å)
B34DD66	51.4 ± 0.9	56.6 ± 0.9	106.7 ± 0.9	~ 297.8
B46DD54	43.6 ± 0.6	44.1 ± 0.6	84.5 ± 0.6	~ 294.7
B63DD37	42.1 ± 0.4	42.6 ± 0.4	74.8 ± 0.4	~ 193.3

B46DD54 and B63DD37 after the first crystallization of P3BT blocks can also be obtained, which are listed in Table 2. On the basis of the comparison of $\bar{d}$ and L in P3BDDTs with varied block ratios, it can be noticed that the ratios of $\bar{d}$ and L have no relationship with the composition of P3BDDTs, verifying that the structures of P3BDDTs are independent from their composition. In the relatively low temperature region, P3DDT blocks with long side chains crystallize in amorphous domains between P3BT crystalline domains, resulting in numerous P3DDT-crystalline subdomains (shown in Scheme 1b). Because of the appearance of newly built P3DDT-crystalline subdomains in the second stage, parameters of $\bar{d}$ and d_{tr} cannot be marked to a specific domain in Scheme 1b.

For both blocks, the degrees of crystallinity are substantially less than 100%, which raise the question: where are the amorphous P3AT chains (the collective signature of the

amorphous P3BT and P3DDT chains, which are miscible and indiscrete)? In the first step of P3BT blocks' crystallization, the amorphous P3AT chains are almost rejected from P3BT crystalline domains into the second domains (i.e., amorphous domains) and transition zones. In the second step, the crystallization of P3DDT blocks in the amorphous domains also drives the amorphous segments mostly out of their crystalline subdomains. Therefore, it is most likely that the amorphous segments exist mainly among the P3DDT crystalline subdomains, as shown in Scheme 1b. In this case, SAXS should show a formation of intensity at a q value corresponding to the interdomain repeat,³⁴ marked as L' in Scheme 1b. Inspection of the Lorentz-corrected 1D SAXS profiles of B34DD66 in the temperature region of 150–130 °C (shown in Figure S4) reveals that there is, indeed, a broad bump centered at $q \sim 0.046 \text{ \AA}^{-1}$, corresponding to the L' value of $\sim 137 \text{ \AA}$.

4. CONCLUSIONS

In this work, we have systematically investigated the microphase separation and crystallization of P3BDDTs by temperature-resolved WAXD, FTIR, and synchrotron SAXS in a stepwise cooling process. Our WAXD and FTIR results revealed that P3BDDTs showed a two-step crystallization route with cooling, that is P3BT blocks with shorter alkyl side chains crystallized first in the high temperature region, followed by the rapid crystallization of P3DDT blocks in the relatively low temperature region. Synchrotron SAXS results demonstrated that the crystallization of P3BT blocks in the high temperature region drove P3BDDTs to microphase separation into lamellar structure consisting of P3BT crystalline domains and P3BT/P3DDT amorphous domains, and the crystallization of P3DDT blocks in the relatively low temperature occurred in the amorphous domains between the P3BT crystalline domains. Analysis of the 1D correlation function derived from SAXS data suggested that the previously crystallized P3BT segments could confine the size of P3DDT crystalline subdomains, and possibly contribute to the rapid increase in the P3DDT crystallinity. Our results shed light on the interplay between crystallization and microphase separation of all-conjugated P3AT diblock copolymers with side-chain lengths of two blocks different by eight carbon atoms, help to provide guidelines for precisely controlling the nanoscale morphology of all-conjugated BCPs to achieve the optimized performances in organic electronic devices, and enrich the understanding of the subject of crystallization in double-crystalline block copolymers.

■ ASSOCIATED CONTENT

Supporting Information

Additional WAXD profiles, complete FTIR spectra, FTIR band assignments, additional SAXS peak intensity changes, and partial SAXS profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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