DOI: 10.1002/masy.200651321

Crystallization Kinetics of Homogeneous and Melt Segregated PE Containing Diblock Copolymers

Alejandro J. Müller,[1] Arnaldo T. Lorenzo,[1] Reina V. Castillo,[1] María Luisa Arnal,[1] Adriana Boschetti-de-Fierro,[2] Volker Abetz[2]*

Summary: The crystallization behavior of four types of polyethylene (PE) containing diblock copolymers with an approximate 50/50 composition has been investigated and compared with their respective PE homopolymers. A glassy block of polystyrene (PS), a rubbery block of poly (D,L-lactide) (PDLA), a semicrystalline block of poly (L-lactide) (PLLA) and a miscible block of (poly(ethylene-*alt*-propylene) (PEP) were used to asses the influence of the degree of confinement and miscibility on the crystallization kinetics of PE. PEP had the largest effect on the crystallization kinetics of the PE block in view of its miscibility. For the strongly segregated systems larger restrictions were imposed by vitreous PS due to hard confinement as compared with the soft confinement of the rubbery PDLA block. A nucleation effect of previously crystallized PLLA on the PE block was detected which offset its depression of the crystallization kinetics of PE.

Keywords: crystallization kinetics; double crystalline diblock copolymers; polyethylene block

Introduction

Over the years, the crystallization behavior of diblock copolymers with one crystallizable block has been extensively studied and it is still a field of much interest,[1–9] however double crystalline diblock copolymers have been discussed to a much lesser extent.[9,10] Diblock copolymers provide well-defined model systems for studying self-assembly because the composition and interactions can be controlled over a wide range.[1] Crystallization processes are influenced by whether the sample is cooled from a microphase-separated melt or from a homogeneous melt. On cooling from the melt, the structural changes due to the crystallization process compete with those due to microphase separation, and the final morphology will depend on whether crystallization is confined, templated or unconfined.[2,9] Additionally, the nature of the covalently bonded block (glassy, rubbery or semicrystalline) is known to affect crystallization kinetics of the neighboring crystalline block.[1,2,9]

In this work, the thermal behaviour of several nearly symmetric polyethylene (PE) containing diblock copolymers with different degrees of segregation strength are studied. Diblock copolymers of PE-*b*-PLDA (polyethylene-*block*-poly(L,D-lactide)), PE-*b*-PLLA (polyethylene-*block*-poly(L-lactide)), PE-*b*-PS (polyethylene-*block*-polystyrene) and PE-*b*-PEP (poly(ethylene-*alt*-propylene)-*block*-polyethylene), with similar weight composition were evaluated. The PLDA block is a mixture of L and D configurational isomers. It can not crystallize and has a T_g value of 55 °C. Both PE and PLLA can crystallize in the PLLA-*b*-PE diblock copolymers. On the other hand, PS and PEP blocks, are both amorphous but their T_g values are higher ($T_g = 100\,^{\circ}C$)

---

[1] Grupo de Polímeros USB, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar. Apartado 89000, Caracas 1080-A, Venezuela
E-mail: amuller@usb.ve

[2] Institut für Polymerforschung, GKSS-Forschungszentrum Geesthacht GmbH, 21502 Geesthacht, Germany

and lower ($T_g = -63\,^\circ C$) than the PE crystallization temperatures. These systems were used in order to evaluate the crystallization behaviour of the PE block when it is covalently attached to different second blocks. The influence of the physical nature of the second block in strongly segregated diblock copolymers on the crystallization kinetics of the PE block was examined (at PE crystallization temperatures PS is glassy, PDLA rubbery and PLLA semi-crystalline). Additionally, the influence of having a miscible block like PEP covalently bonded to the PE block was examined.

Experimental Section

Materials

The synthesis of well defined PE -*b*-PLDA , PE-*b*-PLLA, PE-*b*-PS and PE-*b*-PEP block copolymers has been previously described.[11–14] The PE block has been prepared by hydrogenating a high 1,4-polybutadiene and it can be considered a random copolymer of ethylene and butene (with a low butene content, see Table 1). Table 1 lists the molecular weight characterization data obtained by size exclusion chromatography (SEC) and composition obtained by ^{1}H NMR spectroscopy. The diblock copolymer nomenclature that we have used in Table 1 denotes the PLLA block as L, PLDA block as LD, PS block as S, PEP block as EP and the PE block as E. Additionally, subscripts indicate the approximate composition in weight % and superscripts the approximate number average total molecular weight of the copolymer, in kg/mol.

Differential Scanning Calorimetry (DSC)

Perkin-Elmer DSC-7 and Pyris 1 differential scanning calorimeters were employed. Samples were encapsulated in aluminium pans (mass was approximately 5mg). The calibration was performed with indium and hexatriacontane and all tests were run employing ultra pure nitrogen as purge gas.

The PE isothermal crystallization experiments were also carried out by DSC. The samples were first heated to a temperature of approximately 30 °C higher than the melting point of the PE blocks and kept at that temperature for 3 min in order to erase the thermal history. Then the samples were cooled at 60 °C/min to the isothermal crystallization temperature and the DSC recorded the crystallization process as a function of time. In the case of $L_{46}E_{54}^{50}$ copolymer, the PLLA block was crystallized until saturation (at 130 °C) before performing the PE block isothermal crystallization.[15]

Results and Discussion

The degree of thermodynamic segregation within the block components can be approximated to the following sequence: PE-*b*-PLLA $\sim$ PE-*b*-PDLA $>$ PE-*b*-PS $\gg$ PE-*b*-PEP and the first three systems can be

Table 1.
Molecular Characteristics of the Block Copolymers and Homopolymers.

Copolymers	Exp. Composition$^{a)}$	$\overline{M}_n$ (Kg · mol^{-1}) PE block	$\overline{M}_n$ (Kg · mol^{-1})$^{b)}$ Total copolymer	PE % 1,2 Units	Polydisp.$^{c)}$ *D*
PE^{25}	100	25	24	11.0	1.01
$E_{53}S_{47}^{51}$	53/47	26	51	11.3	1.04
$E_{54}EP_{46}^{53}$	54/46	26	53	11.2	1.02
PE^{28}	100	28	28	7.0	–
$E_{54}L_{46}^{50}$	54/46	27	50	7.2	–
$E_{46}LD_{54}^{60}$	46/54	28	60	7.0	–

a) Experimental compositions as determined by ^{1}H NMR spectroscopy.
b) Experimental Total $\overline{M}_n$ estimated by ^{1}H NMR spectroscopy.
c) Polydispersity index determined by SEC.

considered as strongly segregated in the melt while the last one is either very weakly segregated in the melt or miscible.[9,13–15] Therefore, for nearly symmetric compositions, in the first three cases we have observed lamellar morphologies by TEM (Transmission Electron Microscopy) where crystallization occurs within the microphase separated lamellae without any break-out (no spherulites are formed in these copolymers), as expected for strongly segregated systems. For PE-*b*-PEP, the crystallization occurs from a mixed melt and after crystallization, PE crystalline lamellae were observed in a matrix of mixed amorphous PE/PEP by TEM (TEM results not shown).

Figure 1 shows the DSC cooling (left) and subsequent heating scans (right) at 10 °C/min for the PE containing diblock copolymers under study and for their respective PE precursors: PE^{25} (for the $E_{53}S_{47}^{51}$ and $E_{54}EP_{46}^{53}$) and PE^{28} (for $E_{54}L_{46}^{50}$ and $E_{46}LD_{54}^{60}$). Also, Table 2 lists all relevant transition temperatures and enthalpies extracted from Figure 1. PE^{25} and PE^{28} exhibit peak melting temperatures (T_m) of 98.7 and 107.5 °C respectively, a reflection of their different short chain branching contents (see Table 1 where the 1,2 units content on the parent PB are reported). A difference is also observed in the peak crystallization temperature of the PE's for the same reason (see Figure 1 and Table 2).

Table 2.
Thermal Properties obtained from DSC scans presented in Figure 1 for the PE block within the diblock copolymers and for PE homopolymers.

Copolymer	$T_{c,\ peak}$	ΔH_c	$T_{m,\ peak}$	ΔH_m
	°C	$J \cdot g^{-1}$	°C	$J \cdot g^{-1}$
PE^{25}	85.2	−101	98.7	98
$E_{53}S_{47}^{51}$	74.4	−68	97.9	66
$E_{54}EP_{46}^{53}$	66.2	−79	91.3	76
PE^{28}	94.3	−105	107.5	110
$E_{54}L_{46}^{50}$	88.7	–	104.2	–
$E_{46}LD_{54}^{60}$	88.3	−109	103.2	115

The $E_{54}L_{46}^{50}$ diblock exhibits two well defined fusion endotherms (although PE^{28} exhibits a sharp melting peak followed by a broad tail in the low temperature range in Figure 1), while both blocks crystallized in a single coincident exotherm upon cooling from the melt.[15] The restrictions imposed by the PE block upon the crystallization of the PLLA block caused the coincident crystallization phenomena to occur. This coincident crystallization was confirmed in a previous study,[15] where some fraction of PLLA crystallizes in coincident fashion

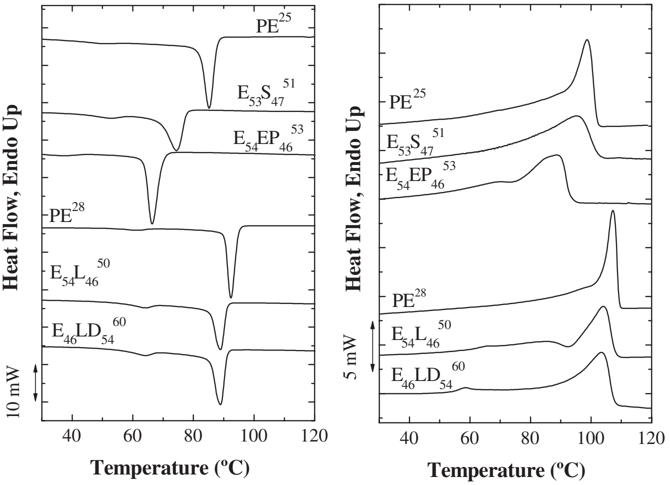

Figure 1.
Left side: DSC cooling scans at 10 °C/min, *Right side:* DSC subsequent heating scans (at 10 °C/min) to the cooling scans presented in the left side.

with PE when is cooled at rates higher than 10 °C/min, while most of the PLLA crystallizes during subsequent heating, this cold crystallization overlaps with the malting of the PE block and produces the apparently bimodal fusion shown in Figure 1, details can be found in ref.[15] The PE block within the $E_{54}L_{46}^{50}$ crystallizes at a peak temperature of 88.7 °C while the PE block within $E_{46}LD_{54}^{60}$ does it at 88.3 °C. If the PLLA block is crystallized until saturation at temperatures where the PE block is molten (130 °C) and then later cool down, a nucleation effect of the PLLA on the PE can be observed.[15] This fact will be reflected further below in the crystallization kinetics of the PE block.

For $E_{53}S_{47}^{51}$, the crystallization of the PE block occurs after its covalently bonded neighbor PS has vitrified and develops within its phase separated lamellar microdomains, therefore strong topological restrictions on the PE chains cause the T_c value to decrease considerably (about 10 °C) as compared to neat PE^{25}. In the $E_{54}EP_{46}^{53}$ diblock copolymer case, a strong diluent effect of the rubbery PEP block over the PE crystallization is clearly observed. Figure 1 and Table 2 show that the difference between the T_m and T_c values of PE^{25} and $E_{54}EP_{46}^{53}$ diblock copolymer is very large. This marked diluent effect is probably due to the miscibility of the amorphous PEP with PE due to similarity in their chemical structures ($\chi_{E/EP} = 7.00 \times 10^{-3}$ at room temperature).[16,17]

We can conclude from this section that the crystallization behavior of the PE block is affected (i.e., T_c is depressed as compared to that exhibited by its equivalent neat PE sample) to a higher degree by the PEP block (a strong diluent effect), and then to a lesser degree by the topological restrictions of the strongly segregated glassy PS, rubbery PLDA and semicrystalline PLLA blocks, in that order of importance. These effects were confirmed by crystallization kinetics and will be clearly explained below.

The data obtained by DSC from the isothermal crystallization of PE's and the PE blocks within all diblocks employed here was analyzed with the Avrami equation[18–27]:

$$1 - V_c(t) = \exp(-kt^n) \qquad \text{(ec. 1)}$$

where: V_c is the relative volumetric transformed fraction (i.e., relative amount of material that has crystallized), n is the Avrami index and k the overall crystallization rate constant (i.e., it contains contributions from both nucleation and growth). The analysis of the data was performed by applying the Avrami equation during the primary crystallization stage, i.e., we have employed a relative crystalline conversion range of 3–20% for all samples.

Figure 2 shows how the Avrami index for the PE samples exhibits a tendency to increase with T_c, such a trend has been related to changes in the nucleation mechanism from instantaneous to more sporadic nucleation when growth dimensionality is kept constant.[25–27] However, the PE Avrami indices are in the range in between 2.5 and 3 corresponding to spherulitic crystallization arising from approximately instantaneous nucleation processes, a result often reported in the literature for polyethylene samples.[23–27]

The PE block within the strongly segregated diblock copolymers ($E_{53}S_{47}^{51}$, $E_{54}L_{46}^{50}$ and $E_{46}LD_{54}^{60}$) exhibit lower values than those observed for PE samples. This decrease in the Avrami index values is due to dimensionality restrictions imposed by the lamellar microdomain morphology confinement. In fact no spherulites are observed for these strongly segregated diblock copolymers with lamellar microdomain morphologies. Therefore, the morphology is reduced to two dimensional lamellar crystallization arrangements within the phase separated microdomains. Changes in the crystallization temperature range to lower values is another evidence of the restrictions that the PE block is facing in order to crystallize, in other words, larger supercoolings are needed to crystallize the PE block within the diblock copolymers as compared with the parent PE. The diluent effect of the PEP block upon PE crystal-

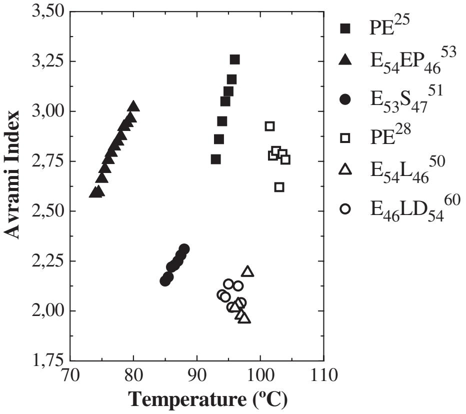

Figure 2.
Avrami index values of the PE homopolymers and the diblock copolymers, obtained by fitting isothermal crystallization data obtained by DSC.

lization produces a large shift to lower T_c values and, in contrast to the strongly segregated copolymers, the Avrami indexes are in the same range as the values shown by PE^{25}. This important result suggest that since PE and PEP are miscible there are no dimensionality restrictions for PE to develop spherulites in the PE-*b*-PEP diblock copolymers, only a strong dilution effect.

Another interesting result is shown in Figure 3, where the inverse of half-crystallization times are plotted as a function of supercooling degree. The supercooling represented in Figure 3 was obtained from values of the equilibrium melting point calculated by Flory's equilibrium theory for copolymer melting[17,18,25–27]:

$$\frac{1}{Tm_c^0} - \frac{1}{Tm^0} = \frac{-R}{\Delta h_u} \ln p \qquad \text{(ec. 2)}$$

where Tm_c^0 is the equilibrium melting temperature of the copolymer, Tm^0 is the equilibrium melting temperature for linear polyethylene, i.e., 145.5 °C, R is the uni-

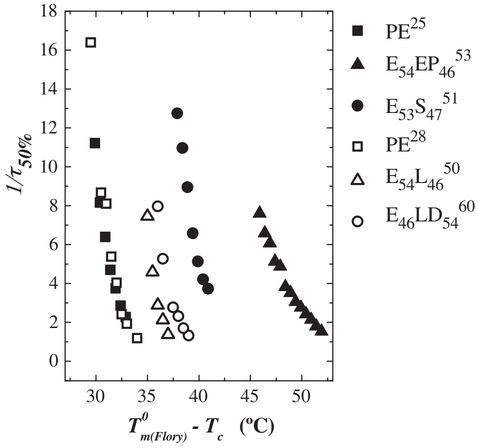

Figure 3.
Variation of the overall crystallization rate expressed as the experimental inverse half-crystallization time as a function of the supercooling degree ($T^0_{m\ (Flory)} - T_c$) for the PE samples and for the PE block within the specified diblock copolymers.

versal gas constant, $\Delta h_u = 960$ cal/mol and $p = X_A$ (in this case, the molar fraction of ethylene for a random copolymer of ethylene and an α-olefin). The values for the equilibrium melting temperatures thus obtained for the PE samples are 125.9 °C and 133.0 °C for PE^{25} and PE^{28}, respectively. These values were employed to calculate the supercooling of each set of samples, i.e., 125.9 °C was employed as the equilibrium melting temperature for PE^{25}, and for the PE block within PE-*b*-PEP and PE-*b*-PS, while 133 °C was employed for the rest of the samples.

In this case, the values of the equilibrium melting temperatures calculated by Flory's theory yielded reasonable results since both PE samples exhibit almost the same crystallization kinetics curve in Figure 3, a fact indicating that the differences in branching content are adequately taken into account by the degree of supercooling in these sets of samples. Figure 3 therefore allows us to establish a valid comparison between the PE block crystallization kinetics of all the diblock copolymers studied, regardless of the 1,2 units content in the PB precursors.

Figure 3 shows that the diluent effect of the PEP block upon the PE block crystallization is stronger than the topological restrictions imposed by the other blocks, since the highest supercooling values are needed in order to crystallize the PE chains. The confinement effect that the glassy PS block has upon the PE crystallization is stronger than restrictions imposed by the rubbery PLDA block or even the semicrystalline PLLA. The larger effect of glassy PS as compared to rubbery PDLA on the PE block crystallization may seem intuitively expected. However, it is interesting to note that in weakly segregated diblock copolymers like poly(p-dioxanone)-block-poly(ε-caprolactone), PPDX-*b*-PCL, the rubbery PCL block had a dramatic effect depressing PPDX crystallization rate by at least one order of magnitude.[30,31] Also, the crystallization kinetics is slower for the PE block covalently bonded to amorphous and rubbery PLDA (within $E_{46}LD_{54}^{60}$) as compared to that of the PE block attached to previously crystallized PLLA (within $E_{54}L_{46}^{50}$). This behavior could be explained if we take into consideration the nucleating influence of PLLA crystals on the PE crystallization, an effect that may cause the acceleration of the overall crystallization kinetics.[15]

Conclusions

The crystallization of the PE block has been shown to be influenced by its neighboring covalently bonded block in the model linear diblock copolymers studied in this work. It was demonstrated that when the PE is covalently bonded to a PEP block, a strong diluent effect is observed upon the PE crystallization causing it to occur at the largest supercooling observed. The confinement effects and topological restrictions caused by the vitreous PS block are stronger than the topological restrictions imposed by the rubbery PLDA block or the semicrystalline PLLA block (which also exhibited a nucleating effect on the PE block) upon the PE block crystallization behavior.

Acknowledgements: We thank Kelly S. Anderson and Marc A. Hillmyer for providing the PE-*b*-PLLA and PDLA-*b*-PE diblock copolymers. The USB team acknowledges financial support from Fonacit through grant S1- 2001000742.

[1] I. W. Hamley, "*The Physics of Block Copolymers*", Oxford University Press, Oxford, **1998**.
[2] Y. L. Loo, R.A. Register: Crystallization within Block Copolymer Mesophases, in: "*Developments in Block Copolymer Science and Technology*", ed by I. W. Hamley, Wiley, New York **2004**.
[3] D. J. Quiram, R. A. Register, G. R. Marchand, A. J. Ryan, *Macromolecules* **1997**, *30*, 8338.
[4] I. W. Hamley, J. P. A. Fairclough, N. J. Terrill, A. J. Ryan, P. M. Lipic, F. S. Bates, E. Towns-Andrews, E.; *Macromolecules* **1996**, *29*, 8835.
[5] H. L. Chen, J. C. Wu, T. L. Lin, J. S. Lin, *Macromolecules* **2001**, *34*, 6936.
[6] V. Abetz, R. Stadler, L. Leibler, *Polymer Bulletin* **1996**, *37*, 135.
[7] H. L. Chen, S. C. Hsiao, T. L. Lin, K. Yamauchi, H. Hasegawa, T. Hsimito, *Macromolecules* **2001**, *34*, 671.
[8] A. J. Müller, V. Balsamo, M. L. Arnal, T. Jakob, H. Schmalz, V. Abetz, *Macromolecules* **2002**, *35*, 3048.

[9] A. J. Müller, V. Balsamo, M. L. Arnal, *Adv. Polym. Sci.* **2005**, *190*, 1.

[10] A. J. Müller, M. L. Arnal, V. Balsamo, Crystallization in Block Copolymers with more than one Crystallizable Block, in press, in the series Lecture Notes in Physics, in: "*Progress in Understanding of Polymer Crystallization*", ed by G. Reiter and G. Strobl, Springer-Verlag, Berlin **2006**.

[11] Y. Wang, M. A. Hillmyer, *J. Polym. Sci. A Polym. Chem.* **2001**, *39*, 2755.

[12] K. S. Anderson, M. A. Hillmyer, *Polymer* **2004**, *45*, 8809.

[13] A. T. Lorenzo, M. L. Arnal, A. J. Müller, A. Boschetti-de-Fierro, V. Abetz, *Eur. Polym. J.* **2006**, *42*, 516.

[14] A. J. Müller, A. T. Lorenzo, M. L. Arnal, A. Boschetti-de-Fierro, V. Abetz, *Macromol. Symp.* **2006**, *240*, 114.

[15] A. J. Müller, R. V. Castillo, M. Hillmyer, *Macromol. Symp.* **2006**, in press.

[16] H. Schmalz, A. J. Müller, V. Abetz, *Macromol. Chem. Phys.* **2003**, *204*, 111.

[17] A. T. Lorenzo, M. L. Arnal, A. J. Müller, A. Boschetti de Fierro, V. Abetz, **2006**, to be published.

[18] L. Mandelkern, R. G. Alamo, in: "Thermodynamic Quantities Governing Melting", in: *Physical Properties of Polymers Handbook;* Mark, J.E.; American Institute of Physics: Woodbury **1996**, p. 119.

[19] M. Avrami, *J. Chem. Phys.* **1939**, *7*, 1103.

[20] M. Avrami, *J. Chem. Phys.* **1940**, *8*, 212.

[21] M. Avrami, *J. Chem. Phys.* **1941**, *9*, 177.

[22] U. R. Evans, *Trans. Faraday. Soc.* **1945**, *41*, 365.

[23] L. Mandelkern, F. A. Quinn, P. J. Flory, *J. Appl. Phys.* **1954**, *25*, 830.

[24] A. T. Lorenzo, M. L. Arnal, J. Albuerne, A. J. Müller, **2006**, submitted.

[25] L. Mandelkern, in: *Crystallization of Polymers;* 2nd ed.;Cambridge University Press: Cambridge **2002**, Vol. *1*.

[26] L. Mandelkern, in: *Physical Properties of Polymers;* 3rd ed.; Mark, J.E.; Cambridge University Press: Cambridge **2004**.

[27] J. M. Shultz, in: *Polymer Crystallization;* Oxford University Press: London **2001**.

[28] A. T. Lorenzo, M. L. Arnal, A. J. Müller, A. Boschetti-de-Fierro, V. Abetz, *Macromol. Chem. Phys.* **2006**, *207*, 39.

[29] P.J. Flory, *Trans. Faraday Soc.* **1955**, *51*, 848.

[30] J. Albuerne, L. Marquez, A. J. Müller, J. M. Raquez, Ph. Degee, Ph. Dubois, V. Castelletto, I. W. Hamley, *Macromolecules* **2003**, *36*, 1633.

[31] A. J. Müller, J. Albuerne, L. Márquez, J.-M. Raquez, Ph. Degée, Ph. Dubois, J. Hobbs, I. W. Hamley, *Faraday Discuss.* **2005**, *128*, 231.