Thermal and Self-Nucleation Behavior of Molecular Complexes Formed by p-Nitrophenol and the Poly(ethylene oxide) End Block within an ABC Triblock Copolymer

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Summary: We have been able to prepare a molecular complex between the poly(ethylene oxide) block of a poly(ethylene)-*b*-poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) triblock copolymer and p-nitrophenol (PNP). The composition of the copolymer employed was: 24% PE, 57% PEP and 19% PEO in weight percent. The pure copolymer exhibited a non-conventional thermal behavior since the PEO block displayed a fractionated crystallization process during cooling. The PEO block /PNP complex did not show any apparent crystallization during cooling, instead cold crystallization during heating was observed and an approximately 30 °C increase in melting point as compared to the neat PEO block within the copolymer. This caused an overlap in the melting regions of the PE block and the PEO block/PNP complex. The self-nucleation of the PE-*b*-PEP-*b*-PEO/PNP complex is very different from that of the neat triblock copolymer. An increased capacity for self-nucleation of the PEO block was produced by the complexation with PNP and therefore the three self-nucleation domains were clearly encountered for both the PE block and for the PEO block/PNP complex. Self-nucleation was able to show that the two crystallizable blocks can be self-nucleated and annealed in an independent way, thereby ascertaining the presence of separate crystalline regions in the triblock copolymer. Through the use of PNP, both the crystallinity and the melting point of the PE-*b*-PEP-*b*-PEO block copolymer employed here can be substantially increased. Similar results were obtained by complexation of the same ABC triblock copolymer with resorcinol.

Introduction

The crystallization of polymers is known to depend very much on parameters like the size of crystallizable domains, the presence of heterogeneities, thermal history and other parameters. While polymers like polypropylene in the bulk state crystallize via the so-called heterogeneous nucleation, in blends it also may crystallize via homogeneous nucleation when the number of crystallizable domains exceeds the number of active heterogeneities originally present in the bulk polymer before dispersion [1-4]. In block

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copolymers with dispersed crystallizable domains (spheres or cylinders) there is a much higher number of domains per unit volume as compared to phase separated polymer blends. Thus in block copolymers there do exist various crystallization mechanisms within one sample, since different crystallizable microdomains will not all be containing the same type of heterogeneity [4-13].

In this contribution we investigate the crystallization behavior of a triblock copolymer in which two short crystallizable end blocks, namely polyethylene (PE) and poly(ethylene oxide) (PEO) are separated by an amorphous poly(ethylene-*alt*-propylene) (PEP) mid block. As a method differential scanning calorimetry (DSC) is applied by means of self nucleation experiments [14-15]. Moreover, it is well-known that PEO homopolymer can form well-defined complexes with low molecular weight components like p-nitrophenol leading to an increase of both melting and crystallization temperatures [16-17]. In the following it will be shown that such complexes can also be formed in a PEO containing block copolymer.

Experimental

The synthesis of the PE-*b*-PEP-*b*-PEO triblock copolymer (24% PE, 57% PEP and 19% PEO in weight percent with an overall M_n of 69 kg/mol) ($E_{24}EP_{57}EO_{19}{}^{69}$) was carried out by living anionic polymerization and subsequent hydrogenation using Wilkinson catalyst ($(Ph_3P)_3Rh(I)Cl$) [18]. Residual catalyst was removed by shortly heating a solution of the triblock copolymer in toluene with a small amount of concentrated aqueous HCl to reflux followed by precipitation into 2-propanol. $E_{24}EP_{57}EO_{19}{}^{69}$/PNP complex was prepared from toluene solution (molar ratio EO/PNP = 3/2). Details about DSC measurements and self-nucleation procedure can be found in refs. 12 and 13, which are based on ref. 14. Ts stands for self-nucleation temperature [12-14].

Results and Discussion

Figure 1 presents the typical crystallization and melting behavior of the $E_{24}EP_{57}EO_{19}{}^{69}$ triblock copolymer. The cooling scan displays an exotherm at around 65 °C where the PE block crystallizes. The PEO block needs a much higher supercooling in order to crystallize in view of a fractionated crystallization that has been reported for similar diblock and triblock copolymers containing small amounts of PEO [5-7, 11-13]. When the PEO component is well dispersed in the form of cylinders or spheres, the number of isolated microdomains (assuming that microphase segregation is complete and has occurred in the melt before crystallization) will be much higher than the number of heterogeneities that can cause nucleation at higher temperatures [11-13]. At least 10^{15} isolated PEO microdomains/cm^3 could be present, while for instance a bulk PEO homopolymer contains less than 10^6 heterogeneities/cm^3 [12-13]. Therefore fractionated crystallization takes place and in the case of the triblock copolymer of Fig. 1, the PEO block can only crystallize at approximately –25 °C (where most of the polymer crystallizes) and also at –45 °C (where only a very small fraction is crystallizing in Fig. 1). The crystallization at –25 °C is produced after nucleation by a weakly active heterogeneity present in the polymer [1, 12-13], while that at –45 °C is most probably due to the crystallization after homogeneous nucleation since PEO vitrifies at 56 °C under similar cooling conditions [1-3, 7, 11-13]. The subsequent melting trace of $E_{24}EP_{57}EO_{19}{}^{69}$ shows the melting endotherms of the PEO and the PE block at temperatures equivalent to those shown by homopolymers of similar molecular weight and microstructure [13].

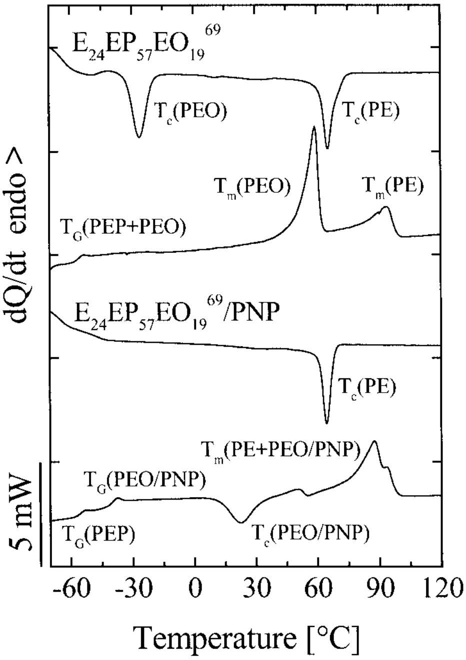

Figure 1. DSC cooling and heating scans at 10 °C/min for $E_{24}EP_{57}EO_{19}{}^{69}$ triblock copolymer (top) and for $E_{24}EP_{57}EO_{19}{}^{69}$/PNP complex (bottom).

Figure 1 also shows the DSC cooling and subsequent heating scans for the

$E_{24}EP_{57}EO_{19}^{69}$/PNP complex. In the cooling trace only the PE block exhibits a crystallization exotherm upon cooling from the melt while the PEO block either does not crystallize or crystallizes in a small amount or in a wide temperature range that cannot be detected. The subsequent heating trace exhibits a very clear Tg at –55 °C that corresponds to the PEP block and a second Tg located at –35 °C that should correspond to the PEO block/PNP molecular complex. At a temperature close to 20 °C a cold crystallization exotherm for the PEO block/PNP complex develops and a very small endotherm can be observed at 55 °C which could be due to the melting of a small fraction of PEO block crystals that could not form part of the complex with PNP. Finally a complex and broad melting endotherm is displayed beyond 75 °C. The high temperature shoulder of this melting endotherm could correspond to the melting of the PE block that now overlaps with the melting of the PEO block/PNP complex. The melting temperature of PEO homopolymer increases when it co-crystallizes with PNP as thicker and stable nonintegral-folded lamellae are formed [16-17]. Previous reports for PEO/PNP complexes of molar ratio 3/2 and with a PEO molecular weight of approximately 6000 g/mol indicate that these complexes have a melting temperature range of 75-95 °C depending on the crystallization temperatures employed [16].

The self-nucleation behavior of the $E_{24}EP_{57}EO_{19}^{69}$/PNP complex is displayed in Figure 2, where the cooling scans from selected Ts temperatures are shown in Fig. 2a while subsequent heatings can be seen in Fig. 2b.

At a Ts of 104 °C or higher melting is complete and Domain I is reached by both the PE block and the PEO block/PNP complex. Only the PE block displays a clear crystallization exotherm upon cooling from 104 °C. A lowering of Ts causes self-nucleation of the PE block within Domain II as indicated by the shift of the crystallization temperature of the PE block to higher temperatures in the DSC cooling scans corresponding to Ts temperatures of 100 °C down to 96 °C. No apparent changes in the subsequent heating traces in Fig. 2b are observed up to Ts = 96 °C as expected for Domain II [13-14].

At a Ts temperature of 94 °C annealing of the PE block starts as Domain III is reached. This can be verified in Fig. 2b where a high temperature peak corresponding to the melting of annealed PE crystals can be observed. Apart from this additional melting peak, the rest of the DSC heating scan remains more or less unchanged indicating that the PEO block/PNP complex has not been altered by the applied heat treatments at Ts greater or equal than 94 °C (i.e., the PEO block/PNP complex is still in Domain I at such Ts temperatures).

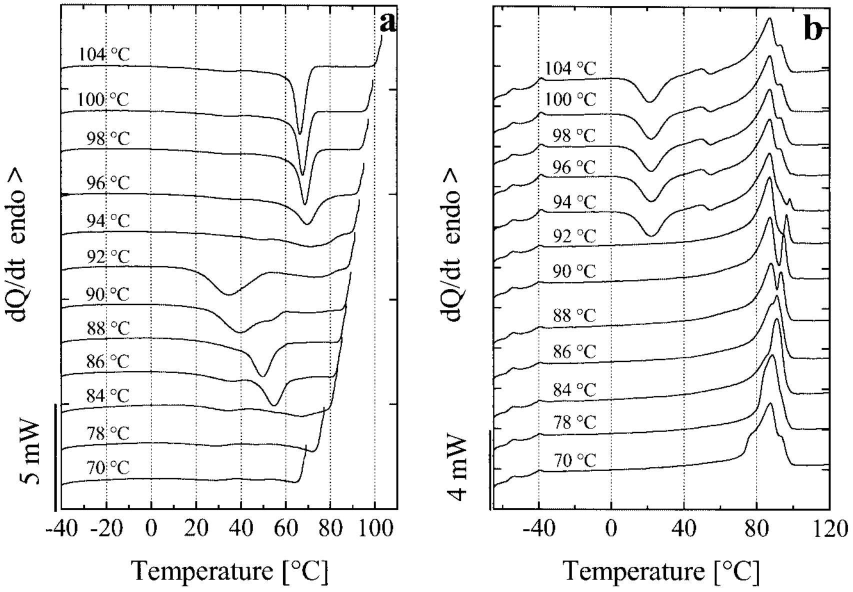

Figure 2. Self-nucleation behavior of $E_{24}EP_{57}EO_{19}^{69}$/PNP complex: a) DSC cooling scans from the indicated Ts temperatures and b) subsequent heating scans.

The PEO block/PNP complex is self-nucleated at a Ts = 92 °C as can be seen in Fig. 2a where a very prominent exotherm that peaks at approximately 35 °C is readily apparent, therefore Domain II is reached for the PEO block/PNP complex. This behavior differs from that of the pure triblock copolymer, where Domain II for the PEO block disappears as a consequence of the fractionated crystallization process (for details of the self-nucleation behavior of $E_{24}EP_{57}EO_{19}^{69}$ see reference 13).

The produced self-nuclei at 92 °C are causing the crystallization of the PEO block/PNP complex during cooling and therefore on a subsequent heating scan (Fig. 2b) no cold crystallization is observed. This heating scan (for Ts = 92 °C) also shows how the amount of annealed PE crystals has grown with a reduction in Ts as compared with the heating scan after self-nucleation at 94 °C. The final transition from Domain II to Domain III for the PEO block/PNP probably occurs at Ts = 84 °C as judged by the immediate crystallization upon cooling from this Ts temperature in Fig. 2a and by the change in the corresponding melting endotherm in Fig. 2b [14].

Similar results were obtained by complexing the PEO block of the $E_{24}EP_{57}EO_{19}^{69}$ triblock copolymer with resorcinol.

Conclusions

We successfully prepared a molecular complex between the PEO block of a $E_{24}EP_{57}EO_{19}^{69}$ triblock copolymer and PNP. The PEO block /PNP complex did not show any apparent crystallization upon cooling from the melt, instead cold crystallization during heating was observed and an approximately 30 °C increase in melting point as compared to the neat PEO block within the copolymer. An increased capacity for self-nucleation of the PEO block was produced by the complexation with PNP and therefore the three self-nucleation domains were clearly observed for both the PE block and the PEO block/PNP complex. Self-nucleation was helpful to ascertain the presence of separate crystalline regions in the triblock copolymer. Through the use of PNP, both the crystallinity and the melting point of the $E_{24}EP_{57}EO_{19}^{69}$ triblock copolymer employed were substantially increased. Similar results were obtained by complexation of the same ABC triblock copolymer with resorcinol.

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