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Confinement Effects on the Crystallization Kinetics and Self-Nucleation of Double Crystalline Poly(p-dioxanone)-*b*-poly(ε-caprolactone) Diblock Copolymers

Alejandro J. Müller,[1] Julio Albuerne,[1] Luis M. Esteves,[1] Leni Marquez,[1] Jean-Marie Raquez,[2] Philippe Degée,[2] Philippe Dubois,[2] Stephen Collins,[3] Ian W. Hamley[3]*

[1]Grupo de Polímeros USB, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela
[2]Laboratory of Polymeric and Composite Materials (LPCM), University of Mons-Hainaut, Place du Parc 20, 7000 Mons, Belgium
[3]Department of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Summary: The morphology, crystallization and self nucleation behavior of double crystalline diblock copolymers of poly(p-dioxanone) (PPDX) and poly(ε-caprolactone) (PCL) with different compositions have been studied by different techniques, including optical microscopy (OM), atomic force microscopy (AFM) and differential scanning calorimetry (DSC). The two blocks crystallize in a single coincident exotherm when cooled from the melt. The self-nucleation technique is able to separate into two exotherms the crystallization of each block. We have gathered evidences indicating that the PPDX block can nucleate the PCL block within the copolymers regardless of the composition. This effect is responsible for the lack of homogeneous nucleation or fractionated crystallization of the PCL block even when it constitutes a minor phase within the copolymer (25% or less). Nevertheless, we were able to show that decreasing amounts of PCL within the diblock copolymer still produces confinement effects that retard the crystallization kinetics of the PCL component and decrease the Avrami index. On the other hand evidence for confinement was also obtained for the PPDX block, since as its content is reduced within the copolymer, a depression in its self-nucleation and annealing temperatures were observed.

Keywords: confinement; diblock copolymers; poly(ε-caprolactone); poly(p-dioxanone); self nucleation

Introduction

Poly(p-dioxanone), PPDX, is a poly(ester-ether) that is biodegradable, bioabsorbable and commercially available as suture material.[1] For some biodegradation applications, the hydrolytic degradation time of PPDX may be too fast and its copolymerization with poly(ε-

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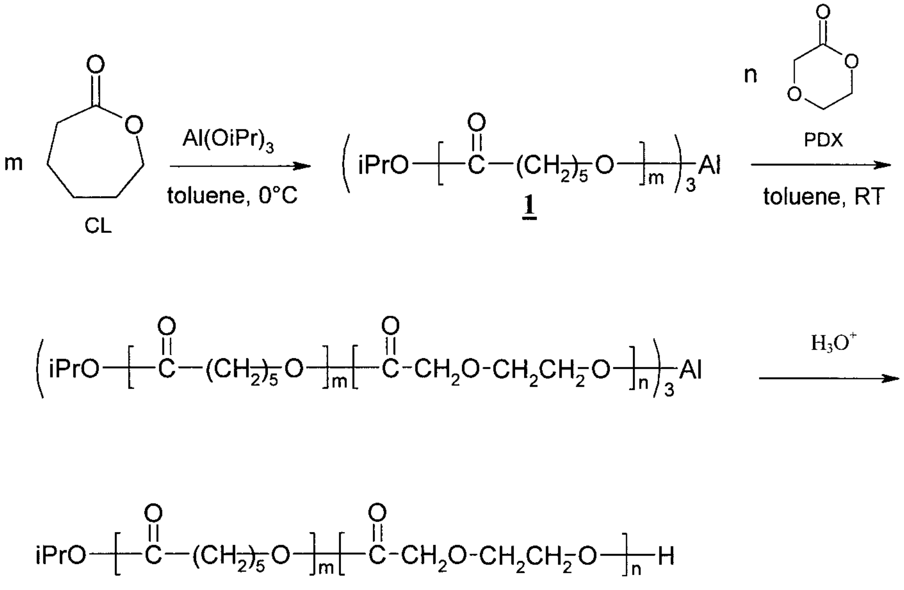
caprolactone), PCL, a more resistant polymer to hydrolysis, allows tuning the lifetime of the polymer for specific applications.[2]

P(CL-*b*-PDX) diblock copolymers are also interesting since they can phase separate in the melt (the order-disorder temperature is most probably above 140 °C[3]), and the two microdomains can later crystallize upon cooling. The crystallization of block copolymer microdomains is a topic that has attracted much recent attention because of intrinsic interest in the crystallization of confined materials and also because the interplay between phase separation and crystallization can be very complicated since it depends on copolymer composition, polymer-polymer interaction parameter, molecular weight and relative position of the thermal transition of each microdomain with respect to the order-disorder transition.[4-6]



P(CL-b-PDX)

Scheme 1. Controlled ring-opening polymerization of 1,4-dioxan-2-one quantitatively initiated by ω-Al alkoxide poly(ε-caprolactone) chains (1) in toluene at room temperature.[7]

The preparation of narrowly polydispersed PCL and PPDX homopolymers employed here has been reported previously.[7] The synthesis of poly(ε-caprolactone-*b*-1,4-dioxan-2-one) block copolymers (P(CL-*b*-PDX)) is summarized in scheme 1. The polymerization of ε-caprolactone was performed in dry toluene at 0°C and was initiated by $Al(OiPr)_3$. After 1h, part of the living poly(ε-caprolactone) (PCL) solution was recovered, purified and characterized by Size Exclusion Chromatography (SEC). In a second step, purified PDX dissolved dry toluene at room temperature was added to the rest of the living PCL in toluene solution under a nitrogen atmosphere. After a given time, the polymerization was stopped by adding a few of drops of HCl (0.1 M). The poly(ε-caprolactone-*b*-1,4-dioxan-2-one) block copolymer (P(CL-b-PDX)) was recovered by precipitation into heptane at room temperature, filtration and drying under vacuum. Catalyst residues were extracted as previously reported.[8] The molar mass of the PPDX block was determined by ^{1}H NMR spectroscopy from the relative intensities of methylene protons of the PDX repeat units at 4.35 ppm and methylene protons of CL repeat units at 2.32 ppm knowing the molar mass of the PCL macroinitiator. The relative proportion of PDX and CL repetitive units also enabled weight fractions to be calculated.

Table 1 lists all materials employed and their molecular weights and polydispersities. The notation employed is explained as follows: the capital letters refer to PPDX and PCL blocks respectively, the superscripts are indicative of the molar mass (in thousands) and the subscripts indicate the weight fractions.

Table 1. Molecular Characteristics of the Materials Employed.

Composition[a]	M_n (PCL)	M_w/M_n	M_n (PPDX)	F_{PCL} (wt)
$D_{23}^{8}C_{77}^{27}$	27 200	1.06	7 500	0.77
$D_{28}^{10}C_{72}^{24}$	24 400	1.16	9 500	0.72
$D_{40}^{5}C_{60}^{7}$	7 100	1.17	4 800	0.60
$D_{55}^{7}C_{45}^{6}$	5 950	1.16	7 300	0.45
$D_{77}^{32}C_{23}^{10}$	10 280	1.07	32 280	0.23
PCL^{11}	11 400	1.07		1.00
$PPDX^{5}$			5 480	0.00

[a] D and C denote PPDX and PCL blocks, respectively; the superscripts are indicative of their molar masses (in thousands), and the subscripts refer to their weight fractions.

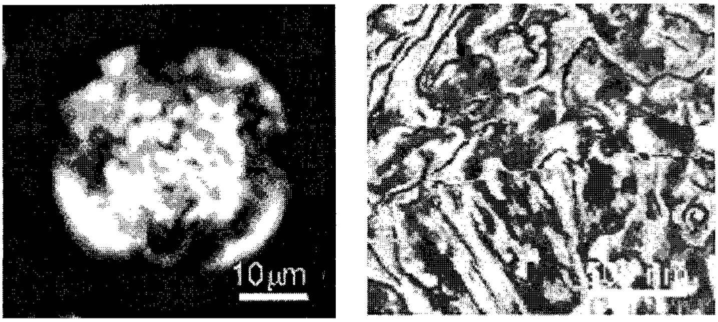
In a previous work[3] we have shown that P(CL-*b*-PDX) diblock copolymers are double crystalline materials, with two well defined melting peaks (whose temperatures are around the values for the homopolymers) and just one coincident crystallization exotherm (upon cooling from the melt) that occurs at lower temperatures than that of PPDX homopolymer crystallization and is independent of copolymer composition. In this coincident crystallization process, the PPDX starts to crystallize first, and then the PCL segment follows, apparently nucleated by the PPDX crystallization. Evidence for this behaviour was obtained from real time WAXS experiments during isothermal crystallization and DSC measurements[3]. In this work, we present results on how the confinement of the PCL block affects its crystallization kinetics even when the nucleation effect of PPDX prevents homogeneous nucleation and fractionated crystallization of the PCL block in copolymers where PCL is present as a minor phase. Another type of confinement effect can be identified for the PPDX block, when it is a minor component, by applying the self-nucleation technique.

Morphology

The susceptibility to degradation of PPDX makes the study of the morphology challenging. The P(CL-*b*-PDX) diblock copolymers cannot be annealed for long times at high temperatures to produce highly ordered morphologies because the PPDX block degrades, and it is similarly susceptible to staining agents.[3] Therefore, the samples are used as synthesized, without any prior thermal treatment. Previous attempts to obtain SAXS patterns in the melt on these samples failed possibly because they are not treated (and the morphology may lack the degree of order required for SAXS to produce a reflection).[3]

Previous Polarized Optical Microscopy (POM) experiments revealed that most samples crystallized with spherulitic superstructures at intermediate to high undercoolings and with granular aggregate superstructures at low undercoolings. The samples for POM studies were prepared by melting (at around 130°C) between two microscope cover slips for 10 min, and then they were quickly cooled to the crystallization temperature, Tc. At this temperature micrographs were taken with a digital camera at different time intervals.

In this work, we have also performed Atomic Force Microscopy (AFM) with a Veeco Instruments Nanoscope III in tapping mode. The samples were spin cast over silica or mica substrates from a 2% weight solution in 1,1,2,2-tetrachloroethane, at 2500 rpm for 1 min. The thermal treatment of the AFM samples was performed using two vacuum ovens, where they were first held in the melt for 3 min at 130°C, and then transferred to the other oven at a constant crystallization temperature, Tc; the samples remained at this temperature for a fixed amount of time before they were cooled down to room temperature to observe them in the AFM.



(a) **(b)**

Figure 1. Spherulitic superstructure of $D_{23}^{8}C_{77}^{27}$ as revealed by: (a) POM during growth at 44°C, and (b) AFM phase contrast image of a sample that was crystallized at 42°C before quenching to room temperature. Note that an inter-spherulitic border runs almost horizontally through the middle of the image.

Figure 1 (a) presents an example (for $D_{23}^{8}C_{77}^{27}$) of the type of spherulitic superstructure that is seen with POM at undercoolings that are high enough to allow the crystallization of both PCL and PPDX microdomains. Figure 1(b) shows an AFM image that reveals that the spherulites are composed of radial lamellae of PCL (since PCL constitutes 77% of the material) that grow until they impinge with one another. The PPDX phase cannot be clearly identified since it is a minor phase that must be located within the interlamellar region of the dominant PCL lamellae where the amorphous PCL phase, together with all of the PPDX, must be accommodated.

Using POM we have identified spherulites in the crystallization region where both blocks crystallize (high undercoolings). Conversely, in the region where just the PPDX segment may crystallize (at Tc above 48°-50°C), POM revealed a transformation from spherulites to granular aggregates (for sample $D_{40}^{5}C_{60}^{7}$) or from rounded spherulites to ellipsoidal ones (for sample $D_{77}^{32}C_{23}^{10}$), or the superstructure cannot be seen (e.g., in sample $D_{23}^{8}C_{77}^{27}$ if the PCL domain is molten, the PPDX cannot form spherulites since it only amounts to 23% by weight and does not form aggregates that are large enough to be seen under POM).

POM allows the growing process of the superstructures to be monitored at different crystallization temperatures, and thus their growing rate (G) can be calculated (Figure 2). At lower temperatures (below 49°C) both blocks can crystallize into mixed spherulites similar to those of Figure 1. It can be appreciated that the growth rates of the diblock copolymers are lower than that exhibited by PCL homopolymer by a factor that is less than ten in this temperature range. However, in the region in which the PCL block is molten, we observe a depression of the growing rate of the copolymers by a factor of 10 as compared to PPDX homopolymer. This is probably due to the presence of the molten PCL in the system, which slows down the PPDX segments as they form the superstructural array. It is interesting to observe that a minimum in growth rate is observed around the transition temperature of 50°C at which both blocks start to crystallize together; it is at this temperature where the difference in undercooling experienced by each block goes through a maximum (i.e., it represents the highest temperature at which the PCL block can crystallize but a rather low crystallization temperature for PPDX).

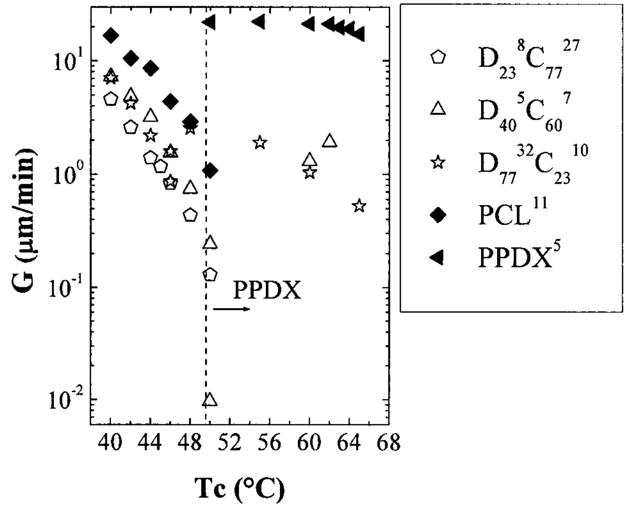


Figure 2. Superstructural growth rate (G) as a function of isothermal crystallization temperature (Tc) for the indicated samples. The dashed line indicates the approximate temperature limit beyond which only the PPDX microdomain can crystallize.

Overall Isothermal Crystallization Kinetics

The overall isothermal crystallization kinetics was studied in a Perkin-Elmer DSC-7. We had previously demonstrated[3] that if both blocks are simultaneously crystallized by quenching the diblock copolymer from the melt directly to Tc, a slower kinetics is observed than when the PPDX block is allowed to retain its crystalline morphology and then the PCL block is crystallized. These experiments demonstrated that a nucleation effect of the PPDX on the PCL was operating. In the first case, we started from the molten state (around 120°C), and then quickly cooled down to the crystallization temperature, in a similar way to that previously described for POM and AFM experiments. The second type of measurement was performed starting from the molten state at 120°C, then cooling down to -25°C (at 10°C/min), only to subsequently heat the sample above the PCL melting point (62°C) for a fixed period of time (70 min), and finally quench it to the crystallization temperature. In the present case, only the second type of procedure was employed where we monitored the PCL block isothermal crystallization after the PPDX had been allowed to fully crystallize. Figure 3 shows the overall crystallization rate, expressed as the inverse of the crystallization half-time, of PCL^{11} and of the PCL block for selected diblock copolymers. Figure 3 shows that when the PCL content in the copolymer is high enough to form the matrix, for $D_{23}{}^{8}C_{77}{}^{27}$ and $D_{40}{}^{5}C_{60}{}^{7}$, the overall crystallization rate of the PCL block is higher than that of PCL^{11}. This result confirms the previous finding that the crystallized PPDX nucleates the PCL; otherwise the acceleration of the overall kinetics (that includes nucleation and growth) could not have been observed since superstructural growth of the PCL block is most likely slower than that of PCL^{11} in view of the evidence provided in Figure 2.

The nucleation effect of the PPDX block seems to be overtaken by topological confinement when the PCL content within the copolymer is lower than 50%. Figure 3 shows how the PCL block of the diblock copolymer with 47% PCL ($D_{53}{}^{21}C_{47}{}^{21}$) and that with 23% PCL ($D_{77}{}^{32}C_{23}{}^{10}$) crystallize at a slower overall rate than neat PCL. It is very interesting that a diblock copolymer like $D_{77}{}^{32}C_{23}{}^{10}$ with only 23% PCL exhibits crystallization of the PCL block in the temperature range shown in Figure 3, which is very similar to that of the heterogeneously nucleated PCL homopolymer. This means that even though the PCL is a minor component it does not nucleate homogeneously nor even display fractionated crystallization.[4-5] We have interpreted this result by considering that the previously crystallized PPDX heterogeneously nucleates the PCL, therefore preventing the nucleation problems of this block component.[3] Another possibility could be that the PCL phase is percolated or interconnecting; however all the evidences suggesting a nucleation effect by the PPDX lead us to the above quoted conclusion. In any case, both effects may be present.

The crystallization temperature range at which the PCL block within $D_{77}{}^{32}C_{23}{}^{10}$ was able to crystallize is comparable to that of PCL homopolymer, indicating that a heterogeneous nucleation mechanism is present. Another corroboration of the heterogeneous nucleation mechanism can be made by calculating the slope of the crystallization half time versus temperature (in a semi-log scale) and comparing its value with that of the PCL homopolymer[9].

In our case, PCL^{11} exhibited a slope of 0.14 min/°C. The crystallization of the PCL blocks within the diblock copolymers exhibited slopes range between 0.13 to 0.24 min/°C and in the case of $D_{77}{}^{32}C_{23}{}^{10}$ the value was 0.20 corroborating a heterogeneous nucleation mechanism for the minor PCL component.

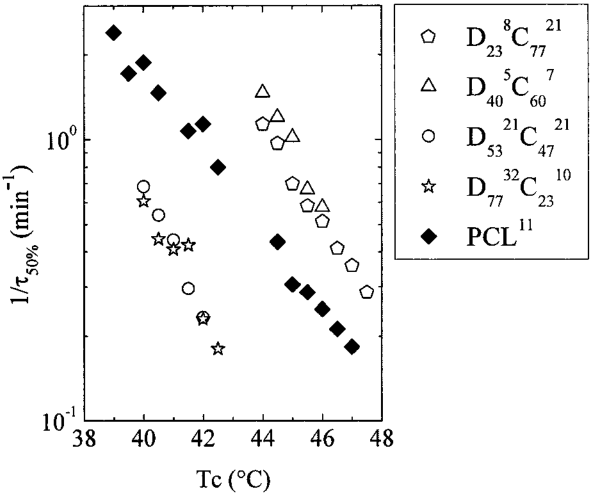


Figure 3. Reciprocal crystallization half-time at different crystallization temperatures, for the PCL homopolymers and the PCL block in the copolymers (the PPDX was previously crystallized according to the procedure stated in the text).

The most important contribution of the present work is that in spite of the nucleation effect of PPDX on PCL, that causes a heterogeneous nucleation mechanism for all the diblock copolymers employed regardless of composition, we can still find evidence for "confinement" for the PCL component. We will also show below that in the composition range where PCL is the major component, PPDX can also exhibit signs of confinement.

In the case of the PCL block, one of the first indicators of confinement is the reduction in the overall crystallization kinetics presented in Figure 3 and discussed above. The second is shown in Figure 4 where the Avrami index, obtained after fitting the Avrami equation to the overall crystallization data[3] obtained by DSC, is plotted as a function of the PCL content in the diblock copolymer. The spreading of the data corresponds to the different crystallization temperatures employed and to differences in molecular weight (we have found higher Avrami indexes in PCL homopolymers of higher molecular weights; this may explain the values displayed by the PCL block within $D_{23}{}^{8}C_{77}{}^{27}$). Nevertheless a clear trend can still be observed; the Avrami index decreases as the PCL content in the copolymer decreases. Such a decrease in Avrami index can be interpreted as a decrease in the dimensionality of growth from spherulites to two-dimensional structures or even to one-dimensional structures (for an sporadic nucleation case). This decrease in growth dimensionality is the result of confinement since the size of the PCL block decreases as its content in the copolymer decreases.

The classical Avrami interpretation takes into account the nucleation and dimensionality of growth during the crystallization process. It is now well known that when a block copolymer is confined into a great number of isolated microdomains (e.g, spheres or cylinders) it crystallizes from homogeneous nuclei that form at the largest possible supercooling.[5] Loo et al.[9] have shown that when homogeneous nucleation takes place, the Avrami index is usually 1. They have interpreted this result by considering that the growth rate is so fast at large supercoolings that only nucleation controls the rate of overall transformation.

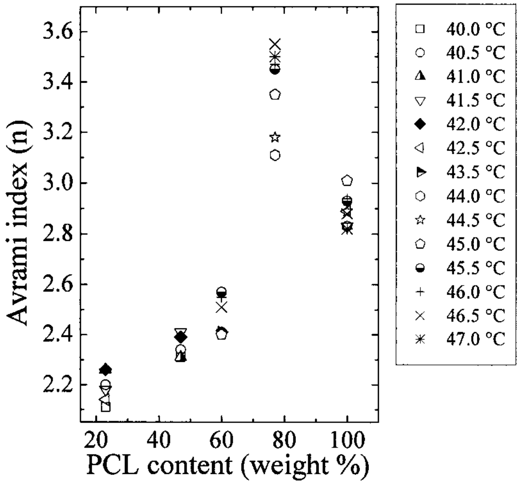


Figure 4. Avrami index as a function of PCL composition, for the isothermal crystallization of the PCL block at different temperatures (the PPDX was previously crystallized according to the procedure stated in the text). The 100% values correspond to PCL[11].

Another evidence that in our case the PCL block is not homogeneously nucleated is the fact that even for $D_{77}^{32}C_{23}^{10}$ the Avrami index was not found to be 1. Nevertheless, for this copolymer, Figure 4 shows that the Avrami index is of the order of 2, and this could correspond to one-dimensional crystals grown from sporadic nuclei, or two-dimensional growth from instantaneous nuclei. As the PCL content in the copolymer increases the Avrami index increases to values that are similar to those of PCL homopolymer, i.e., around 3, that indicate spherulitic growth from instantaneous nuclei, since the spherulites in such cases are easily observed in POM.

Self Nucleation

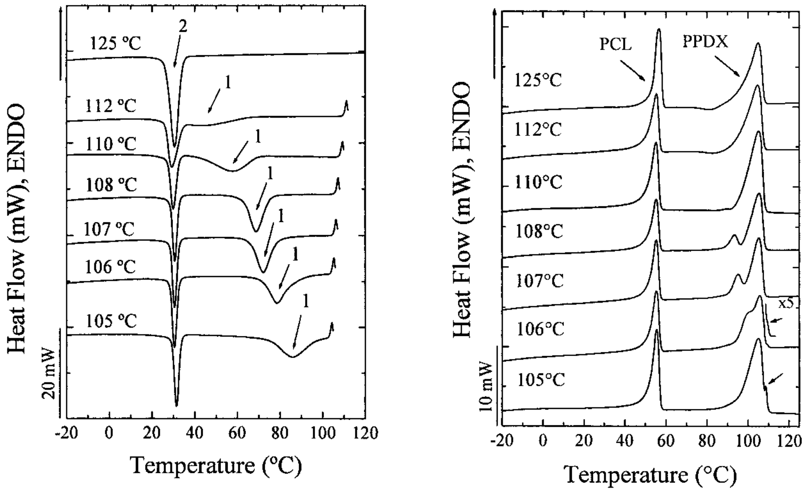
The self-nucleation technique was employed in order to ascertain the self-nucleation temperature Domains for the homopolymers and copolymers. Details of the experimental procedure can be found in previous works.[5]

Samples are first heated to a temperature high enough to completely melt the polymer in order to erase thermal history; then they are cooled at 10 °C/min down to –25 °C to provide them with a standard thermal history. Then they are heated to a temperature denoted Ts (or self-nucleation temperature) and isothermally kept there for 3 min. After treatment at Ts, the sample is cooled down to –25 °C (examples of such cooling scans can be seen in Figure 5) and subsequently heated at 10 °C/min until full melting occurs. Depending on Ts, the sample can be in one of three general Domains: In Domain I the sample is completely molten; in Domain II the sample is self-nucleated since Ts is high enough to melt almost all crystals but low enough to leave small fragments that can act as self-nuclei (or to induce memory effects) upon subsequent cooling and therefore the nucleation density can be enormously increased; in Domain III the sample is partially molten so that self-nucleation and annealing of unmelted crystals will take place at Ts.

Figure 5 (a) shows DSC cooling scans after 3 min at Ts for $D_{55}^{7}C_{45}^{6}$. At 125°C the Ts is too high and the sample is said to be in Domain I or complete melting Domain. Notice how after complete melting, the DSC cooling scan exhibits a single crystallization exotherm where both PPDX and PCL crystallize in a coincident fashion[3]. The origin of such coincident crystallization is related to the decrease in growth rate experience by the PPDX block when it tries to crystallize at low undercoolings (in the region where PCL has not started to crystallize).[3] Figure 5(b) shows the subsequent heating scans after the cooling runs shown in Figure 5(a). The two melting endotherms are due to the melting of the PCL component (at lower temperatures) and the PPDX component (at higher temperatures).

A novel result is shown in Figure 5(a) thanks to the self-nucleation technique. When a Ts of 112°C is used, only the PPDX is self-nucleated (since PCL is molten at that temperature, see Figure 5(b)) and upon cooling from 112°C a new high temperature exotherm, labeled 1 in Figure 5(a), starts to develop while the PCL component still crystallizes at lower temperatures (exotherm 2). The PPDX block of $D_{55}^{7}C_{45}^{6}$ at 112°C is in Domain II or self-nucleation Domain. Lowering Ts leads to a clear separation of the crystallization of the PPDX and the PCL block in temperature.

The location of Domain III is easily detected by observing the subsequent heating scans of Figure 5 (b).[5, 10] At a Ts temperature of 106°C a very small high temperature melting peak signaled with an arrow can be seen that is the trademark of the first signs of annealing at Ts. The PPDX block of $D_{55}^{7}C_{45}^{6}$ at 106°C is in Domain III or the self-nucleation and annealing Domain. For the PPDX block of $D_{55}^{7}C_{45}^{6}$, Figure 5 demonstrates that all three self-nucleation Domains can be observed.



(a) (b)

Figure 5. DSC cooling scans (10°C/min) after 3 minutes holding time at the indicated Ts temperatures for $D_{55}^{7}C_{45}^{6}$. (a) Ts Temperature range where only the PPDX block can be self-nucleated. (b) Subsequent melting.

Müller et al. have previously shown[5, 10-11] that Domain II disappears for systems where the crystallizable block (PE, PCL or PEO) is strongly confined into small isolated microdomains. For self-nucleation to occur, a higher density of self-nuclei is then necessary and self-nucleation can only take place when Ts is lowered well into Domain III, where already annealing of remaining crystallites takes place. This is a direct result of the extremely high number density of microdomains that need to be self-nucleated when the crystallizable block is confined within small isolated microdomains.

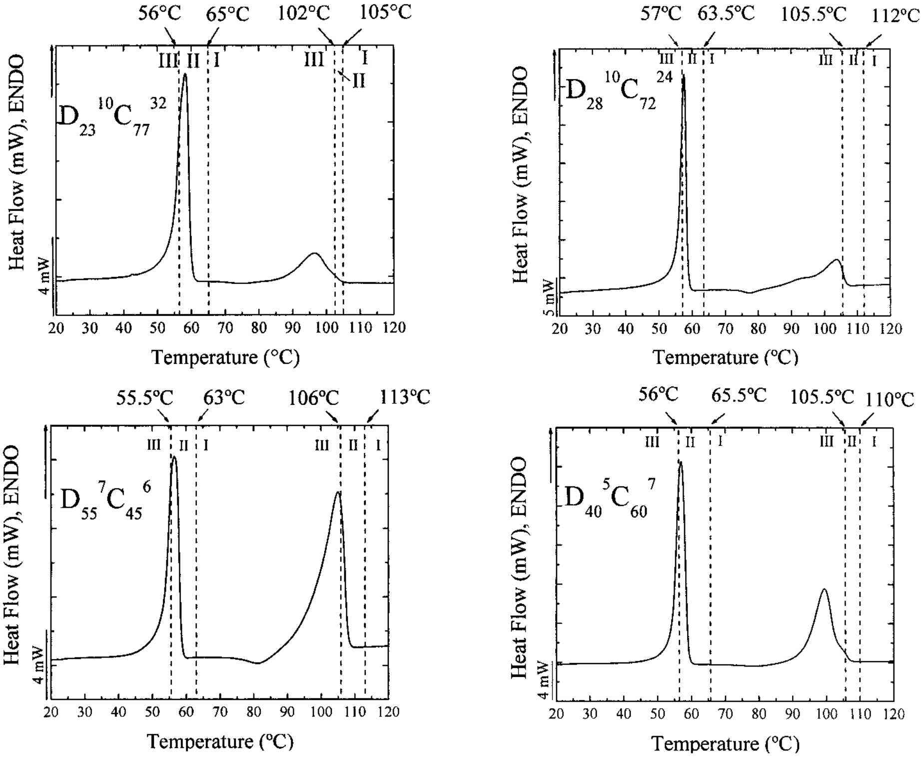


Figure 6. Self nucleation domains for PPDX-*b*-PCL diblock copolymers of different compositions. The temperature boundaries between the domains as well as the compositions are denoted.

Examples of the location of the self-nucleation Domains are shown in Figure 6 for a PPDX homopolymer and 3 diblock copolymers of varying compositions. The examples of Figure 6 illustrate an important finding since the three self-nucleation Domains were observed for both

PPDX and PCL blocks within all diblock copolymers examined regardless of composition. This is yet another evidence that homogeneous nucleation is not taking place for either the PPDX or the PCL blocks because Domain II was always observed.[5] Once more, even if Domain II were present for all copolymers examined, we found another evidence of confinement since the temperatures for the transition between Domain I and II, and between Domain II and III, for the PPDX block were found to increase as the PCL content in the copolymer decreases. This indicates that the processes of self-nucleation and annealing are increasingly more difficult as the PPDX is confined in smaller quantities in a matrix of PCL. A detailed study on the self-nucleation behaviour of these copolymers will soon be reported.

Conclusions

P(CL-*b*-PDX) diblock copolymers of a wide composition range have been studied by DSC, POM and AFM. The two blocks crystallize in a single coincident exotherm when cooled from the melt. The self-nucleation technique was able to separate the crystallization of each block into two exotherms depending on the self-nucleation temperature employed. We have gathered evidence indicating that the PPDX block can nucleate the PCL block within the copolymers regardless of composition. This effect is responsible for the lack of homogeneous nucleation or fractionated crystallization of the PCL block even when it constitutes a minor phase within the copolymer (25% or less). It also accounts for the presence of the three self-nucleation Domains in both the PCL and the PPDX block regardless of composition. Nevertheless, we were able to show that decreasing the amount of PCL within the diblock copolymer still produces confinement effects that retard the crystallization kinetics of the PCL component and decrease its Avrami index. For copolymers with a majority of PCL, decreasing amounts of PPDX within the copolymer make the self-nucleation and annealing of this block component more difficult, thereby reflecting confinement restrictions.

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