CRYSTALLIZATION AND MELTING OF POLY(ETHYLENE OXIDE) CONFINED IN NANOSTRUCTURED PARTICLES WITH CROSS-LINKED SHELLS OF POLYBUTADIENE

Wei-ping Gao, Yu Bai, Er-qiang Chen** and Qi-feng Zhou
Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Abstract Small fixed aggregates of a poly(ethylene oxide)-block-polybutadiene diblock copolymer (PEO-b-PB) in THF solution were obtained by adding a selective solvent for PB blocks, followed by cross-linking the PB shells. The morphologies of the nanostructured particles with a cross-linked shell were investigated by atomic force microscopy and transmission electron microscopy. The average behaviors of the PEO crystallization and melting confined within the nanostructured particles were studied by using differential scanning calorimetry experiments. For the deeply cross-linked sample (SCL-1), the crystallization of the PEO blocks was fully confined. The individual nanoparticles only crystallized at very low crystallization temperatures ($T_{cs}$), wherein the homogenous primary nucleation determined the overall crystallization rate. For the lightly cross-linked sample (SCL-2), the confinement effect was $T_c$ dependent. At $T_c \leq 42^\circ$C, the crystallization and melting behaviors of SCL-2 were similar to those of the pure PEO-b-PB diblock copolymer. At $T_c > 42^\circ$C, SCL-2 could form PEO lamellae thicker than those of the pure PEO-b-PB crystallized at the same $T_c$.

Keywords: Diblock copolymer; Aggregates; Cross-linking; Confined crystallization and melting.

INTRODUCTION
Polymer crystallization and melting have been extensively studied over the last five decades and many researchers have provided new findings which have added to our understanding of this stimulating topic\cite{1-3}. The long chain nature of polymers makes their mechanism of crystallization and crystal morphology substantially different from those of small molecules. Although a fully extended chain crystal with minimum free energy represents the ultimate equilibrium crystal, the kinetic pathway of polymer crystallization usually leads to the formation of folded-chain crystals in thermodynamically metastable states, which exhibit the morphology of thin lamellae. The melting temperature ($T_m$) of the lamellar crystals is increased with increasing the lamellar thickness (fold length).

Recently, there has been a growing interest on the study of the crystallization and melting of crystalline-amorphous diblock copolymers\cite{4-19}. It is well known that diblock copolymers may present micro-phase separation structures\cite{20}. In the strong and medium segregation limit regimes, which are away from the order-disorder transition (ODT) of the diblock copolymer, a variety of ordered phase morphologies such as lamellae, gyroids, cylinders (hexagonal), and spheres (body-centered cubic) on a length scale of a few tens of nanometers, have been identified. For the phase transition of crystalline-amorphous diblock copolymers, one should consider three thermal events which may affect one another\cite{31}: self-organization of the diblock copolymer, vitrification of the amorphous block, and crystallization of the crystalline block. Therefore, three temperature parameters can be employed to describe their interrelationships: the order-disorder transition temperature, $T_{ODT}$, the glass transition...
temperature of the amorphous blocks, $T_{g}^a$, and the crystallization temperature of the crystalline blocks, $T_c$ (always lower than the $T_m$ of the crystalline blocks). In the case of $T_{ODT} > T_c > T_{g}^a$, phase structures and morphologies are basically dominated by the crystalline blocks. Disregarding the initially ordered phase morphologies formed below $T_{ODT}$, crystallization of the crystalline blocks may occur with little morphological constraint of the ordered phase, leading to lamellar morphology. Therefore, the confinement arisen form the microphase separation is "soft". In the case of $T_{ODT} > T_g^a > T_c$, the crystallization of the crystalline blocks occurs within the ordered phase morphology, and is completely confined ("hard" confinement) due to the rapid vitrification of amorphous blocks that retains the initially ordered phase morphology. The "soft" confinement may change into a "hard" one using chemical modification of the amorphous blocks. For example, in poly($\varepsilon$-caprolactone)-$b$-polybutadiene (PCL-$b$-PB) diblock copolymer, the PB blocks become solid-like after cross-linking, and thus, crystallization of PCL block could only take place under certain "hard" confined phase morphology[21].

Disregarding the various confinement geometries formed by microphase separation of the crystalline-amorphous block copolymers, both theoretical[22–24] and experimental studies have revealed that chain-folding principle is valid for the crystallization of the crystalline blocks. Therefore, in solid state, the amorphous blocks are tethered on the crystal fold surfaces. When the crystalline blocks tend to form thicker lamellae, i.e. decrease the fold numbers, the area occupied by each amorphous block at the surface becomes smaller, leading to a higher tethering density. Increasing the lamellar thickness will ultimately cause the stretching of the amorphous blocks, which is unfavorable in entropy. Therefore, the interaction between an enthalpic driving force to minimize the fold surface energy and the entropic term from stretching of the amorphous blocks also plays an important role to determine the thermodynamic properties of the final folded-chain crystals[15, 22–24].

In this paper, we studied the confinement effects on the crystallization and melting of a poly(ethylene oxide)-$b$-polybutadiene (PEO-$b$-PB) diblock copolymer. Instead of using the bulk phase morphology as the templates to construct the nano-confined environment, we assembled the diblock copolymer in a selective solvent at first[25]. The small aggregates were then fixed by cross-linking the shells to obtain the confinement conditions[25–28]. Upon controlling the cross-linking density of the PB, we were able to manipulate the "soft" and "hard" confinements, leading to different crystallization and melting behaviors of the PEO therein. Moreover, cross-linking could also change the conformational entropy of the PB, which would affect the lamellar thickness and thus the melting of PEO blocks. The average behaviors of the crystallization and melting of PEO blocks within the nanostructured particles with cross-linked shells were investigated by differential scanning calorimetry (DSC) in great detail.

**EXPERIMENTAL**

**Synthesis of Diblock Copolymer**

The chemical structure and synthesis of the PEO-$b$-PB diblock copolymer to be studied are shown in Scheme 1. The hydroxyl-terminated PB homopolymer (PB-OH), which was kindly supplied by Prof. Wan-tai Yang at Beijing University of Chemical Technology, was obtained through the anionic polymerization of butadiene in cyclohexane using n-butyllithium as the initiator. The polymerization was terminated by adding ethylene oxide. The resulted PB-OH fraction had a number average molecular weight ($M_n$) of 5,100 g/mol and polydispersity ($d_w$) of 1.13, and was used as received. A low molecular weight PEO fraction [$\alpha,\omega$-hydroxy-methoxy-poly(ethylene oxide)] (HO—(CH$_2$CH$_2$O)$_n$—CH$_3$) was purchased from Aldrich. After careful purification and fractionation, the $M_n$ and $d_w$ of the PEO fraction were found to be 5,100 g/mol and 1.04, respectively. The hydroxyl end group of the linear PEO was reacted with succinic anhydride to produce the carboxyl-terminated PEO (PEO-COOH). The synthesis was carried out in dichloromethane at 40°C. A strong dehydrant, 1,3-dicyclohexylcarbodiimide (DCC), was required to act as reactant in the coupling reaction. After the completion of reaction, the unreacted homopolymers were removed by precipitation and column chromatography on silica gel with toluene/THF as eluent. The $M_n$ and $d_w$ of the final product of the diblock copolymer are 1.04 × 10$^4$ and 1.06, respectively.
A gel permeation chromatograph (GPC, Waters 150C) was applied to determine the molecular weight (MW) and MW distribution of the samples. For the PEO homopolymer, the GPC was calibrated by the standards of low MW PEO fractions. Fourier transform infrared spectroscopy (FTIR, Vector 22) and $^1$H-NMR (Bruker ARX400 spectrometer, DCCl$_3$ as the solvent and TMS as internal standard) measurements were carried out to elucidate the chemical structure of PEO-$b$-PB diblock copolymer. The $^1$H NMR was also used to estimate the total MW of the diblock copolymer and the composition of PEO and PB in the block copolymer. The NMR measured weight fraction of the PEO ($f_{EO}$) is 0.5.

**Cross-linking of the Nanostructured Particles**

The PEO-$b$-PB diblock copolymer was first dissolved in THF at 15°C, to give a concentration of 0.1% (W/V). During stirring, a selective solvent of ethyl ether, which is a good solvent for PB and a non-solvent for PEO, was slowly added to the solution. The clear solution gradually turned into bluish. The ultimate volume ratio of the common/selective solvent (THF/ethyl ether) was 1/15. After the solution was further stirred for 12 h, the cross-linking agent, disulfur dichloride (S$_2$Cl$_2$) was added. In order to produce PB shells with different cross-linking densities, two different amounts of S$_2$Cl$_2$ were used, wherein the volume ratios of S$_2$Cl$_2$/solution (V/V) were adjusted to 1.5 × 10$^{-5}$:1 and 3 × 10$^{-5}$:1, to yield SCL-1 and SCL-2 two samples, respectively. Under vigorous magnetic stirring, the cross-linking reactions were carried out at 15°C for 3 d and then at 21°C for 5 d. Afterwards, most of the solvents were removed by evaporation followed by adding 2-propanol to precipitate the shell cross-linked aggregates. The samples were further rinsed several times with 2-propanol. The sulfur contents of SCL-1 and SCL-2 were measured to be 23.5 wt% and 3.8 wt% by elemental analysis (EA, Elementar Vario EL), respectively. The detail structures of cross-linking were not examined. Therefore, only sulfur contents were used as a relative measurement of the cross-linking density of PB shells for SCL-1 and SCL-2. Before the crystallization and melting studies, the samples were completely dried in vacuum for at least 3 d.

**Equipment and Experiments**

An atomic force microscope (AFM, DI NanoScope IIIa) in tapping mode was employed to characterize the shape, size of the samples dried on fresh mica surfaces. In AFM experiments, the scanning rate was ranged between 1 and 3 Hz, and both the height and phase images were recorded. For the AFM observation, a small amount of the solutions containing the PEO-$b$-PB aggregates with or without cross-linking were directly spread on fresh mica surface. After the solvents were removed, the samples were further dried under vacuum. A transmission electron microscope (TEM, JEM-100CX) with an accelerating voltage of 100 kV was used for morphological studies. A solution of the nanostructured particles with cross-linked PB shells was dropped on the surface of a carbon film on the TEM grids. After the solution drop was completely dried, the TEM samples were melted at 80°C for 5 min followed by isothermal crystallization at 40°C. In order to enhance the contrast between the shells and cores under TEM observation, the samples on the carbon films of TEM copper grids were stained by OsO$_4$. Since the PB blocks contained unsaturated structures, they were stained heavier than the PEO blocks.
Wide-angle X-ray diffraction (WAXD, Bruker D8discover equipped with GADDS detector) was employed to examine the PEO crystalline structure of the dried nanostructured particles with cross-linked shells at room temperature. DSC (Seiko SII 6200) with a mechanical refrigerator (Haake, EK90/SII, the attainable lowest temperature is –80°C) was utilized to study the average crystallization and melting behavior of the nanostructured particles. The DSC was calibrated with standards such as indium. The samples with typical amount of about 2–4 mg were encapsulated in sealed aluminum pans. Isothermal crystallization was conducted by quenching the samples from the isotropic melt to a preset crystallization temperature ($T_c$). In the low undercooling ($\Delta T$) region, a self-seeding technique was used to promote the overall isothermal crystallization rate \cite{29}. The samples were annealed at a selected self-seeding temperature ($T_s$) for 10 min, followed by rapidly quenching to a preset $T_c$. The melting behaviors of the crystallized samples were recorded by directly heating the samples from the $T_c$ to the temperature higher than $T_m$. The melting peak temperatures were used to represent the $T_m$s of the samples.

RESULTS AND DISCUSSION

The Morphologies of Nanostructured Particles

In both the molten and solid state, the symmetric PEO-$b$-PB diblock copolymer we studied possesses the thermodynamically equilibrium phase morphology of lamella \cite{15}. The self-assembly of the diblock copolymer in selective solvent may form alternative structures \cite{25}. During the addition of selective solvent of ethyl ether into the THF solution, the system turned into bluish, indicating the formation of small aggregates of PEO-$b$-PB diblock copolymers. Because ethyl ether is commonly used as a nonsolvent for PEO, by adding a little amount of ethyl ether into a THF solution of PEO homopolymer ($e.g.$, PEO ($M_n = 5,100$ g/mol) solution with a concentration of 0.1% ($W/V$)), it could easily cause the polymer to precipitate. However, the bluish solutions we obtained were rather stable for months, implying that the small aggregates of the diblock copolymer could prevent coagulation. When ethyl ether was dropped into the solution at 15°C, two different processes might occur: 1) direct crystallization of PEO and 2) micellization of the diblock copolymer. In case 1, the PEO blocks crystallize very fast at low $T_c$ (15°C), resulting in the formation of tiny crystallites. In addition to the PB blocks tethered on the lamellar fold surfaces, the “over spilled” PB at the lamellar perimeters can partially cover on the lamellar side surfaces, and thus inhibit the crystal lateral growth \cite{30}. In case 2, the micellization due to the addition of selective solvent for PB will result in the formation of micelles with PEO as the cores and PB as the shells. Since PEO is quite dense within the cores, the micellization may assist the PEO crystallization. However, the shells of PB prevent the formation of large PEO lamellae. Both two processes can produce small aggregates of the diblock copolymer. However, we could not identify exactly what has happened in the solution during the addition of ethyl ether. A further investigation is in progress.

Figures 1(a) and 1(b) are the AFM height images of the samples SCL-1 and SCL-2 dried on the fresh surfaces of mica. For comparison, Fig. 1(c) shows the AFM height image of sample obtained by casting the solution of PEO-$b$-PB aggregates without cross-linking on mica surface. We found that without cross-linking, the small aggregates of PEO-$b$-PB formed in solution would be destroyed during solvent evaporation and finally, the dendritic monolayers with a thickness of nearly 17 nm were obtained (Fig. 1c). On the contrary, the particle morphologies shown in Figs. 1(a) and 1(b) indicate that the cross-linking can successfully retain the aggregates, even when the solvents were completely removed. The particles of the SCL-1 and SCL-2 possess the lateral size ranged from 80–160 nm. For both the SCL-1 and SCL-2 samples, the particle heights were measured to be 15–20 nm, which is almost identical to that of the PEO-$b$-PB monolayer on mica surface. The DSC and WAXD experiments showed that the PEO blocks in the as-dried particles were crystallized. Moreover, on the basis of WAXD results, we found that the PEO blocks in the particles crystallize to form the same monoclinic structure as that in PEO homopolymer.
Crystallization of PEO Confined in PB

Crystallization and Melting of PEO Blocks in Nanostructured Particles

As mentioned above, the sulfur contents of the SCL-1 and SCL-2 are 23.5 wt% and 3.8 wt%, respectively. Therefore, the PB shells of SCL-1 are cross-linked much deeper than those of SCL-2. The glass transition behaviors of the amorphous shells of SCL-1 and SCL-2 were also studied by using DSC cooling experiments conducted at a cooling rate of $-10$ K/min. For SCL-1, the glass transition of the cross-linked PB occurred between 0°C and $-30°C$. Since the glass transition was overlapped with the crystallization process during cooling, the glass transition temperature ($T_g$) of SCL-1 could not be precisely determined. The $T_g$ of SCL-2 was lower than $-40°C$. In the entire temperature region from 80–$-40°C$ examined (Although the mechanical refrigerator of the DSC instrument has a cooling limit of $-80°C$, when its temperature was lower to below $-40°C$, the controlling of cooling rate could not be further retained), the glass transition of the cross-linked PB shell was not observable.

The average behaviors of PEO crystallization and melting within the nanostructured particles were examined using DSC. Figures 2(a)–2(c) are the DSC cooling traces of pure PEO-$b$-PB, SCL-2, and SCL-1, respectively, under different cooling rates. The samples were held at 80°C for 5 min before cooling, where the PEO crystals were completely melted. For PEO-$b$-PB (Fig. 2a), multiple exothermic peaks are observed during the nonisothermal crystallization process, wherein the onset crystallization temperature increases from nearly 37–42°C when the cooling rate is changed from $-10$ K/min to $-1$ K/min. For SCL-2 (Fig. 2b), the DSC cooling traces exhibit single exothermic peak. However, SCL-2 shows that its onset crystallization temperature is similar to that of PEO-$b$-PB at their corresponding cooling rate. For SCL-1 (Fig. 2c), all the onset crystallization temperatures appear below $-5°C$, irrespective of the cooling rate. Figure 2(d) shows the DSC heating traces of SCL-1, SCL-2, and PEO-$b$-PB after they are cooled from 80°C at the rate of $-1$ K/min. The $T_m$s of the three samples are 48, 51, and 52°C, respectively. Compared with PEO-$b$-PB, SCL-1 and SCL-2 exhibit much broader melting peaks, the peak widths of which increase with increasing the sulfur content of the samples.

As shown in Fig. 2(c), SCL-1 can only crystallize when the temperature cooled to below $-5°C$. In isothermal crystallization experiments, we also found that crystallization of SCL-1 took place at sufficiently low $T_c$. When $T_c$ was between 0°C and $-10°C$, the isothermal crystallization rate was extremely slow. Further lowering the $T_c$ led to very fast crystallization. The SCL-1 crystals obtained at different $T_c$ exhibited broad melting endotherms with the peak temperatures near 48°C, which were very similar to that shown in Fig. 2(d). We noted that the highest applicable $T_c$ for SCL-1 was located at temperature region of its glass transition, where the confinement became “hard”. This observation indicated that crystallization of the PEO blocks is strongly confined within the individual nanostructured particles. In the bulk states, it has been found that the crystallization of crystalline blocks confined in the spheres of the microphase separation morphology also requires sufficient high undercoolings ($\Delta T_s$)\cite{7,16-19}. The nano-sized spheres embedded in the amorphous matrix are separated from each other. Moreover, the macroscopic impurities cannot be contained within the nanospheres. Therefore, the crystal growth in an individual sphere can not advance to others, and principally, every sphere needs its own crystal
nucleus. The nucleation process is dominantly homogeneous, and the very high nucleation density can only be achieved at very low $T_c$. In SCL-1, the deep cross-linking of PB shells makes the PEO blocks fully confined within the particles. Therefore, the PEO blocks can only crystallize at a $T_c$ lower than $-5 \degree C$.

**Figure 2** DSC cooling curves of PEO-b-PB (a), SCL-2 (b) and SCL-1 (c) obtained using different cooling rates, and the DSC melting curves of SCL-1, SCL-2 and PEO-b-PB (d) after cooling from 80°C at the cooling rate of $-1 \text{ K/min}$. The heating rate is 10 K/min.

**Figure 3** DSC melting curves of PEO-b-PB (a) and SCL-2 (b) isothermally crystallized at different $T_c$s. The heating rate is 10 K/min.

Figure 2 indicates that in the DSC cooling/heating experiments, SCL-2 behaves more or less similar to the PEO-b-PB. Therefore, isothermal crystallization was used to illustrate the confinement effect in SCL-2. Figures 3(a) and 3(b) are two sets of DSC melting traces for PEO-b-PB and SCL-2, respectively, isothermally crystallized at different $T_c$s. At $T_c$ below 42°C, except the peak broadening, SCL-2 exhibits almost the same melting behavior as PEO-b-PB, wherein their $T_m$s are around 52.5°C. Furthermore, using the heat of fusion of 7.89 kJ/mol ($\Delta H_f$ for low molecular weight PEO fractions with 100% crystallinity) as reference, SCL-2 possesses the normalized crystallinity of approximately 70%, which is only 10% lower than PEO-b-PB.
However, as shown in Fig. 3, when $T_c$ is increased to higher than 42°C, the difference between SCL-2 and PEO-b-PB becomes pronounced. In this $T_c$ region, self-seeding method was utilized to promote the isothermal crystallization process. Complete crystallization of the PEO-b-PB results in a constant crystallinity of nearly 80%. However, the crystallinity of SCL-2 is dramatically decreased with increasing $T_c$, disregarding the prolonged isothermal crystallization time. For both samples, elevation of $T_c$ will lead to an increase of $T_m$. Compared with PEO-b-PB, the $T_m$ of SCL-2 becomes higher after crystallization at same $T_c$. For example, at $T_c$ of 50°C, the $T_m$ for SCL-2 is 58.2°C, which is 3°C higher than that of PEO-b-PB.

![Fig. 4](image)

**Fig. 4** The double logarithmic plots of Avrami analysis for PEO-b-PB (a) and SCL-2 (b) isothermally crystallized at different $T_c$.

$n$ is the Avrami exponent.

The different behaviors of SCL-2 crystallization at $T_c$s below and above 42°C indicate that the confinement effect is $T_c$ dependent. We expected that there might be some “holes” in the PB shells of SCL-2 due to the light cross-linking. In this case, when the sample is melted at 80°C, the PEO blocks of neighboring particles can partially merge together through the holes on the amorphous shells, resulting in the formation of continuous PEO domains with many defects. Therefore, at low $T_c$ region ($T_c \leq 42°C$), the SCL-2 crystallization follows the kinetics as the PEO-b-PB does. According to the isothermal crystallization curves recorded by DSC, the overall crystallization kinetics at different $T_c$s can be obtained using Avrami analysis. Figures 4(a) and 4(b) represent the double logarithmic plots for PEO-b-PB and SCL-2, respectively, crystallized at $T_c \leq 42°C$. The apparent crystallinity ($X_c$) was calculated using the total latent heat of the exothermic peak as the reference. As shown in Fig. 4, all the measured Avrami exponents ($n$) of the two samples are close to 3, corresponding to three-dimensional crystal growth with athermal nucleation or crystallization confined in two-dimensional lamellae with thermal nucleation\[31\]. The Avrami analysis implies that after melting, SCL-2 may contain layer-like PEO domains with large lateral size. This is evidenced by the TEM image (Fig. 5) of SCL-2 nanoparticles packed together on the carbon film, which were first treated at 80°C for 5 min followed by isothermal crystallization at 40°C. In Fig. 5, the dark lines due to OsO$_4$ staining represent the PB boundaries between different domains. Some large domains with the lateral size of 0.5–1 μm can be observed.

For both SCL-2 and PEO-b-PB, $T_m$s start to increase when $T_c$ exceeds 42°C, indicating the increase of PEO lamellar thickness\[15\]. In this $T_c$ region ($T_c > 42°C$), it is intriguing that after crystallization at a same $T_c$, SCL-2 exhibits $T_m$s higher than those of the PEO-b-PB. One of the reasons should be that the cross-linking of PB decreases the entropy of SCL-2 in melt state. Therefore, compared with PEO-b-PB, the $ΔS$ of the melting for SCL-2 is smaller, leading to higher $T_m$s. On the other hand, the higher $T_m$ may also imply that the SCL-2 forms thicker lamellae. For SCL-2, the cross-linking might pull some of the PB blocks closer to one another in the shells compared with that in the non-cross-linked samples. Therefore, during crystallization, the PB blocks can be arranged with a higher tethering density at the PEO fold surface, allowing some of the PEO block to form thicker lamellae with higher $T_m$. However, it is interesting to note that as the $T_m$ increases with increasing $T_c$, the crystallinity of SCL-2 decreases. We speculate that the formation of thicker lamellae may deform the PB shells to
certain extent. In this case, some portion of PEO blocks stays in an unfavorable condition of crystallization. These PEO blocks lose their translational motion due to the connected cross-linked PB shells. Therefore, they can not adjust themselves to the proper positions on crystal growth front and fit in the crystal lattice. This might cause the decrease of crystallinity.

Fig. 5 TEM image of the SCL-2 after isothermally melt crystallized at 40°C

**Annealing Behaviors of PEO Blocks in Nanostructured Particles**

For both SCL-1 and SCL-2, the confinement effects were further examined in the DSC heating experiments using different heating rates and isothermal annealing. The DSC heating results at different heating rates for PEO-b-PB and SCL-2 samples completely crystallized at 34°C are depicted in Figs. 6(a) and 6(b). For PEO-b-PB (Fig. 6a), a single melting peak is observed during fast heating. However, a shoulder on the high temperature side of the melting peak can be recognized at the heating rate of 4 K/min, which gradually develops into a peak when the heating rate is further lowered. The higher melting peak on Fig. 6(a) is associated with thicker lamellae of PEO, which are formed via thickening of the original lamellae during slow heating (annealing) process\(^{[15]}\). This indicates that the confinement of PB layers is rather "soft", wherein the crystal thickening of PEO can move the amorphous layers on the top and bottom fold surfaces apart from each other. As shown in Fig. 6(b), SCL-2 only shows one melting peak which narrows with decreasing heating rate. The onset of the melting process shifts to higher temperature when the heating rate is lowered, whereas the temperatures of the peak maximum keep nearly a constant at 52°C. This indicates the perfection of the crystals of SCL-2 originally formed at 34°C. However, no significant lamellar thickening can take place within the confined environment of SCL-2. Therefore, although slightly cross-linked, the amorphous shells of SCL-2 limit the changing of crystal morphology during heating.

**Fig. 6** DSC melting curves recorded at different heating rates for PEO-b-PB (a) and SCL-2 (b) isothermally crystallized at 34°C

Figure 7 is a set of DSC heating traces of a SCL-1 sample crystallized at -30°C followed by annealing at 40°C with different annealing times. With increasing the annealing time, the melting peak becomes narrower,
accompanied with an increase of peak area. Moreover, the peak significantly shifts to higher temperature. Note the annealing temperature of 40°C is higher than the $T_g$ of the amorphous shells in SCL-1, where the shells become relatively “soft”. Therefore, the rather imperfect PEO crystals rapidly formed at very low $T_c$ can be reorganized upon annealing. However, compared with the melting curves shown in Fig. 6, this process is much slower than that of PEO-b-PB and SCL-2.

![DSC melting curves of SCL-1 isothermally crystallized at -30°C followed by annealing at 40°C for different times](image)
The heating rate is 10 K/min.

**CONCLUSION**

Small aggregates of PEO-b-PB in THF solution could be obtained by adding a selective solvent of PB blocks. Further using S$_2$Cl$_2$ as the cross-linking agent, we could successfully fix the aggregates with different cross-linking density of the PB shells. The average behaviors of the PEO crystallization and melting confined within the nanostructured particles were studied by DSC experiments. For the deeply cross-linked sample (SCL-1), the experimental results revealed that the PEO blocks were fully confined. The nanoparticles only crystallized at very low $T_c$, wherein the homogeneous primary nucleation determined the crystallization rate. For the lightly cross-linked sample (SCL-2), the confinement was not complete, and the confinement effect on crystallization was found to be $T_c$ dependent. At $T_c \leq 42°C$, the crystallization of SCL-2 followed the same kinetics as the pure PEO-b-PB diblock copolymer. At $T_c > 42°C$, the SCL-2 could form PEO lamellae thicker than those of PEO-b-PB crystallized at the same $T_c$. The cross-linking between PB blocks may pull the blocks closer to one another and decrease the entropy of PB, allowing the PB blocks accommodate closer on the PEO lamellar fold surface. Therefore, the PEO fold number is decreased, resulting in thicker lamellae with higher $T_m$.

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