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Crystallization and vitrification effect in a poly(styrene)-*g*-poly(ethylene oxide) graft copolymer

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Abstract

Crystallization and solid state structure of a poly(styrene)-graft-poly(ethylene oxide) (PS-*g*-PEO) graft copolymer with crystallizable side chains were studied using simultaneous small angle X-ray scattering/wide angle X-ray scattering/differential scanning calorimetry (SAXS/WAXS/DSC). It is found that the glass transition temperature (T_g) of PS main chain is remarkably higher than that of PS homopolymer. The start cooling temperature (T_o) has a great influence on crystallization of the PEO side-chain. When the graft copolymer is cooled from the temperature above T_g, phase separation is suppressed due to the low mobility of the PS main chain and the homogeneous melt is vitrified. The unfavorable conformation of the rigid main chain results in a single crystallization peak and lower crystallinity. When PS-*g*-PEO is only heated to a temperature lower than the T_g and then cooled, phase separation is retained. Both the PEO side chains with high and low crystallizability can crystallize in the phase-separated state, leading to double crystallization peaks and higher crystallinity. The effect of solvent on crystallization of the graft copolymer was also examined. It is observed that addition of toluene reduces the T_g of the PS main chain and leads to the disappearance of the vitrification effect.

Keywords: Poly(styrene)-*g*-poly(ethylene oxide) graft copolymer; Crystallization; Glass transition

1. Introduction

Graft copolymer has a wide range of applications. It can be used as compatibilizer of blends, [1–5] polymer surfactant [6–13] and surface modifier [14–19]. The properties of graft copolymer associated with these applications have been extensively studied. By contrast, the bulk properties of graft copolymer are rarely reported except for side-chain liquid crystal polymers. In fact, study on the bulk properties of graft copolymer can help us to understand how the coupled main chain and side-chain affect each other, particularly when one of them is crystallizable. Mihaylova et al. [20] studied the bulk structure of some graft copolymers with rigid main chains and crystallizable PEO side chains. Their results indicate that crystallization of the side chain can lead to ordering of the main chain to some extent and the rigid main chain also exerts some stress on the side chain and some new WAXS peaks are produced. Yao et al. [21] found that in poly(vinyl alcohol)-*g*-poly(methyl methacrylate) (PVA-*g*-PMMA) graft copolymer the hard PVA crystalline domain enhanced the T_g of the side-chain PMMA. Side-chain liquid crystal polymer is also one type of graft copolymer [22]. In side-chain liquid crystal polymer the glass transition temperature of the main chain is usually lower than the phase transition temperature and melting temperature of the side chain, and thus the formation of liquid crystal phase from the homogeneous melt is less hindered by the main chain. In this paper, we synthesized a poly(styrene)-graft-poly(ethylene oxide) (PS-*g*-PEO) graft copolymer, in which the side chain is crystallizable and the T_g of the main chain PS is higher than the crystallization temperature of PEO. The effects of T_g on crystallization and phase separation were investigated by simultaneous small angle X-ray scattering/wide angle X-ray scattering/differential scanning calorimetry (SAXS/WAXS/DSC).

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2. Experimental

2.1. Synthesis of the PS-g-PEO copolymer

Polystyrene-graft-[ω-ethyl-poly(ethylene oxide)] (PS-*g*-EPEO) were synthesized by free radical copolymerization of styrene monomer with α-acryloyl-ω-ethyl poly(ethylene oxide) macromonomer [23]. The products were purified by means of fractional precipitation technique using methanol/butanone as precipitant/solvent pair. The bulk composition of the graft copolymers was then determined by UV spectrometry (UV-240 Shimadzu, Japan). The characteristic adsorption of PS in the 260 nm region is frequently used to evaluate the styrene content of styrene-based copolymer [24]. In order to eliminate the unstructured background adsorption of EPEO in the graft copolymer, a calibration curve based on the first derivative UV spectroscopy was established using a set of solutions of pure PS of known concentration as standards (Knauer GPC standard sample, $M_n = 92,600$):

$$\Delta(\mathrm{d}A/\mathrm{d}\lambda) = 1.9676C - 0.00484 \quad (0.2 < \Delta(\mathrm{d}A/\mathrm{d}\lambda) < 1.1,\ R = 0.999) \tag{1}$$

where $\Delta(\mathrm{d}A/\mathrm{d}\lambda)$ was obtained by so-called peak-to-peak method [24] and C is the concentration of PS in mg/ml.

The number-average-molecular weight (M_n) and the polydispersity index (MWD) were measured by vapor pressure osmometry (VPO) (Knauer VPO) and gel-permeation chromatography (GPC) (Waters-208), respectively. VPO analysis indicated that M_n of the graft copolymers is 8560. The bulk composition (bulk density in wt%) is 50.0%.

2.2. DSC experiments

The non-isothermal crystallization and subsequent melting behavior of the graft copolymer were carried out on a Perkin–Elmer Pyris-1 DSC calorimeter. The PS-*g*-PEO graft copolymer was cooled from the desired temperature at a rate of 10 °C/min to 0 °C and hold for 1 min, then was heated to 150 °C at a rate of 10 °C/min.

2.3. Time resolved SAXS/WAXS/DSC

The simultaneous time-resolved SAXS/WAXS/DSC experiments were carried out on beamlines 8.2 of the SRS at the Daresbury, Warrington, UK. The camera was equipped with a multiwire quadrant SAXS detector located at 3.5 m from the sample position and a curved knife-edge WAXS detector that covered 120° of arc at a radius of 0.2 m. A Linkam apparatus with liquid nitrogen cooler was used to heat and cool the sample. The thermal procedures applied to the sample are the same as that in the DSC experiments. The data were collected in 6 s frames separated by a waiting-time of 10 μs. The invariant (Q) can be calculated by integration of Lorentz-corrected scattering intensity $I(q)q^2$ versus q from $q = 0$ to $q = \infty$. However, this need the extrapolation of $I(q)$ data to $q = 0$ and to $q = \infty$. Alternatively, only relative invariant (Q') was calculated according to following equation: [25]

$$Q' = \int_{q1}^{q2} I(q)q^2 \mathrm{d}q \tag{2}$$

where q_1 and q_2 are the q values of the first reliable data and the data where $\mathrm{I}(q)q^2$ is constant, are 0.007 and 0.20 Å^{-1}, respectively.

The crystallinity (X_c) of PEO domain in the graft copolymer was calculated from WAXS patterns based on Eq. (3):

$$X_c = \frac{A^{\mathrm{peak}}}{A^{\mathrm{total}} w_{\mathrm{EO}}} \tag{3}$$

where A^{peak} and A^{total} are the area of crystalline peaks and the total area, respectively, w_{EO} is the weight fraction of PEO in the graft copolymer. A^{peak} and A^{total} were obtained by XFIT program supplied by CCP13.

3. Results and discussion

The graft copolymer was precipitated with non-solvent after purification and dried in vacuum at 140 °C overnight, then was cooled and stored at room temperature. Fig. 1 shows the crystallization DSC trace of as-stored PS-*g*-PEO cooled from 70 °C and subsequent melting trace. Two crystallization peaks are observed in Fig. 1. Double crystallization peaks become more evident at a slower cooling rate. By contrast, when PS-*g*-PEO is heated to 150 °C and then cooled, only single crystallization peak is observed, as shown in Fig. 2. This result shows that crystallization behavior of PS-*g*-PEO is strongly dependent on start cooling temperature (T_o). The inserted picture in Fig. 2 represents the enlarged heating DSC curve of

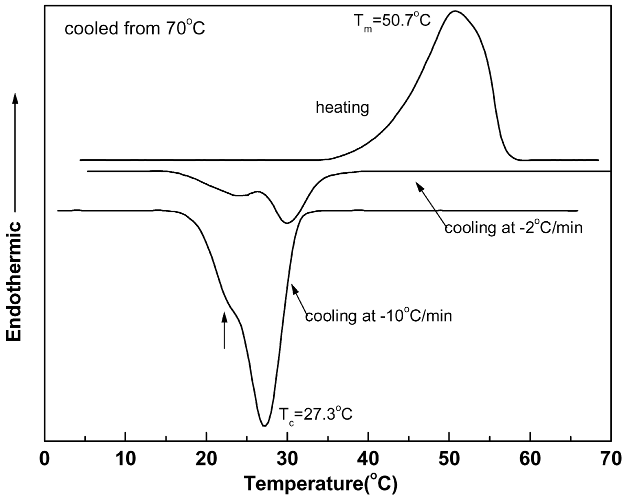

Fig. 1. Cooling and subsequent heating DSC curves of PS-*g*-PEO graft copolymer cooled from 70 °C.

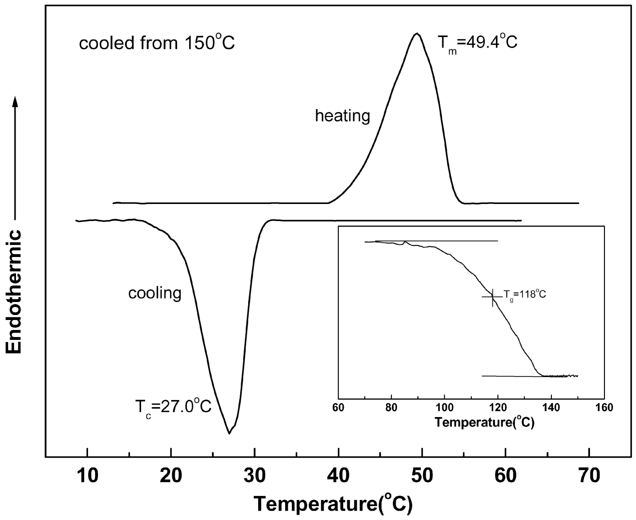

Fig. 2. Cooling and subsequent heating DSC curves of PS-*g*-PEO graft copolymer cooled from 150 °C.

PS-*g*-PEO in the range of 70–150 °C. A decrease in heat capacity due to glass transition of the PS main chain is observed in this temperature range. The glass transition temperature (T_g) of the PS is located at 118 °C, determined by the half change of heat capacity. Even ignoring the low molecular weight of PS main chain in the present work, such a T_g is still remarkably higher than the T_g of PS homopolymer, which is usually about 100 °C. This indicates that grafting of side chains reduces the mobility of the main chains and enhances the T_g of the main chains. Yao et al. [21] found that the crystalline main chains also increased the T_g of the side chains in poly(vinyl alcohol)-*g*-poly(methyl methacrylate) (PVA-*g*-PMMA) graft copolymer. As a result, the main chain and side chain reduce the mobility each other in a graft copolymer.

Since the two start cooling temperatures applied in the present work, 70 and 150 °C, are lower and higher than the T_g of the PS main chain, respectively, we speculate that the effect of T_o on the crystallization behavior of the PEO side chain is related to the T_g of the PS main chain. Therefore, time resolved SAXS and WAXS were used to verify this speculation.

3.1. SAXS/WAXS results

Fig. 3 shows the WAXS patterns of PS-*g*-PEO cooled from 70 and 150 °C. It is observed that the WAXS patterns of the graft copolymer are similar to those of PEO homopolymer, with two peaks at 19.4 and 23.9° corresponding to (120) and (032 + 112) reflections, respectively. The graft copolymer cooled from 70 °C is found to have higher crystallinity than that cooled from 150 °C, showing that T_o also affects crystallinity. The variations of crystallinity with temperature during cooling are shown in Fig. 4 and the differential curves are also depicted. Two stepwise evolutions of X_c are observed for the PS-*g*-PEO cooled from

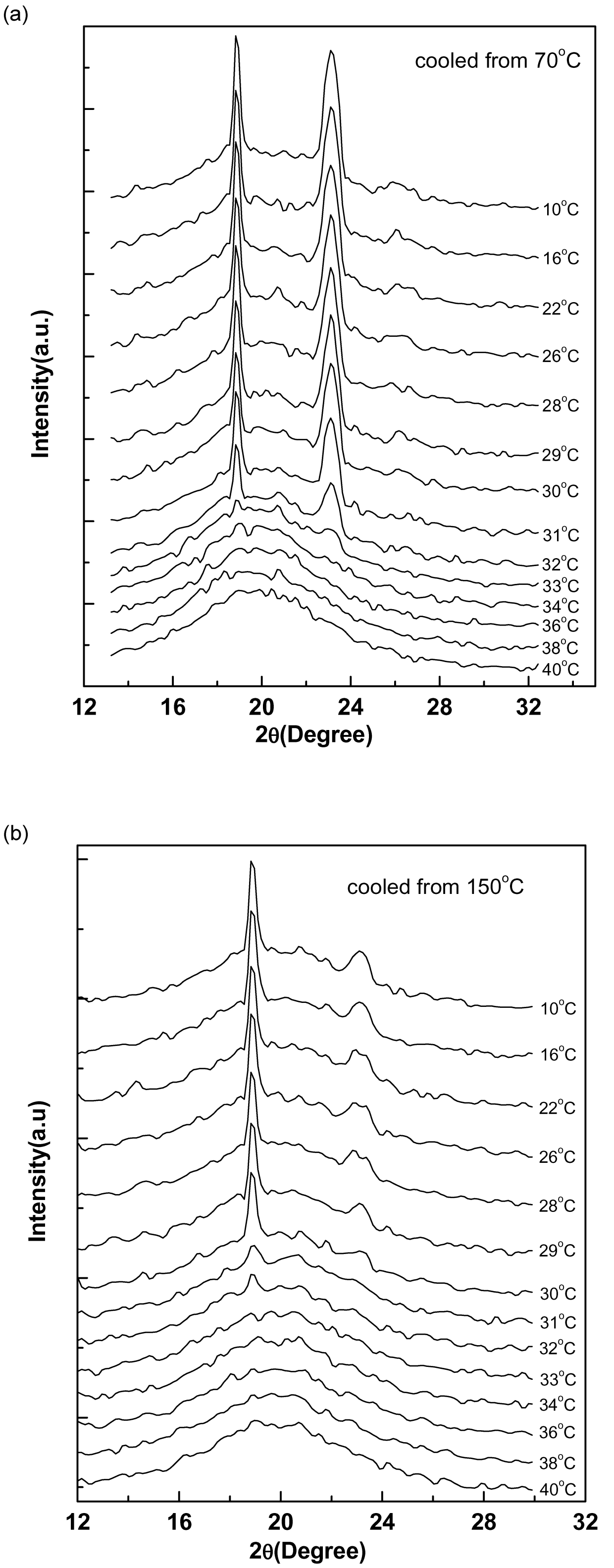

Fig. 3. WAXS patterns of PS-*g*-PEO graft copolymer during cooling. (a) Cooled from 70 °C; (b) cooled from 150 °C.

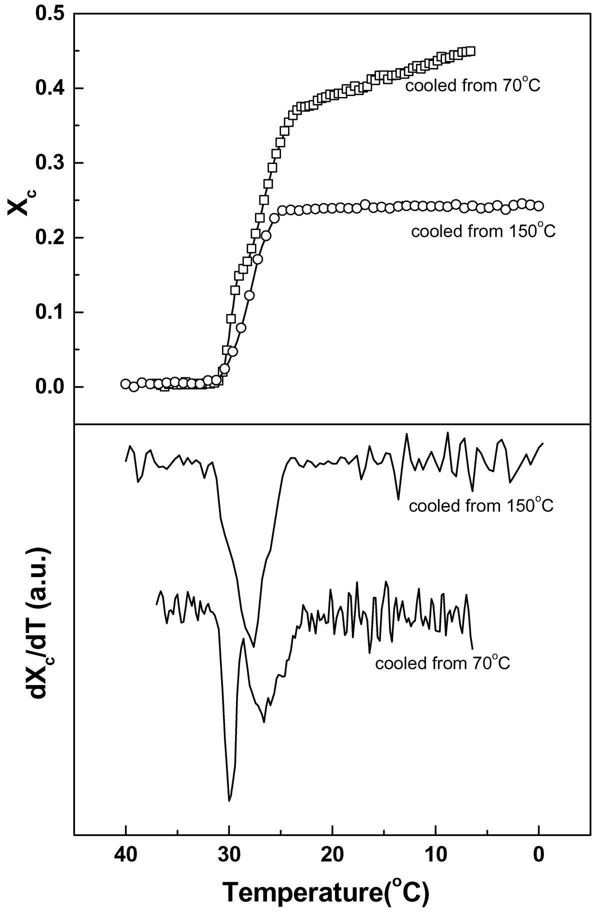

Fig. 4. Changes of crystallinity (X_c) and differential curves of X_c with temperature for PS-*g*-PEO graft copolymer during cooling.

70 °C and accordingly two peaks appear in the differential curve. This agrees well with DSC result. By contrast, the PS-*g*-PEO cooled from 150 °C only exhibits single step change of X_c and thus single peak in the differential curve of X_c.

The SAXS profiles for PS-*g*-PEO cooled from 70 and 150 °C, respectively, are shown in Fig. 5. For the sample cooled from 70 °C it seems that there is no SAXS peak in the melt, but a weak SAXS peak appears after crystallization (Fig. 5(a)). It is striking that the SAXS peak is not obvious for the sample cooled from 150 °C even after crystallization (Fig. 5(b)).

The changes of relative invariant during crystallization are shown in Fig. 6 [26]. In phase-separated state, the invariant can also be calculated from volume fractions of two phases, ϕ_{EO} and ϕ_S, and the square of the electron density difference between the two phases $\Delta\eta^2$: [27]

$$Q' = K\phi_{EO}\phi_S\Delta\eta^2 \tag{4}$$

It can be seen from Fig. 6 that Q' increases after crystallization due to the increase of the electron density in the PEO phase. The influence of T_o on Q' is similar to the influence on X_c. Fig. 7 shows the change of relative invariant in the subsequent melting process after the

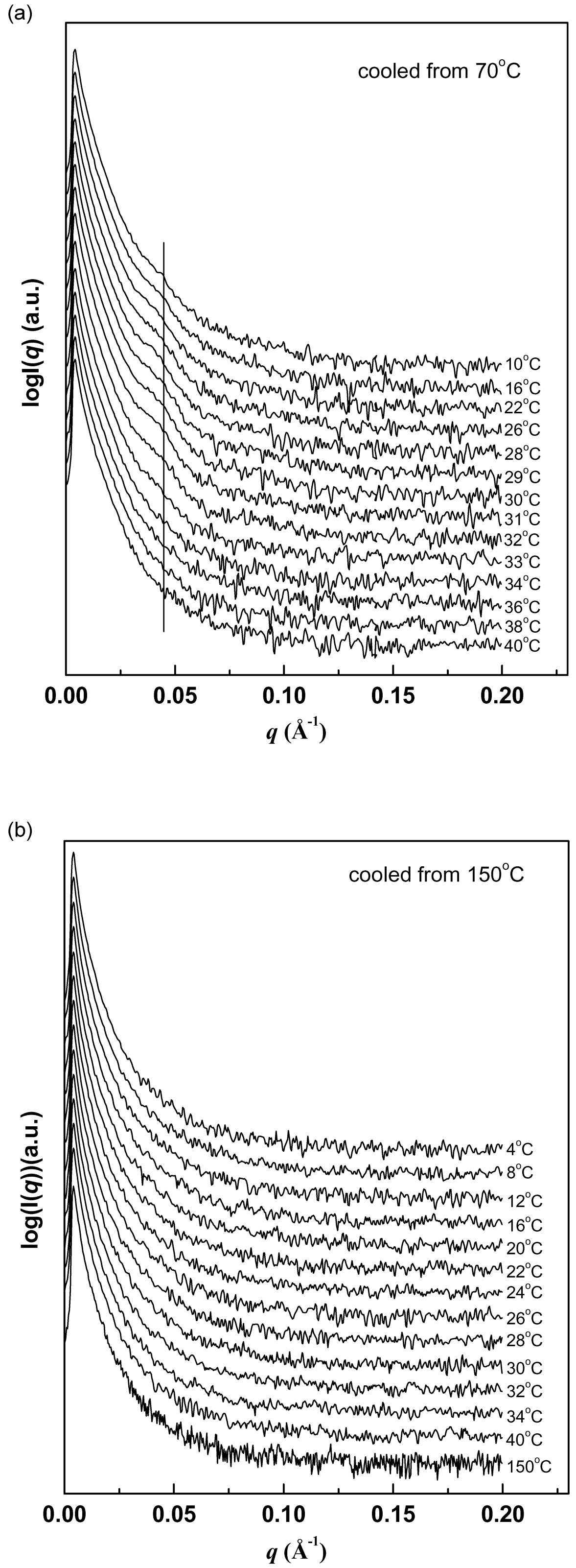

Fig. 5. SAXS profiles of PS-*g*-PEO graft copolymer during cooling. (a) Cooled from 70 °C; (b) cooled from 150 °C.

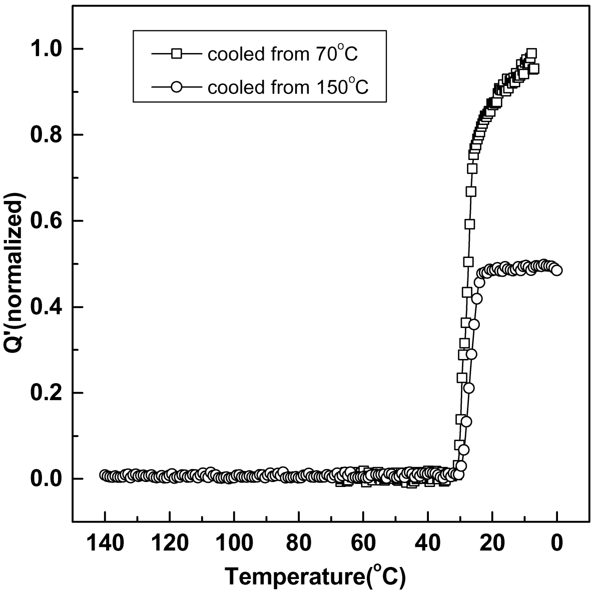

Fig. 6. Changes of relative invariant (Q') during cooling.

samples are cooled from 70 and 150 °C, respectively [26]. One can see that melting of the PEO crystals leads to a drastic decrease in Q'. Moreover, we also observe a remarkable decrease in Q' when the temperature exceeds the T_g of the PS main chain, irrespective of the T_o. This implies that phase-separation is at least partially retained after melting of the PEO crystals, though no SAXS peak is observed. The PS-*g*-PEO becomes homogeneous melt only above the T_g of the PS main chain. On the other hand, we cannot observe any increase in Q' before crystallization takes place when the sample is cooled from the melt (Fig. 6). Therefore, we can judge that the true phase separation temperature is between the T_g of PS main chain and T_c of PEO. Upon heating, the phase-separation state is vitrified between $T_m < T < T_g$ and it becomes homogeneous above T_g. When the graft copolymer is cooled from 150 °C, phase separation is suppressed due to the vitrification effect of the glassy main chain and phase separation is induced by crystallization of the PEO side chain. This shows that crystallization is a very strong drive force to phase separation and can overcome the vitrification of the glassy main chain.

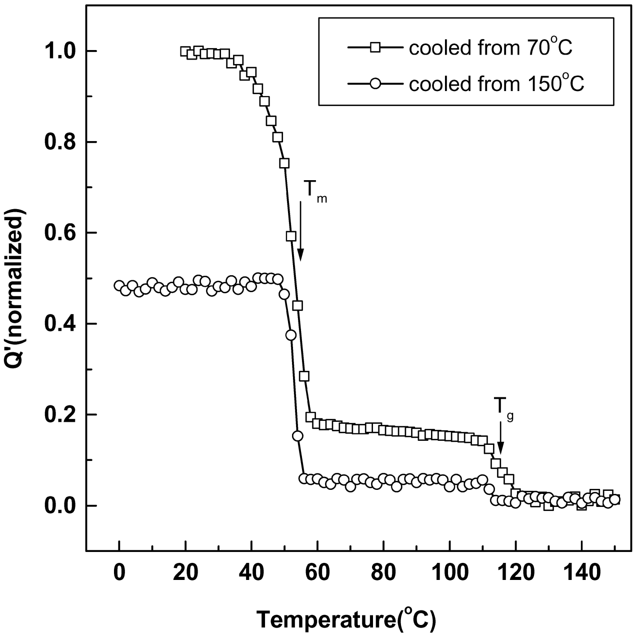

Fig. 7. Changes of relative invariant (Q') in the heating process after crystallization.

The results of SAXS/WAXS/DSC reveal that effect of start cooling temperature on crystallization of the PEO side chain is due to vitrification and depression of phase separation by the glassy main chain. When the graft copolymer is only heated to 70 °C and then cooled, PEO crystallizes from phase-separated melt and the conformation of the main chain is favorable to crystallization of PEO side chain. As a result, both PEO chains with high crystallizability (crystallizing at higher T_c) and lower crystallizability (crystallizing at lower T_c) can crystallize, leading to two crystallization peaks. The existence of PEO chains with different crystallizability probably originates from structural inhomogeneity, since the PS-*g*-PEO is synthesized through common radical polymerization. On the other hand, when cooled from 150 °C, above the T_g of PS, PEO crystallizes from homogeneous melt. The aggregation of PEO side chains requires the corresponding conformational change of the main chains but this is difficult to happen because the T_c is lower than the T_g of the PS main chains. With the unfavorable conformation of the PS main chain only the PEO side chains with high crystallizability can crystallize. The PEO side chains with lower crystallizability crystallize very slowly and cannot be detected by DSC. Accordingly, single crystallization peak appears in DSC cooling trace and the graft copolymer crystallized has a lower crystallinity. It should be noted that crystallization of PEO side chains with lower crystallizability does proceed below the T_g of the PS main chain, though at a slow rate, which is reflected by the enhanced crystallinity after long-term storage.

3.2. The effect of solvent

To reduce the glass transition temperature of the PS main chain, selective solvent for PS toluene was added into the graft copolymer. The weight percentage of solvent in the mixture of solvent and graft copolymer is 26.7%. The glass transition temperature of the PS main chain in the presence of solvent can be estimated using following equation: [28]

$$\frac{1}{T_g} = \frac{w_{PS}}{(T_g)_{PS}} + \frac{w_{solvent}}{(T_g)_{solvent}} \qquad (5)$$

Based on the assumption that solvent is exclusively present in the PS domain and the melting point (−93 °C) is taken as the T_g of the solvent toluene, the T_g of the PS main

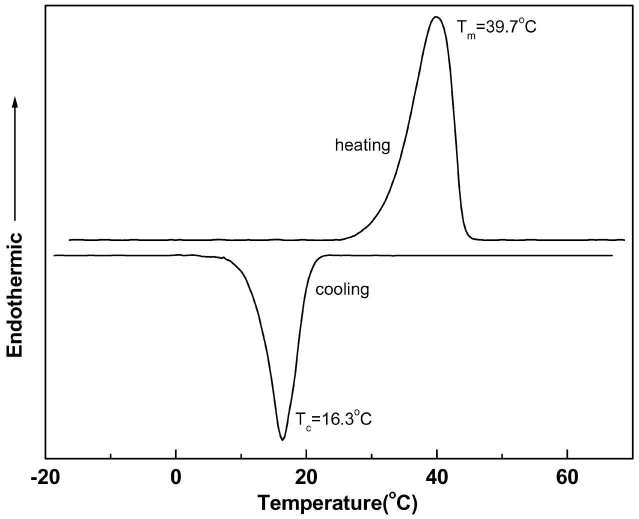

Fig. 8. Cooling and subsequent heating DSC curves of the mixture of PS-*g*-PEO graft copolymer with toluene.

chain in this graft copolymer containing solvent is about -30 °C.

Fig. 8 shows the DSC trace of such a mixture cooled from 70 °C and subsequent melting trace. It is found that the crystallization peak temperature of this mixture is 16.3 °C, higher than the T_g of the PS main chain. Only single crystallization peak is observed in Fig. 8, which is quite different from the neat graft copolymer without solvent. The crystallization and melting peaks also become much sharper after addition of toluene, indicating that more uniform PEO crystallites are formed. The SAXS and WAXS profiles during cooling of the solvent-containing PS-*g*-PEO are shown in Fig. 9. One can see that the SAXS peaks become more evident after crystallization when compared to the neat graft copolymer, possibly because toluene reduces the density of the PS domains and enlarges the electron density difference between the PEO domains and the PS domains. The WAXS peaks corresponding to (032 + 112) reflections are also very strong. The changes of crystallinity and relative invariant with temperature during cooling and corresponding differential curves are depicted in Fig. 10. Again single step change of X_c and Q' is found and single peaks appear in the differential curves. This shows that all the PEO side chains with different crystallizability crystallize at a relatively fast rate and cannot be distinguished by DSC. The crystallinity of PEO in the mixture of PS-*g*-PEO with toluene after complete crystallization is 0.52, similar to the neat graft copolymer, showing that PEO domains does not contain toluene and crystallinity of PEO is not affected by solvent.

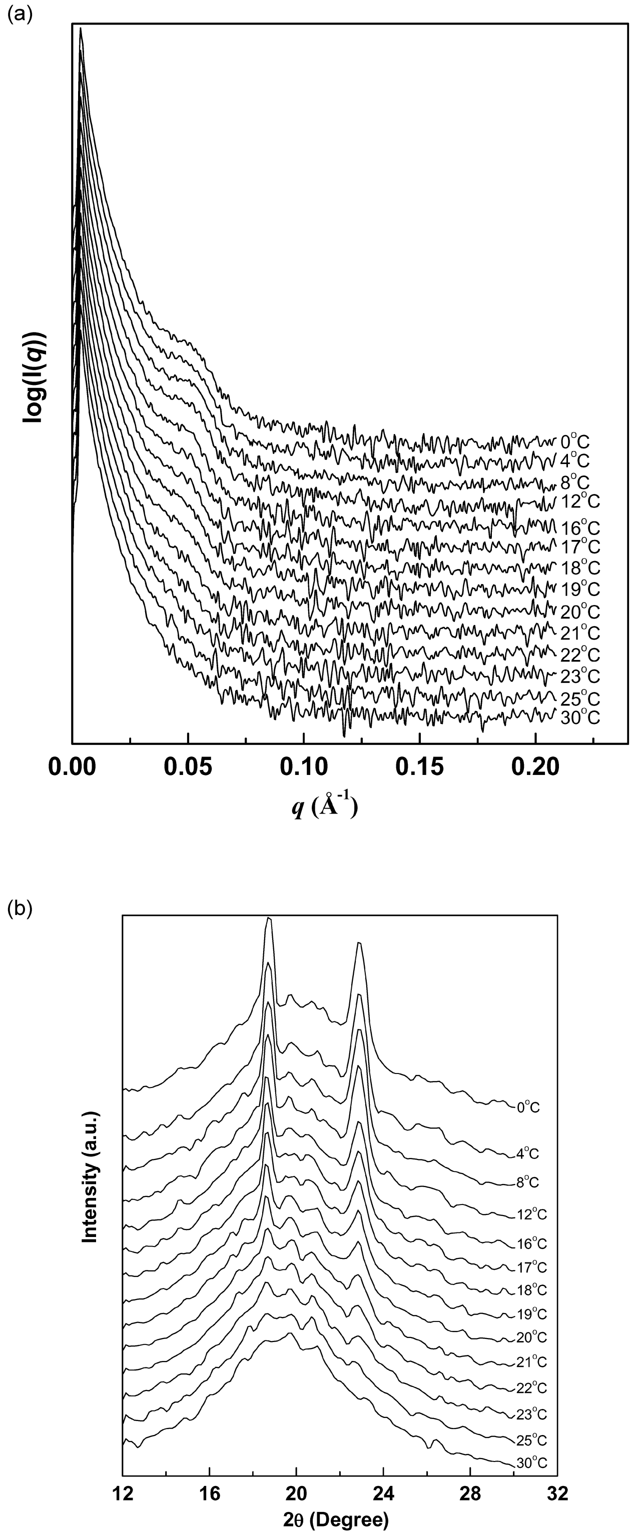

Fig. 9. SAXS and WAXS patterns during cooling for the mixture of PS-*g*-PEO graft copolymer with toluene.

4. Conclusion

Crystallization behaviors of PS-*g*-PEO graft copolymer are quite different when cooled from below and above the T_g of the PS main chain, originating from the vitrification effect of the main chain on phase separation. When cooled from above T_g, phase separation is depressed by the low mobility of the main chain and the PEO side chains crystallize from

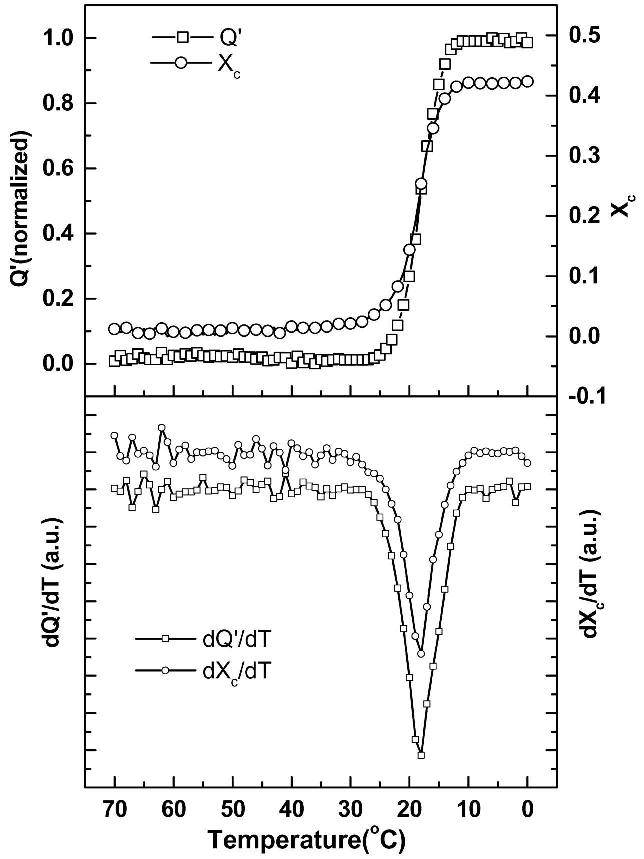

Fig. 10. Changes of X_c and Q' during cooling for the mixture of PS-*g*-PEO graft copolymer with toluene.

homogeneous melt, while cooled from below T_g, phase separation is retained and PEO side chains crystallize from phase-separated melt. Addition of selective solvent for the main chain, the T_g of the main chain is reduced and the vitrification effect disappears.

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