Macromolecules

Volume 40, Number 6 March 20, 2007

Communications to the Editor

The Two Crystallization Modes of Mesophase Forming Polymers

Juan P. Fernández-Blázquez, Jesús Pérez-Manzano, Antonio Bello, and Ernesto Pérez*

Instituto de Ciencia y Tecnología de Polímeros (CSIC),
Juan de la Cierva 3, 28006 Madrid, Spain

Received December 5, 2006

Introduction. There has been in recent years an increasing interest in the study of the initial stages of polymer crystallization, with the underlying idea of being a multistage process via an intermediate mesomorphic phase.[1−3] Foundations for this scheme are based on the Ostwald's rule of stages, formulated more than 100 years ago.[4] This empirical rule states that a phase transformation will proceed through metastable states, whenever they exist, and it has been recently invoked in the crystallization of different materials[5] and specifically for polymer crystallization[1,2] by combining both phase stability and kinetic considerations. Thus, to the initial concept that metastable phases will evolve faster than the corresponding stable phases, it has been also realized that although the bulk free energy of the crystal phase is below that for the metastable one; however, the situation can be inverted for small sizes, owing to surface free energy considerations. In such case, for instance, the crystal formation will be preceded by a mesomorphic structure which is the most stable one at the nanometric level.[1,2]

This scenario may have important technological consequences when considering that the transient intermediate phase might exert a certain influence on the structure of the final product. For instance, lamellar thickness may reflect a memory of that mesomorphic phase.[1]

These considerations have been applied to classical semicrystalline polymers, where the transient phase is really a metastable one and experimental evidence of its intermediate formation is rather elusive. However, it seems obvious to proceed to the corresponding study of mesophase-forming polymers, i.e., those polymers where the mesophase can be readily observed before the final crystallization, as it happens in many thermotropic polymers.

The picture will be even more complete if it were possible to analyze a system where the crystal formation could be controlled in such a way that it can be attained with or without the intermediate formation of mesophase. Unfortunately, not many systems exhibit this behavior, since now we face the opposite problem: it is usually extremely difficult to avoid the formation of the mesophase due to the rapid kinetics of the liquid crystallization process.

We have succeeded, however, in the control of such mesophase kinetics. Thus, poly(heptamethylene *p*,*p*′-bibenzoate), P7MB, is a liquid crystalline polymer where the mesogenic bibenzoate units are responsible for its thermotropic behavior, and on cooling from the isotropic melt, a low ordered smectic mesophase is obtained, which subsequently transforms into a three-dimensional crystal.[6−10] P7MB is a typical liquid crystalline polymer where the mesophase displays a rapid kinetics of formation. However, by preparing copolymers of heptamethylene glycol with different amounts of bibenzoate and terephthalate units, the mesophase formation can be controlled, owing to the nonmesogenic character of the terephthalate groups. Thus, we have shown[11] that considerable amounts of these terephthalate units can be inserted (up to around 40−50 mol %) without destroying completely the mesophase formation ability (at the usual cooling rates of the calorimeter).

We report here the preliminary results obtained for one of such copolymers, named as C7TB1, with 10 mol % terephthalate units (see Chart 1 for structural formula).

Experimental Section. The details for the synthesis and characterization of C7TB1 and P7MB have been previously reported.[11]

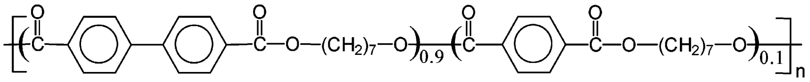
The thermal transitions were analyzed in a Perkin-Elmer DSC7 calorimeter connected to a cooling system and calibrated with different standards. A scanning rate of 20 °C/min was used. Variable-temperature X-ray scattering experiments at wide (WAXS), middle (MAXS), and small-angle scattering (SAXS) were performed by employing synchrotron radiation in the soft-

---

* Corresponding author. E-mail: ernestop@ictp.csic.es.

10.1021/ma062788x CCC: $37.00

Chart 1



condensed matter beamline A2 at HASYLAB (Hamburg, Germany). The experimental details can be found in the Supporting Information.

Results and Discussion. Figure 1 shows the DSC curves of copolymer C7TB1 and homopolymer P7MB. It can be observed that, on cooling from the isotropic melt, P7MB presents two exotherms, centered at 138 and 95 °C, with enthalpies of 18 and 15 J/g, respectively. They correspond[6−11] to the transition from the isotropic melt to a smectic mesophase and from this mesophase to a three-dimensional crystal, respectively.

The subsequent melting curve indicates that P7MB shows monotropic behavior: the crystal melts directly into the isotropic phase and a single endotherm is exhibited, centered at 168 °C, with an enthalpy of 33 J/g. Nevertheless, the isotropization of the mesophase can be observed if the sample is immediately heated after cooling from the melt down only to a temperature where the crystal is not yet formed.[6] For the present P7MB sample, a value of 162 °C was obtained for the isotropization temperature, with an enthalpy of around 18.5 J/g.

Copolymer C7TB1 shows a DSC cooling curve (upper frame of Figure 1) rather similar to the one of P7MB, but with somewhat lower transition temperatures (and enthalpies): 112 and 81 °C, with 15 and 14 J/g, respectively. It has been shown that these two transitions have the same origin than those for P7MB.[11] It is important to note that the two transitions are rather sharp and perfectly well-defined, in contrast to other similar copolymers.

In the subsequent melting curve of C7TB1, two overlapped endotherms are observed (at 144 and 150 °C) with a total enthalpy of 29 J/g. These two peaks may be due either to enantiotropic behavior or to melting/recrystallization processes. The synchrotron results are in favor of this second possibility, since the mesophase is not observed on melting. However, and performing a similar experiment to that for P7MB, i.e., cooling down from the isotropic melt just after the mesophase formation exotherm (down to around 105 °C), the isotropization of the mesophase can be observed in the subsequent melting, centered at 129 °C, involving an enthalpy of around 14 J/g.

It follows, therefore, that while the introduction of 10 mol % terephthalate units decreases the melting temperature, T_m, from 168 to 144 °C, the depression is considerably higher for the isotropization temperature, T_i, which changes from 162 °C for P7MB to 129 °C for C7TB1.

From these transition temperatures and the corresponding enthalpies, ΔH, the phase diagrams can be obtained, by estimating the free energy, ΔF, of the various phases in relation to the isotropic state[7,12,13] by applying the approximation

$$\Delta F = \Delta H(T_m - T)T/T_m^2$$

Although this equation has some limitations,[13] it can be used at least for semiquantitative purposes. The corresponding free energy diagrams for P7MB and C7TB1, estimated with that equation, are shown in Figure 2. They appear to be qualitatively rather similar, and the monotropic transition of the crystal in the two polymers is characterized by the crossing of the curves corresponding to the crystal and to the mesophase at a temperature higher than the isotropization point.

It is obvious that although the more stable phase will be that one with the lowest free energy, kinetic considerations will also affect to the formation of a certain phase, even without invoking surface free energy effects due to small sizes. In principle, and when cooling from the isotropic melt, there is a certain interval $\Delta T = T_m - T_i$ where the crystal phase should be formed directly, without the intermediate mesophase. That interval is only 6 °C for P7MB, but it has been considerably amplified to 15 °C for C7TB1. However, the crystallization of P7MB at the corresponding so low undercoolings will take many hours or days, as deduced from the extrapolation of the crystallization rates at several isothermal temperatures. On the contrary, since the ΔT

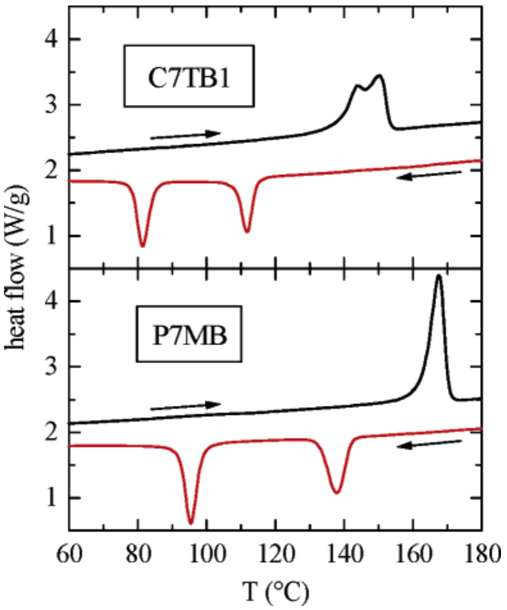


Figure 1. DSC curves for P7MB (lower frame) and C7TB1 (upper frame) corresponding to the cooling from the isotropic melt and the subsequent melting. Scanning rate: 20 °C/min.

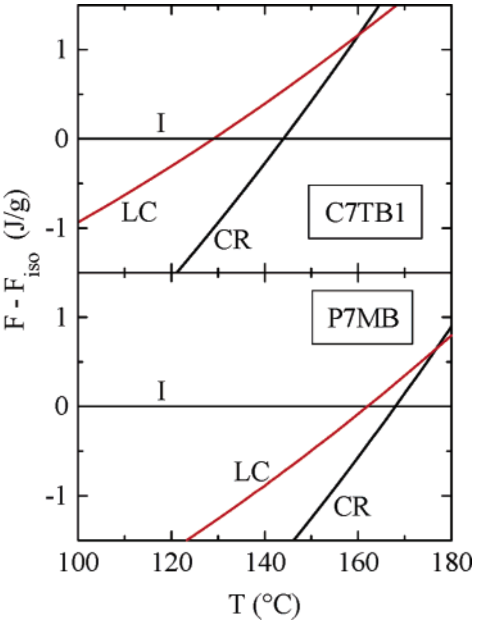


Figure 2. Free energy diagrams corresponding to P7MB (lower frame) and C7TB1 (upper frame). I = isotropic melt; LC = mesophase; CR = crystal phase.

gap is much higher for C7TB1, this polymer can be crystallized from the melt with easily measurable rates, as shown below, at temperatures around 130−135 °C. At lower temperatures, the mesophase is formed first, previously to the final crystallization, and the two exotherms are observed in the corresponding isothermal experiments.

This aspect has been analyzed by performing real-time synchrotron experiments in C7TB1. The corresponding results for two selected isothermal crystallization temperatures (starting from the isotropic melt and quenching down to the isothermal temperature) are presented in Figure 3. The upper part of the figure, corresponding to the experiment at 115 °C, indicates that in the first frame after temperature stabilization the smectic mesophase is already almost completely formed, characterized by an amorphous-like broad halo in the WAXS diffractogram, a narrow MAXS peak centered at 1.72 nm, and the absence of long spacing in the SAXS channels. After a few frames, however, several diffractions begin to appear in the WAXS diagrams, together with the observation of a long spacing and a small, but appreciable, shift in the MAXS diffraction, down to a value of 1.69 nm. This corresponds to the crystallization from the mesophase, which is completed after around 7 min.

Rather different is the behavior for the isothermal temperature of 130 °C, as observed in the lower part of Figure 3. Thus, the sample is initially in its isotropic state, characterized by the absence of any MAXS or SAXS peak, and only the amorphous broad peak is obtained in the WAXS diagram. After around 3 min of isothermal crystallization, several diffraction peaks appear in the WAXS diffractograms, together with the observation of a long spacing. Moreover, a rather wide MAXS peak is also observed. The interpretation is, therefore, that now the crystal phase has been formed directly from the isotropic melt, since there is no sign of the smectic mesophase, which will be characterized by the observation of the smectic MAXS peak, with no long spacing.

Other several interesting aspects can be deduced from Figure 3, especially in relation to the width of the MAXS peaks. Thus, the first frames of the experiment at 115 °C show a MAXS peak with a full width at half-maximum of around 0.021 nm^{-1}. After crystallization, the peak becomes slightly wider: 0.023 nm^{-1}. Therefore, a correlation length of around 43 nm is obtained from this crystal peak with the aid of the Scherrer equation.[14]

On the other hand, the similarity of the widths and positions of the smectic and crystalline MAXS peaks indicates that the crystallization from the mesophase seems to proceed with little disruption of the initial smectic domains in the direction of the macromolecular axis.

On the contrary, the MAXS crystal peak obtained at 130 °C, although it is centered at 1.68 ± 0.01 nm, i.e., at approximately the same value as that for the crystallization at 115 °C; however, it shows a much higher width: 0.065 ± 0.005 nm^{-1}, which corresponds to a correlation length of only around 15 nm. It follows, therefore, that when the crystal is formed directly from the isotropic melt, much lower correlation lengths are obtained. In fact, preliminary experiments in a sample of poly(heptamethylene terephthalate), the corresponding homopolymer without mesogenic groups, show a crystal MAXS peak centered at around 1.34 nm and a width of 0.125 nm^{-1} (see Supporting Information). The importance of the intermediate mesophase for the crystal correlation lengths is evident, and it seems to reflect a certain memory effect of the mesomorphic state.

From these correlation length values we face the eventual paradox of obtaining somehow a better ordering in the sample crystallized at lower temperature. However, it is also interesting to analyze the SAXS diagrams. Surprisingly clear and lengthy long spacings are observed for C7TB1, despite being a copolymer, in the two isothermal crystallizations, as observed in Figure 3. A long spacing of 20 ± 1 nm is deduced for the experiment at 115 °C, while a considerably higher value, 27 ± 1 nm, is obtained for the crystallization temperature of 130 °C. Nevertheless, since the long spacing is supposed to be measured along the macromolecular chains, as it happens also for the correlation length deduced from the crystal MAXS peak (corresponding to the 001 diffraction), it could be expected that the long spacing might also reflect the influence of the intermediate mesophase. Obviously, this is not the case, since those two magnitudes display opposite behaviors. Thus, the expectation of higher values of the long spacing at higher crystallization temperatures is now fulfilled.

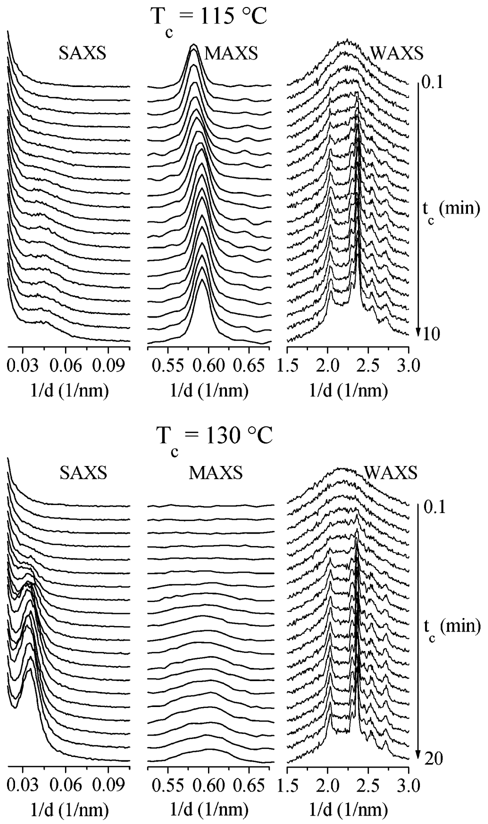


Figure 3. SAXS/MAXS/WAXS synchrotron profiles corresponding to two experiments of C7TB1 isothermally crystallized (starting from the isotropic melt) at 115 °C (upper part) and at 130 °C (lower part), as a function of the crystallization time, t_c.

Evidently, it should be more appropriate to carry out the previous discussion with lamellar thicknesses instead of long spacings. However, the crystallinity degrees deduced from the final WAXS diffractograms of the two experiments are identical inside the experimental error: 0.33 ± 0.04 for both crystallization temperatures. Therefore, the corresponding lamellar thicknesses are expected to show a relative increase on passing from 115 to 130 °C rather similar (or identical) to that observed for the long spacings.

The interesting issue now is to envisage a morphological picture having taken into account these experimental findings, especially for the crystallization at 115 °C: correlation lengths along the macromolecular axis of more than 43 nm and lamellar thicknesses of only 6−7 nm (values deduced from the long spacing and the crystallinity degree, by applying a simple two-phase model). The differences are much smaller in the case of crystallizing at 130 °C: a correlation length of 15 nm and an estimated lamellar thickness of around 9 nm. We plan to perform additional experiments in order to get a further insight into this question.

In conclusion, it follows from the experiments outlined here that copolyester C7TB1 is a very appropriate system to analyze the crystal formation with or without an intermediate mesophase, and it can be considered as a rather good reference model for explaining the different crystallization behaviors. Thus, copolymers with higher content of the nonmesogenic terephthalate unit can be prepared where the ΔT gap is increasingly higher, so that the direct crystallization from the isotropic phase is more easily observed, while the mesophase formation is more and more restricted. Finally, a regular semicrystalline polymer may be characterized by a phase diagram where the mesophase free energy line has been shifted to a much lower temperature in relation to the crystal free energy, so that the ΔT gap will be very high, although, in principle, a mesophase may be obtained at considerably high undercoolings and fast crystallization rates.

Therefore, two extreme cases can be envisaged: (1) at sufficiently low rates (or high crystallization temperatures) any crystallizable polymer system will lead to the thermodynamically more stable crystal phase without the intermediate formation of a mesophase. Evidently, for regular liquid-crystalline polymers this may imply times on the order of many hours or days. (2) At sufficiently high rates, a mesomorphic phase may be always formed first, even in the case of regular semicrystalline polymers, since both kinetic considerations and stabilization of small sizes due to surface free energy effects are favoring such mesophase. In fact, this is in connection with the very active research field of nanoscaled properties: it is becoming well apparent that many properties display an abrupt change when domain sizes fall into the nanometric level.

In order to probe this more interesting second case, just sufficiently high cooling rates and fast detection procedures are needed. Fortunately, the experimental techniques are showing a continuous improvement, so that the corresponding experiments will become readily available in the near future. The main issue is the influence of the mesomorphic phase characteristics on the final properties.

On the other hand, and returning to the Ostwald's rule of stages, it is obvious that it only applies to the mentioned second case.

More experiments at several temperatures and rates and in other polymer systems with different mesophase-forming ability are being planned in order to obtain further information, with special focus on the possible influence of the intermediate mesophase on the final properties of the polymer material.

Acknowledgment. The financial support of MEC (Project MAT2004-06999-C02-01) is gratefully acknowledged. The synchrotron work was supported by the European Community-Research Infrastructure Action Contract RII3-CT-2004-506008.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Keller, A.; Hikosaka, M.; Rastogi, S.; Toda, A.; Barham, P. J.; Goldbeck-Wood, G. *J. Mater. Sci.* **1994**, *29*, 2579.
(2) (a) Strobl, G. *Prog. Polym. Sci.* **2006**, *31*, 398. (b) Strobl, G. *Eur. Phys. J.* **2000**, *3*, 165.
(3) Stribeck, N.; Bayer, R.; Bösecke, P.; Almendarez-Camarillo, A. *Polymer* **2005**, *46*, 2579.
(4) Ostwald, W. *Z. Phys. Chem. (Munich)* **1897**, *22*, 286.
(5) Stoica, C.; Verwer, P.; Meekes, H.; Vlieg, E.; van Hoof, P. J. C. M.; Kaspersen, F. M. *Int. J. Pharm.* **2006**, *309*, 16.
(6) Pérez, E.; Bello, A.; Marugán, M. M.; Pereña, J. M. *Polym. Commun.* **1990**, *31*, 386.
(7) Bello, A.; Riande, E.; Pérez, E.; Marugán, M. M.; Pereña, J. M. *Macromolecules* **1993**, *26*, 1072.
(8) Pérez, E. Liquid crystalline polymers: Polyesters of bibenzoic acid. In *The Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 5, p 3711.
(9) Todorova, G. K.; Krasteva, M. N.; Pérez, E.; Pereña, J. M.; Bello, A. *Macromolecules* **2004**, *37*, 118.
(10) Watanabe, J.; Hayashi, M.; Nakata, Y.; Niori, T.; Tokita, M. *Prog. Polym. Sci.* **1997**, *22*, 1053.
(11) Pérez-Manzano, J.; Fernández-Blázquez, J. P.; Bello, A.; Pérez, E. *Polym. Bull. (Berlin)* **2006**, *56*, 571.
(12) Hoffman, J. D. *J. Chem. Phys.* **1958**, *29*, 1192.
(13) Suzuki, T.; Kovacs, A. J. *Polym. J.* **1970**, *1*, 82.
(14) (a) Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969. (b) Baltá-Calleja, F. J.; Vonk, C. G. *X-Ray Scattering of Synthetic Polymers*; Elsevier: Amsterdam, 1989.

MA062788X