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Control of the confined and unconfined crystallization in glassy-crystalline poly(vinylcyclohexane)-*b*-poly(ethylene)-*b*-poly-(vinylcyclohexane) triblock copolymer in solution

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Abstract

The influence of the solvent evaporation rate on the crystallization of the poly(vinylcyclohexane)-*b*-poly(ethylene)-*b*-poly(vinylcyclohexane) (PVCH–PE–PVCH) triblock copolymer with the high T_g of PVCH segment in chloroform was investigated. The competition between the crystallization of PE block and the vitrification of PVCH in the triblock copolymer was controlled through changing the solvent evaporation rate in the solution system at different temperatures (T_e). It was found that the melting temperature (T_m) of PVCH–PE–PVCH samples increased with increasing the T_e when the T_e was lower than the solvent boiling point (bp), depending on the crystalline temperatures. However, when T_e was just a little above the solvent bp, two melting peaks, which corresponding to the fusion of the confined and unconfined crystals, respectively, were observed on the DSC curves of the samples. As T_e increased to be higher temperature, only one lower melting peak, which corresponding to the fusion of the confined crystals, existed for each samples. It was also found that the crystallinity (X_c) of the samples decreased gradually when T_e was lower than the solvent bp, and then decreased suddenly when T_e was just a little above the solvent bp, finally reached a plateau (about 13.5%) at higher T_e. The changes in X_c of the samples depend on the evaporating time in the solution. The results should be related to the competition between the crystallization of PE block in solvent and the vitrification of PVCH block with the solvent evaporation. Furthermore, the competition was controlled through changing the solvent evaporation rate. The confined and unconfined crystallization of the samples could be freely adjusted.

Keywords: PVCH–PE–PVCH; Confined crystallization; Solution

1. Introduction

In recent years, the confined crystallization behaviors in semicrystalline block copolymers have been the subject of many papers [1–20]. Some authors have extensively investigated the phase structures and final morphologies, which adopted by an amorphous–crystalline block copolymer bulk, not only depend on the Flory–Huggins interaction parameter (χ), the degree of polymerization (N) and the composition (f) of the block copolymer, but also depend on the competitions among microphase separation of block copolymer, vitrification of the amorphous block and crystallization of the crystallizable block [21–24]. At the same time, those competitions can be adjusted in many cases by some ways.

Hamley and co-workers [6,12,25,26] reported that for a series of crystalline-amorphous diblock copolymers of poly-(ethylene) and either poly(ethyl-ethylene) or poly(ethylene–propylene) (PE–PEE, or PE–PEP) systems, the competition always induced microphase separation overwhelmed by PE crystallization when cooled from melt due to the lower glassy transition temperature (T_g) of the amorphous components. Consequently, the final morphologies of the samples were always lamellar structures. Similar results were also found by Nojima et al. [27,28], for low molecular weight poly(ε-caprolactone)-*b*-polybutadiene (PCL–PB). Li et al. [29] investigated the competition between microphase separation and crystallization in an asymmetric poly(ethylene oxide)-*b*-polystyrene (PEO–PS) diblock copolymer. It was found that PEO crystallization always dominated over the microphase separation at large supercooling. While at small supercooling, the kinetic rates of microphase separation and PEO crystallization were comparable, so that the competition between those two processes determined the morphologies of the crystallization and microphase separation.

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Poly(vinylcyclohexane)-*b*-poly(ethylene)-*b*-poly(vinylcyclohexane) (PVCH–PE–PVCH) was a typical glassy-crystalline triblock copolymer having the order–disorder transition temperature (T_{ODT}) of ca. 260 °C. Loo et al. [30,31] examined the melt crystallization behavior of PVCH–PE diblock copolymer. The results showed that the microphase separation always preceded the PE crystallization when the sample was cooled from melt, and the ordered microphase-separated structures were effectively fixed by the PVCH due to the high T_g ($\sim$140 °C). As the result, the PE crystallization was only confined within the nanometer scale microstructures. Weimann et al. [32] revealed that the T_m and X_c of the PVCH–PE–PVCH triblock copolymer were much lower than that of PVCH–PE diblock copolymer due to the double fixed PE chain ends and topological constraints in triblock copolymer. Obviously, these studies focused on the confined crystallizations of PVCH–PE or PVCH–PE–PVCH within the microphase-separated structures; i.e. under a space confinement condition. If the competition between microphase separation and crystallization in these block copolymers is changeable, better understanding should be given on how and why the confined crystallizations occur. However, it could not be adjusted for the melt system.

Many works [33,34] demonstrated that solvent could change the competition between microphase separation and crystallization in an amorphous–crystalline block copolymer. Cohen et al. [33] investigated this phenomenon by casting the poly(styrene)-*b*-poly(ethylene) (PS–PE) diblock copolymer from solution. They showed that the microphase separation firstly occurred when solvent was removed at a temperature above the T_m(PE), resulting in a confined crystallization of the PE within the microdomains. However, when solvent was cast below the T_m(PE), the PE crystallization preceded microphase separation and no obvious ordered microstructures were observed. The polyethylene-*b*-poly(ethylene-*alt*-propylene)-polyethylene (PE–PEP–PE) triblock copolymer was also used by Séguléla et al. [34] to study this competitive phenomenon when solvent-cast was done above or below the T_m(PE). So it is expected that the competition between microphase separation and crystallization would be changed for PVCH–PE–PVCH triblock copolymer in the solution.

In this work, in order to get better understanding on confined and unconfined crystallization of PVCH–PE–PVCH triblock copolymer system, the crystallization behavior of the triblock copolymers in chloroform will be investigated, and the effect of the competition during the solvent evaporation process on the crystallization is also examined.

2. Experimental

2.1. Materials

The lamellar ordered triblock copolymer, PVCH–PE–PVCH ($\bar{M}_w = 40,000$, $\bar{M}_w(\text{PE}) = 16,000$, polydispersity index (PDI) < 1.10 [32]) with the PE weight fraction (w_E) of 0.40, was from Dow Chem. Co. The commercially available chloroform (AR) (bp = 61.2 °C) was used as solvent. All the block copolymers and solvent were used without further purification.

2.2. Evaporating experiments

The PVCH–PE–PVCH triblock copolymers were dissolved in chloroform to prepare solutions in flask with the concentration of 0.01 g/mL at the solvent bp temperature. And then, the solutions were rapidly removed to a water bath and evaporated at various fixed temperatures (T_e) (with the temperature error of ±1 °C) for 24 h, respectively. Finally, the obtained samples were dried at room temperature over 24 h under vacuum in order to eliminate the residual chloroform.

The evaporating experiments were also quantitatively performed at $T_e = 76$ °C through controlling the amount of the evaporated solvent by changing the size of the glass tube as exit of the flask. These samples were also dried at room temperature for 24 h under vacuum after the solvent was evaporated for 24 h. The evaporated solvent was collected and the average rate of solvent evaporation ($\bar{R}_e$) was calculated by fitting the curve of the amount of the solvent versus time, i.e. the slope of the straight curve was $\bar{R}_e$.

2.3. Differential scanning calorimetry (DSC)

The melting temperature (T_m) and the enthalpy of melting (ΔH_m) of the samples were obtained on heating at 10 °C/min from room temperature to 160 °C by using a Shimadzu DSC-60 calibrated with indium and Zn. The crystallinity (X_c) was then calculated from ΔH_m by using,

$$X_c = \frac{\Delta H_m}{w_E \Delta H_m^0} \tag{1}$$

where w_E is the weight fraction of PE component, and ΔH_m^0 is the theoretical heat of fusion of 100% crystalline linear polyethylene (taken as 277.1 J/g) [35].

2.4. Wide-angle X-ray scattering (WAXS)

Wide-angle X-ray scattering (WAXS) measurements were performed using a Rigaku D/max-RB Cu Kα X-rays ($\lambda = 1.54$ Å) originated from a generator operating at 40 kV and 120 mA. Measurements were continuously made at room temperature in the range $10° < 2\theta < 40°$, in 4°/min.

3. Results and discussion

3.1. Melting temperature and crystallinity

The PVCH–PE–PVCH triblock copolymer samples crystallized from the chloroform solvent at different evaporating temperatures (T_e) were examined by using DSC. The changes of the T_m and the X_c of the samples were investigated. Fig. 1 shows typical DSC thermograms of the samples. It is obviously that the T_m of the samples were gradually shifted to the higher temperature with increasing the T_e at first, and then decreased.

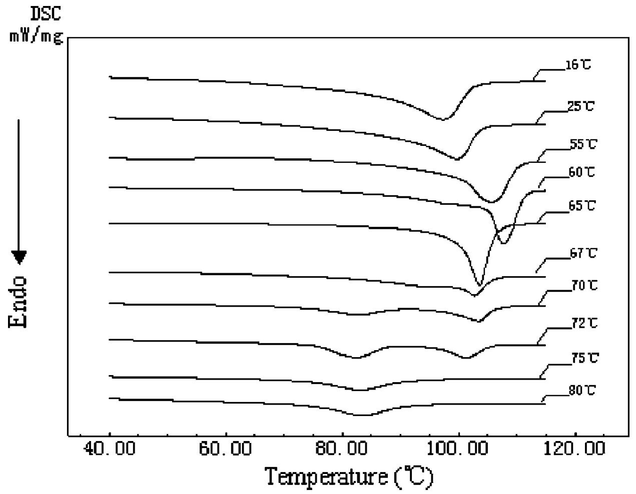

Fig. 1. DSC thermograms of the samples crystallized from the chloroform solvent at different T_e.

It should be noted that two melting peaks were observed for the samples when T_e was a little above the boiling point of the solvent. A new lower T_m appeared in the DSC curves. However, the higher melting peaks disappeared at higher T_e.

Fig. 2 shows the changes of the T_m and X_c of the samples crystallized at different T_e. According to the T_e, the changes could be divided into three regions: I, lower than the solvent bp; II, a little above the solvent bp; III, higher than the solvent bp.

In region I, the T_m of the samples monotonously increases from 97 to 108 °C with increasing the T_e. When the T_e is close to the solvent bp, the T_m reaches the maximum value (ca. 108 °C) approximately corresponding to the T_m of the neat PE homopolymer hydrogenated from poly(1,4-butadiene) which is equal to the PE block in the triblock copolymer [30,31]. This result implies that the PE block could freely crystallize from the solution in this case. The T_m depends on the crystallization temperature, so the higher the crystallization temperature, the higher the T_m is.

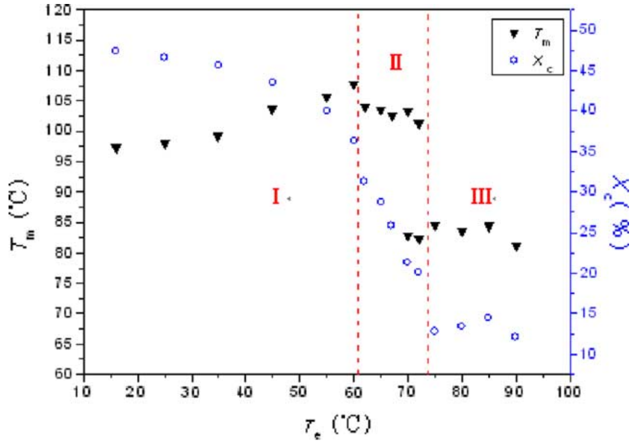

Fig. 2. Plots of the T_m and X_c data of the samples versus T_e.

In region II, The T_m slightly decreased with increasing the T_e. However, two melting peaks, at 83 and 103 °C, at 82 and 101 °C, are observed on each DSC curves for the samples crystallized at $T_e = 70$ and 72 °C, respectively. It is easily considered that the rate of solvent evaporation is quick in this case, so the vitrification of the PVCH block occurred before the crystallization of the samples completed from the solution. This is also proved by the fact of the sharp decrease in X_c of the samples in this region. It is well known that the crystallization of PE is very fast, the sample crystallized before the vitrification of the PVCH block with the solvent evaporation should have higher T_m close to that in region I. If the crystallization occurred after the vitrification of the PVCH block with the solvent evaporation, it should be confined by the fixed nanometer scale phase separated structure, leading to the lower T_m of the samples which corresponding to that of PVCH–PE–PVCH triblock copolymer crystallized from melt by cooling [30–32] as mentioned above. It is obviously that a competition between the crystallization and the vitrification of the sample exists in the system. If the crystallization and the vitrification occur simultaneously just like this case, the unconfined and confined crystals with the higher and lower T_m should co-exist in the resulted samples.

When the T_e was raised above 75 °C, just one melting peak which corresponding to the lower T_m of appeared for each samples at about 84 °C in region III. It demonstrates that only the confined crystals formed for the case of the vitrification preceding the crystallization due to the higher T_e and faster rate of the solvent evaporation.

It is interesting that the tendency of the changes in X_c could also be divided into the same three regions as the changes in T_m. In region I, a gradual decrease in X_c with increasing the T_e should be attributed to the shortened crystallization time in the solution due to the faster evaporation. Then a sharp reduction appears in region II, owing to the shorter crystallization time and confined crystallization. Finally a lowest plateau of the X_c (about 13.5%) appears in region III with further increasing T_e because of the complete confined crystallization.

These results show that the competition between the crystallization of the PE block and the vitrification of the PVCH block in the solution with the solvent evaporation plays a very important role in the formation of the unconfined and confined crystals. If the crystallization precedes the vitrification, the PE crystallization is free in the solution. In other words, the PE crystallization is not restricted by the double PE chain ends linked to PVCH block and the fixed nanometer scale phase separated structure in the triblock copolymer, leading to the higher T_m. On the other hand, if the PVCH block is vitrified firstly, the PE chains are restricted at both ends by the PVCH block and by and the fixed nanometer scale phase separated structure in the triblock copolymer. So the crystallization of the PE chains is completely confined, and the T_m is lower. However, if the crystallization and the vitrification occur simultaneously and the rates of the processes are comparable, the crystallization of PE block will be partly confined, resulting in the unconfined and confined crystals coexisted in the samples.

3.2. Control of the competition between crystallization and vitrification

Above results imply that if the solvent evaporation is controllable, the competition between the crystallization of the PE block and the vitrification of the PVCH block should be adjusted. Therefore, the confined and unconfined crystallization of the samples could be controlled.

In order to realize the control of the crystallization of the samples in solution, the competition was controlled through changing the rate of solvent evaporation ($\bar{R}_e$) which was defined in Section 2.

Fig. 3 shows the DSC thermograms of the samples crystallized from a quantitative solvent evaporation at T_e = 76 °C for 24 h. With increasing the $\bar{R}_e$ from 0.73 to 1.23 mL/min, the lower T_m (corresponding to the confined crystals) increased gradually. However, the higher T_m (the unconfined crystals) gradually diminished. These results suggest that the proportion of the unconfined and confined crystals in the samples could be changed, i.e. the faster the $\bar{R}_e$ was, the more the confined crystals were.

It is also should be noted that the T_m of the unconfined crystals first increased slightly with increasing solvent evaporation rates from 0.73 to 0.99 mL/min in Fig. 3. It should be ascribed to the effect of annealing at 76 °C after the solvent was completely removed from the solution system. Because the evaporation and annealing time was fixed to be 24 h as described in Section 2, so the faster the solvent evaporation was, the longer the annealing time at 76 °C for sample crystallization was. As a result, the T_m of the unconfined crystals increased. However, with the further increase of the solvent evaporation rates to 1.20 and 1.23 mL/min, the T_m decreased slightly because the enhanced confined crystals would affect the unconfined crystals.

Fig. 4 shows the changes of the crystallinity for the confined crystallization ($X_c(C)$) and unconfined crystallization (X_c(Un)), and for the total crystallinity ($X_c(C)+X_c$(Un)) in samples with increasing the $\bar{R}_e$ at 76 °C. It is obvious that the $X_c(C)$ is monotonously increased, but both the X_c(Un) and the total crystallinity are monotonously decreased. The results manifest that the proportion of the confined and the unconfined is controllable through changing the $\bar{R}_e$.

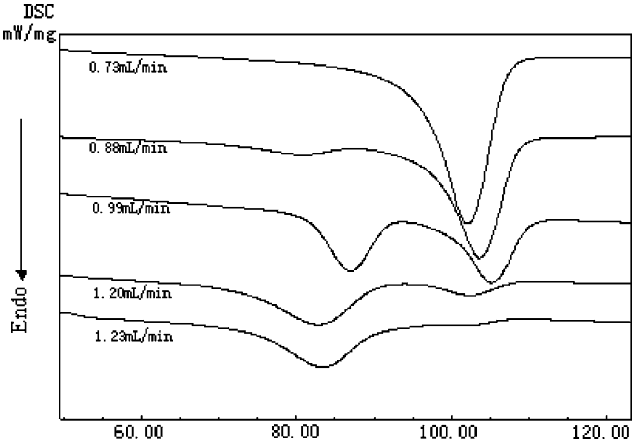

Fig. 3. The DSC thermograms of the samples crystallized at 76 °C for various $\bar{R}_e$.

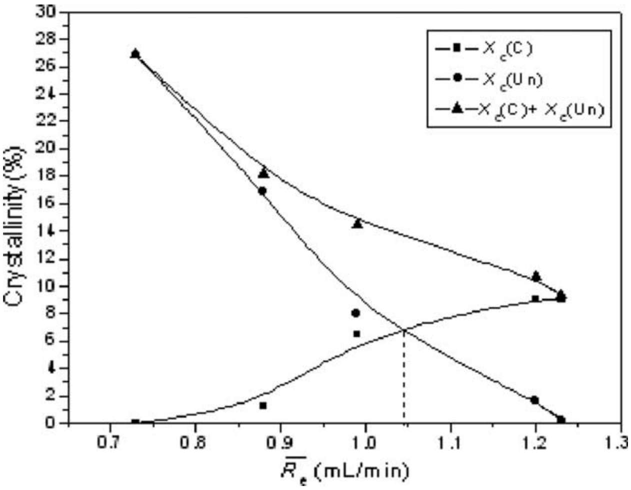

Fig. 4. The changes of the crystallinity of the confined crystallization ($X_c(C)$), the unconfined crystallization (X_c(Un)) and the total crystallinity ($X_c(C)+X_c$(Un)) of the samples with $\bar{R}_e$ at 76 °C.

It should be noted that there is a cross point in the $X_c(C)$ curve and X_c(Un) curve where the $\bar{R}_e$ is about 1.05 mL/min. At this point, the $X_c(C)$ is equal to the X_c(Un), which indicates that the proportions of the confined crystallization and the unconfined (freely) crystallization are both 50% in the system.

3.3. Crystal structures

There is still ambiguity whether the different T_m for the unconfined and confined crystals is due to the different crystal structures in the samples. WAXS was carried out for the samples.

Fig. 5 shows the typical WAXS results of the samples at different T_e. It is evident that the amorphous PE, (110) and (200) reflections are all recorded at 18, 21 and 24° for each sample, respectively. It shows that the PE block of all samples

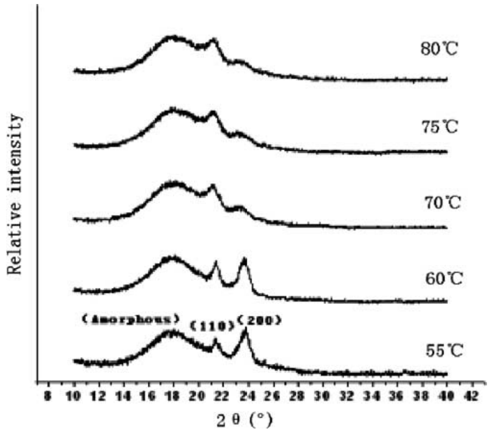

Fig. 5. WAXS analysis of the samples crystallized at different T_e.

crystallized in its usual orthorhombic form, indicating that the two T_m in the samples are not due to the different crystal types. On the other hand, the result also suggests that the confinement of the PE block by the glassy PVCH block does not significantly distort the PE crystals structure, corresponding to those reported by Hamley et al. [1,2] and Weimman et al. [32], respectively, for the crystallization of a lamellar ordered PVCH–PE diblock copolymer and a lamellar PVCH–PE–PVCH triblock copolymer. However, the relative intensity of (200) reflections became smaller at higher T_e ($\geq 70\,^{\circ}\mathrm{C}$). It suggests that the PE crystals preferred to grow along (110) orientation and the (200) orientation was inhibited when PE crystallization was confined by glassy PVCH at higher T_e.

4. Conclusion

The competition between the crystallization of PE block and the vitrification of PVCH block in PVCH–PE–PVCH triblock copolymer could be controlled in the solution. Therefore, the confined and unconfined crystallization in the system could be easily adjusted by changing the solvent evaporation rate. The crystal's structure of the confined crystallization was not changed comparing with that of the unconfined crystallization, although its (200) orientation was inhibited when PE crystallization was confined by glassy PVCH at higher evaporating temperatures.

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