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Crystallization and Physical Ageing of Poly (2-vinyl pyridine)-*b*-poly(ethylene oxide) Diblock Copolymers

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Summary: A set of melt miscible Poly(2-vinyl pyridine)-*b*-Poly(ethylene oxide) (P2VP-*b*-PEO) block copolymers of different compositions were studied. Transmission electron microscopy shows phase separation in the materials during the crystallization process of the PEO block as crystalline lamellae are observed for all compositions evaluated. The isothermal crystallization kinetics of PEO is progressively retarded as the P2VP content in the copolymer increases, since P2VP hinders molecular mobility in the miscible amorphous phase. Polarized light optical microscopy demonstrated that the glassy P2VP block has a negative effect on the secondary nucleation of the PEO. Finally, physical ageing experiments performed in the glassy state of the amorphous mixed phase, at different ageing times, demonstrated that a nucleating effect can be induced in the glassy state as a consequence of the reorganization of the amorphous regions. This nucleating effect significantly alters the cold crystallization rate upon subsequent heating above the glass transition temperature.

Keywords: block copolymers; crystallization; morphology; physical ageing; poly(ethylene oxide)

Introduction

Block copolymers with a crystallizable component have been extensively studied in recent years.[1–3] Firstly, because the block copolymers have the ability to self-organize in a large variety of fascinating morphologies on the scale of micro and nanometers (commonly referred to as microdomains, *MDs*), and secondly, because the final morphology has been found to be path-dependent, based on whether the crystallization occurs from a homogeneous state or a microphase-separated one.[1-3]

In this work, we have employed a series of poly (2-vinyl pyridine)-*block*-poly(ethylene oxide) diblock copolymers, P2VP-*b*-PEO, in a wide composition range. These diblock copolymers are characterized by having an amorphous block with a relatively high glass transition temperature (Tg) (i.e., P2VP) and a highly flexible and crystallizable covalently linked counterpart (i.e., PEO). These diblock copolymers are known to be miscible in the melt and in the amorphous state.[4] Therefore, the crystallization of the PEO block is expected to be dramatically affected by P2VP content.

The objective of the present work is to study the crystallization kinetics of the PEO block within these P2VP-*b*-PEO diblock copolymers since the crystallization window (highly dependent on the Tg value of the mixed amorphous phase) should vary in a significant way with copolymer composition. Additionally, as it will be shown

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below, these copolymers offer a good opportunity to study the effect of physical ageing on the subsequent crystallization of PEO.

Experimental Part

Materials

diblock copolymers of poly (ethylene oxide) (EO^{yy}_{xx}) and poly(2-vinyl pyridine) ($2VP^{yy}_{xx}$) were studied: $EO^{19}_{76}2VP^{6}_{24}$, $EO^{11}_{35}2VP^{20}_{65}$, $EO^{40}_{50}2VP^{40}_{50}$ and the homopolymers PEO^{2}, PEO^{5} and PEO^{27}, where the superscripts(yy) indicate the number average molecular mass (in kg/mol), and the subscripts (xx) indicate the weight composition (%) for each block. These materials where synthesized by sequential addition of the monomers using anionic polymerization high vacuum techniques and benzyl potassium as initiator.[5] The polydispersity index of all samples prepared range between 1.03 and 1.07.

Differential Scanning Calorimetry (DSC)

a Perkin-Elmer DSC PYRIS 1 using ultra pure nitrogen as inert medium was employed. The heating rate was 20 °C/min. Isothermal crystallization plus standard cooling and heating scans were evaluated.

The physical ageing essays were performed as follows: The sample was melted at 100 °C for 3 minutes. Then, it was quenched from the melt (at 60 °C/min) to the ageing temperature (T_{ageing}) and it was held at this first T_{ageing} for a given ageing time (from 2.2 to 300 min), then the sample was heated from T_{ageing} to 100 °C at 20 °C/min.

Morphology

The morphology was studied by polarized light optical microscopy (PLOM), using a Zeiss MC-80 optical microscopy with a Linkam TP-91 hot stage, and by transmission electron microscopy (TEM) with a JEOL 1220 operated at 100 kV. For TEM, thin films were prepared and isothermally crystallized at 40 °C for 6 hours.

Results and Discussion

It is important to recognize that P2VP and PEO are miscible in the molecular mass range employed in this work since their Flory-Huggins interaction parameter (χ) is very close to zero (the solubility parameters are similar). We have performed Tg measurements by DSC and we have shown that only one Tg is detected that follows the Flory-Fox equation closely (data not shown). These results are consistent with the reported miscibility of the components.[4]

Standard DSC heating and cooling runs are presented in Figure 1. As the P2VP content in the diblock copolymers increases, a depression of both the crystallization and melting temperatures can be observed. Since the components are miscible, increasing the amount of P2VP decreases the diffusion of the PEO chains to the crystallization front. The diffusion restrictions become so large that at a 50/50 composition, the PEO block can no longer crystallize during cooling from the melt. However, a nucleation process apparently occurs during vitrification, since in the subsequent heating run, the PEO block exhibits cold crystallization followed by melting.

Another important result is the effect of the molecular mass (M_n) upon the crystallization and melting behavior of the semicrystalline PEO. In the molecular mass range examined, the crystallization and melting temperature increase with M_n as expected.[6] The isothermal crystallization kinetics behavior is presented in Figure 2. The spherulitic growth rate was determined by PLOM and the overall crystallization rate (including both nucleation and growth) was determined by DSC and it is represented in Figure 2 as the inverse of the experimental half crystallization time. The crystallization rate is a function of the molecular mass of the PEO as expected.

The isothermal crystallization results are consistent with the standard DSC data discussed previously. It is important to point out the fact that both transformation rates, the overall and the spherulitic

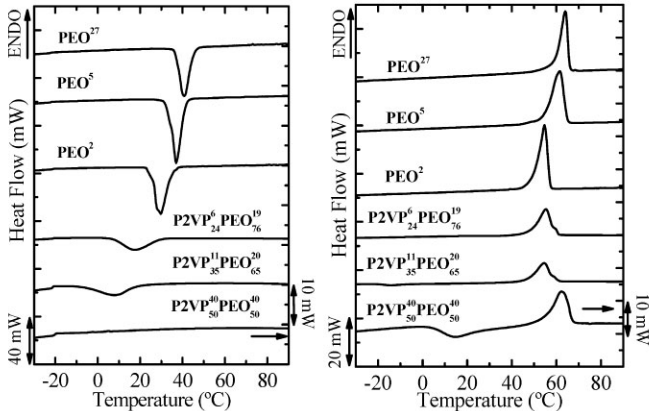

Figure 1.
Standard DSC cooling (left) and heating (right) scans (at 20 °C/min) for the homopolymers and block copolymers indicated.

crystallization rates, followed the same trend as function of the composition of the block copolymer and as function of the molecular mass of the PEO homopolymers. The increase in supercooling needed to crystallize PEO within the diblock copolymers as compared to neat PEO samples is caused by two effects: the topological restrictions imposed by chain tethering and the diffusion hindrance caused by the miscibility with the more rigid P2VP chains. In fact, as the PEO content within the block copolymers decreases, more supercooling is needed for crystallization as the Tg of the material increases and the crystallization window narrows.

TEM micrographs for different diblock copolymers samples are presented in Figure 3. Regardless of composition, only PEO crystalline lamellae structures are

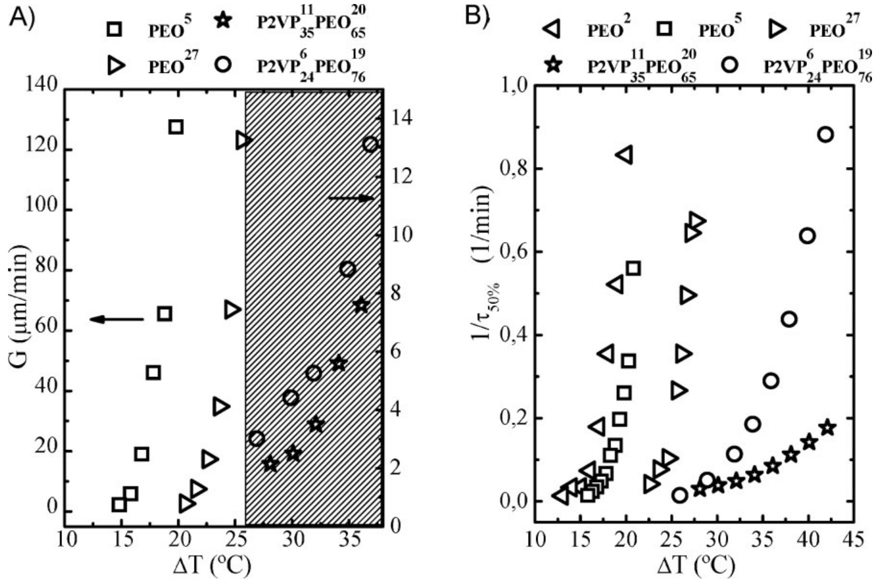

Figure 2.
Spherulitic (A) and Overall (B) crystallization rates for the homopolymers and block copolymers indicated.

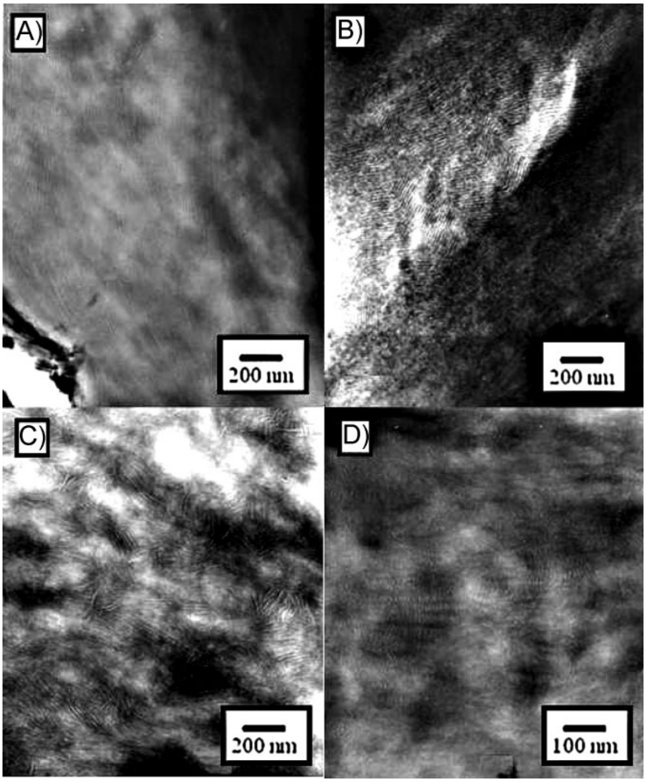

Figure 3.
TEM micrographs for $P2VP^{40}_{50}PEO^{40}_{50}$ (A and B), $P2VP^{6}_{24}PEO^{19}_{76}$ (C) and $P2VP^{11}_{35}PEO^{20}_{65}$ (D).

observed. These results are consistent with the expectation of crystallization from a single phase melt of diblock copolymers in the weak segregation regime or fully miscible [1,3]. Once more, these results verify that both components are miscible in the melt and in the amorphous regions of the sample after PEO crystallizes. Small angle X-ray scattering experiments are fully consistent with this interpretation (results not shown).

PLOM observations for $EO^{11}_{35}2VP^{20}_{65}$ and $EO^{19}_{76}2VP^{6}_{24}$ revealed that the samples exhibited two different crystalline superstructures sometimes at identical crystallization temperatures (see Figure 4 for two typical examples): the expected spherulitic superstructure (although as in Figure 4 (left) sometimes they tended to have not perfectly circular interfaces with the melt) and a single crystal like morphology. These kinds of superstructures have been previously reported in the literature in similar copolymers [7]. The single crystal like morphology has been attributed [7] to the inhibition of secondary nucleation of PEO by the glassy P2VP block. One interesting result that has been found in the present work is that both types of structure (spherulites and single crystals) exhibited the same growth rate at the same isothermal crystallization temperature, a fact that could be expected since G values reflect exclusively the growth of already nucleated structures.

As previously shown in Figure 1, the PEO block within $P2VP^{40}_{50}PEO^{40}_{50}$ does not crystallize upon cooling from the melt (although it can undergo nucleation, possibly during vitrification) but undergoes cold crystallization when subsequently heated. In order to investigate this behavior

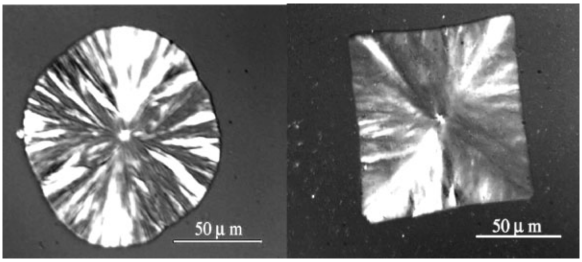

Figure 4.
PLOM morphologies found for the P2VP$^{6}_{24}$PEO$^{19}_{76}$ copolymer during isothermal crystallization at 43 °C (left) and 45 °C (right).

in more detail, we performed isothermal annealing at temperatures lower than Tg to induce physical ageing. After this isothermal annealing, the sample was heated at 20 °C/min in order to register its cold crystallization and final melting. An example of the results obtained is presented in Figure 5. As annealing time increases, the cold crystallization peak shifts to lower temperatures, a sign of nucleation when the crystallization proceeds from the amorphous state. Figure 5 also shows how the size of the cold crystallization exotherm increases, as the sample is able to crystallize more during the heating process.

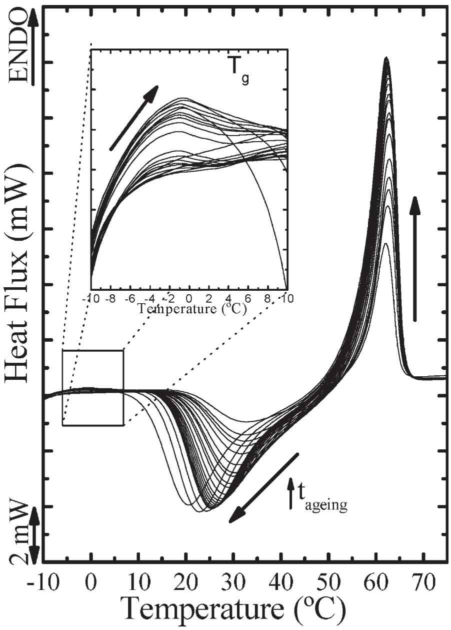

Figure 5.
DSC heating scans, at 20 °C/min, after physical ageing at −15 °C for different annealing times: from 2.2 to 300 min.

The changes in the rate of cold crystallization can be attributed to an increase in the number of active nuclei in the sample caused by the rearrangement of the amorphous zone due to the ageing process. A similar behavior has also been reported for poly (*L*-lactic Acid) and for poly (ethylene terephthalate).[8] Pan et al. [8] found that the reorganization process that occurs by physical ageing changes the conformation of the PLLA chains from gauche-gauche (gg) to gauche-trans (gt), which is a state that promotes the crystallization when the sample is heated above its glass transition temperature (Tg).[8,9] The increase in the rate of crystallization can be evaluated by following the cold crystallization peak temperature (Tp) (see Figure 6) as function of the ageing time. Figure 6 also shows another interesting result for the ageing behavior of this block copolymer, since as the difference between the ageing temperature and the Tg value was greater (i.e., as the ageing temperature is lowered) the cold crystallization enthalpy (ΔHp) reached a maximum value faster (i.e., at lower ageing times). This peculiar enhanced nucleation is still under investigation.

Conclusions

As the P2VP content within the diblock copolymer P2VP-*b*-PEO increased, the

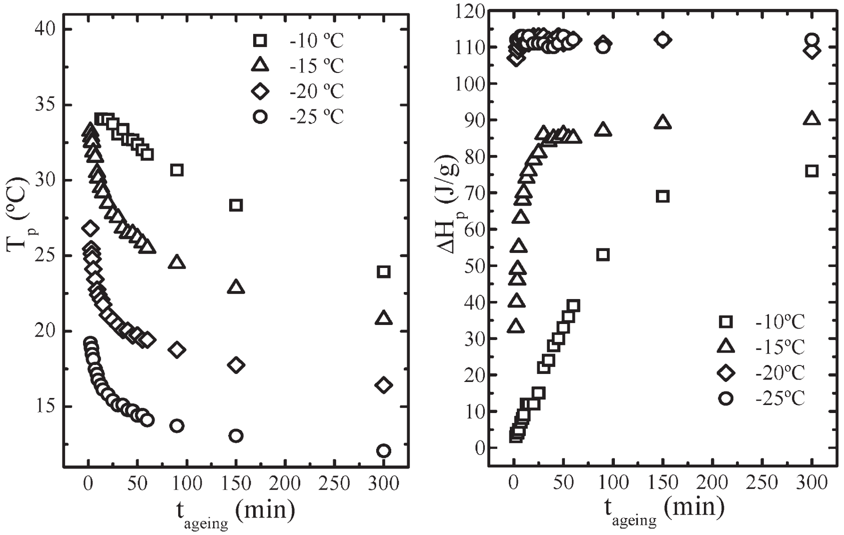

Figure 6.
Variations in the peak cold crystallization temperature (Tp) and in the cold crystallization enthalpy (ΔHp) as a function of the ageing time for $P2VP_{50}^{40}PEO_{50}^{40}$.

crystallization and melting temperatures of the PEO block were lower as a result of the miscibility between both components. The overall crystallization rate as well as the spherulitic growth rate decreased as the content of P2VP increased, indicating the diffusion restrictions encountered by the PEO component during its crystallization. Also, the presence of the glassy P2VP block inhibited the secondary nucleation of the PEO (at low supercoolings) and produced a single crystal-like morphology. Physical ageing experiments were performed and it was found that the time and the temperature for the ageing process affected the PEO nucleation process and changed the dynamics of the cold crystallization behavior for the $P2VP_{50}^{40}PEO_{50}^{40}$ diblock copolymer.

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