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EVIDENCES OF THE CRYSTALLINE MEMORY AND RECRYSTALLISATION CAPACITY OF BISPHENOL-A POLYCARBONATE

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Abstract

Bisphenol-A polycarbonate (BAPC) was crystallised by exposure to acetone vapours for a period of 9 h; it developed a 20% crystallinity according to WAXS measurements. The samples of semi-crystalline BAPC were then submitted to a series of thermal treatments including annealing, self-nucleation and subsequent isothermal crystallizations. The results showed that the polymer possesses a remarkable crystalline memory and a much faster recrystallization and reorganization capacity (lamellar thickening) than its very low thermal crystallization rate. This peculiar crystallization behaviour probably stems from its rigid backbone molecular structure.

Keywords: crystalline memory, polycarbonate, self-nucleation

Introduction

Bisphenol-A Polycarbonate (BAPC) is a linear polymer with a stiff backbone so that even though it is thermodynamically capable of crystallization, it is generally obtained under usual processing conditions in the amorphous state in view of its extremely slow crystallization rate [1]. Previous studies have indicated that at least 8 days are needed at 463 K (the reported temperature for the maximum crystallization rate [2–3]) under a nitrogen atmosphere for the first spherulites to appear in very thin films [4].

Several methods have been used to accelerate the process of crystallization. The most common include the exposure to poor solvents or solvent vapours [5–7], and the incorporation of plasticizers [8–9]. These methods induce a substantial lowering of the T_g of the polymer and greatly enhance the molecular mo-

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bility of the macromolecules thereby reducing the time needed for crystallization from days to hours. The quickest method is exposure to solvent or solvent vapours and it also has the added advantages that the crystallization occurs at room temperature and that the solvent can be removed later more effectively.

In a previous work we have studied the melting behaviour, the mechanical properties and the fracture morphology of BAPC crystallized by exposure to acetone vapours [6]. The first signs of crystallization appeared after two hours of exposure to acetone vapours at room temperature, the maximum crystallinity was achieved after 48 h exposure and was measured to be 24% by Wide Angle X-ray Scattering (WAXS). In this work it was reported that the fusion endotherm displayed two peaks (at 463 K and 483 K) arising from the presence of two mean lamellar thicknesses as indicated by Small Angle X-ray Scattering (SAXS) experiments and partial melting runs in the DSC. When an annealing was performed at 473 K in a sample with an original crystallinity degree of 24%, it was found that after 3 min at that temperature, the crystallinity dropped to 11% and a single melting peak was obtained upon heating in the DSC curve. However, if longer annealing times were used, the partially crystalline BAPC was found to be able to recrystallize and a recovery in the crystallinity degree to 20% was achieved in a period of 30 h annealing. Furthermore, DSC and SAXS evidence indicated that substantial lamellar thickening occurred.

The above quoted results indicated the potential for recrystallization in a very slowly crystallizing material. The present work aims to further explore the process of recrystallization and its possible influence on the fusion and/or annealing of semi-crystalline BAPC. At the same time, the related subject of crystalline memory of the polymer will be explored by using the self-nucleation technique [10].

Experimental

The bisphenol-A polycarbonate (PC) used in this work was the Makrolon 3203 manufactured by Bayer. Its viscosimetric average molecular weight was 32.700 g mol^{-1}. The amorphous as-received PC was compression moulded into 1 mm thick sheets in a Carver Laboratory press, at 523 K and 2000 psi. Before moulding the material was dried under vacuum at 353 K during 24 h.

The method used to crystallize the material was to expose the PC to acetone vapours for 9 h. This time was enough for the BAPC to develop a crystallinity of 20% as determined by WAXS after drying. After exposure to acetone vapours, the samples were submitted to a slow and progressive drying procedure designed to avoid the appearance of bubbles in the samples and also to obtain samples free of acetone. The following drying protocol was followed:

1) One day at room temperature in a convection oven.
2) One week at room temperature and 150 mbar vacuum.

3) While under vacuum: progressive heating at 10 K/day from room temperature up to 418 K.

4) 48 h at 438 K (i.e., at a temperature above the glass transition temperature of the amorphous material which is approximately 423 K). This step guarantees that almost all of the residual acetone is eliminated. Any traces left did not affect the crystallization rate, the thermal or the mechanical properties of the material [6, 7, 11].

The percentage crystallinity was determined by Wide Angle X-ray Scattering by the method proposed by Hermans and Weidinger [12] for PC. The WAXS measurements were performed in a Philips 1730 X-ray generator equipped with a vacuum vertical diffractometer.

A Perkin-Elmer DSC-7 was used to determine the melting behaviour of all samples. The sample mass chosen was 14–15 mg and all tests were performed at 10 K/min under a nitrogen atmosphere. DSC crystallinity determinations always yielded lower values than WAXS and are relatived to the value of the heat of fusion of a 100% crystalline value, we therefore report the experimentally measured fusion enthalpies.

Annealings were performed on semi-crystalline BAPC samples (SC-BAPC). In the first type of annealing experiments performed, the samples were heated up to the annealing temperature at 10 K min^{-1} and then held isothermally at that temperature for 5 min, after which they were cooled down to ambient temperature at a nominal rate of 200 K min^{-1}. Then heating runs at 10 K min^{-1} were conducted. The annealing temperatures were 455, 462, 473, 483 and 490 K.

In the second type of annealing experiments, the SC-BAPC samples were heated to the annealing temperatures and the annealing time was varied.

In the self-nucleation experiments the SC-BAPC samples were heated up to a self-nucleation temperature for 5 min and then brought to a temperature of 463 K (since this is the temperature at which the thermal crystallization rate of BAPC is maximum [2, 3]) where isothermal crystallization were made under a nitrogen atmosphere, for a period of 12 h. After that time, the samples were quenched to 323 K and subsequent heating runs were conducted at 10 K min^{-1}. Self-nucleation was performed for a series of temperatures starting at 463 K and up to 508 K, in this wide temperature range, all the possible domains described by Fillon *et al.* were covered [10]. At temperatures above the upper foot of the melting endotherm only a constant and minimal number of nuclei remain in the melt (domain I); at temperatures in the upper part of the melting range (above the melting peak of the sample) crystal fragments remain and can act as nuclei in later crystallization stages at lower temperatures (domain II) and at temperatures below the melting peak, incomplete melting takes place, causing self-nucleation and annealing (domain III).

The chosen heating rate for the dynamic DSC experiments was always 10 K min^{-1} but some experiments were also performed at 20 K min^{-1} and it was concluded that the qualitative trends found were independent of the heating rate.

Results and discussion

Figure 1 shows DSC heating scans of the original sample (i.e. the SC-BAPC of 20% crystallinity) and of the SC-BAPC samples annealed for 5 min at the indicated temperatures (T_a). The original sample displays the double melting endotherm previously reported [6, 7] with peaks at approximately 462 and 483 K, and attributed to two mean lamellar thicknesses. The result of annealing at the chosen temperatures is very clear from the scans presented in Fig. 1; there is a partial melting of the crystals whose fusion temperature is below T_a (and a concomitant drop in the enthalpy of fusion) and an annealing process of the remaining crystals. The first two temperatures used, 455 and 462 K only affect the first melting peak since they are probably too low to cause significant lamellar thickening of the second type of lamellae present in the material that melt at higher temperatures in view of their greater mean lamellar thickness [6]. At a T_a of nearly 473 K (the temperature between the two melting peaks) the partial melting eliminates all the crystals that melt in the first peak leaving only those that melt in the second peak.

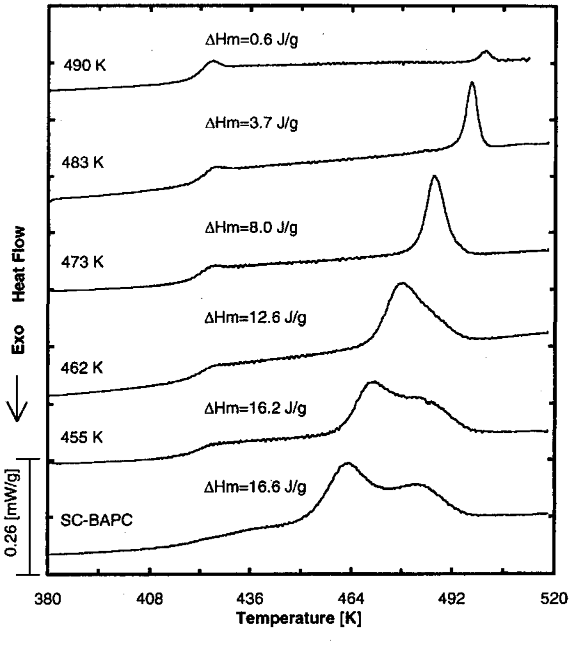

Fig. 1 DSC heating curves of the original sample (SC-BAPC) and SC-BAPC samples after

The evidence that the BAPC crystals can reorganize during the 5 min annealing process is more clearly seen in Fig. 1, when the DSC scans corresponding to the highest annealing temperatures are examined. As mentioned above, the total melting enthalpies are reduced as T_a increases due to the partial melting process (Fig. 1). For a T_a of 483 K, a process of lamellar thickening must have occurred since the remaining crystals after annealing now melt at higher temperatures than any of the crystals originally present in the SC-BAPC sample. If a T_a of 490 K is used, one would expect an almost complete melting of the original SC-BAPC sample since this temperature is very near the end of the upper foot of the melting endotherm. Figure 1 shows that the few crystals that remained after such treatment were substantially annealed and now melt at much higher temperatures.

The reorganization capacity of the BAPC crystals is remarkable since even with exposure to acetone vapours one has to wait two hours for the first crystals to appear and nevertheless, once they are present in the sample, only 5 min at a suitable temperature are enough to cause substantial morphological changes. This reorganization capacity is even more evident in the results of the self-nucleation experiments presented below.

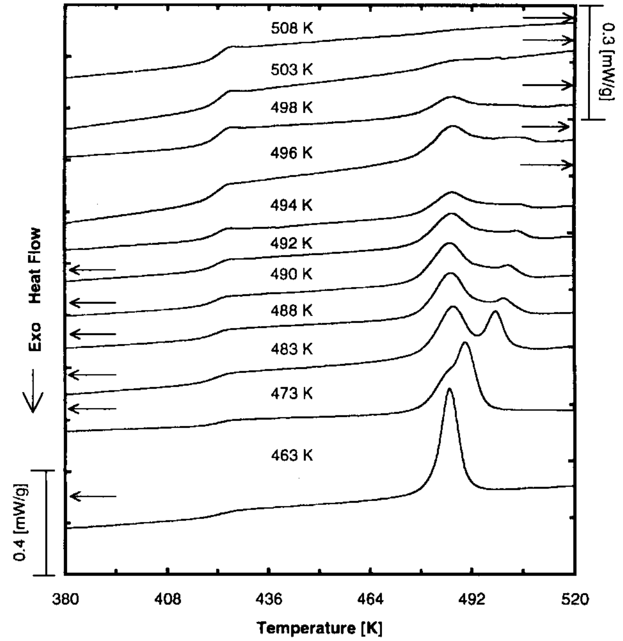

Fig. 2 DSC heating scans of SC-BAPC samples after self-nucleation at the indicated temperatures and subsequent isothermal crystallization (for 12 h at 463 K)

In the self-nucleation experiments, the original sample was annealed for 5 min at a temperature that will be denoted T_s and then immediately brought to

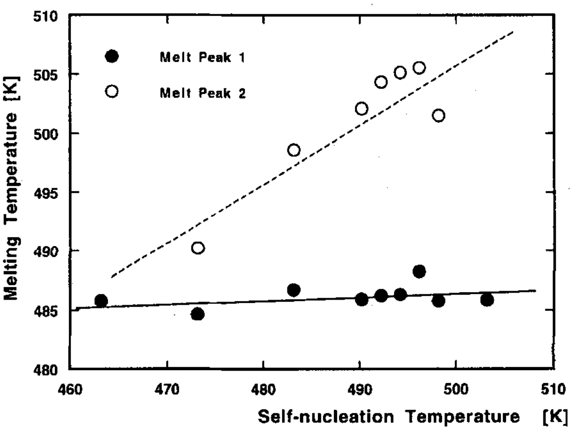

Fig. 3 Melting points *vs.* self-nucleation temperatures for the samples of Fig. 2

463 K in order to crystallize the sample isothermally for a period of 12 h, at the end of this period the sample was quenched to 323 K. Figure 2 shows the DSC heating scans after such treatment at the indicated T_s temperatures. At a T_s of 463 K, this treatment is identical with the annealings of Fig. 1 but performed for 12 h instead of 5 min (see below and Fig. 5). Upon increasing T_s, a complex process is developed, that can be generally described as the formation of a melting peak at 483 K followed by a new second melting peak whose temperature is highly dependent on the T_s values.

It should be noted that an amorphous sample is not capable of crystallizing thermally by exposure to 463 K for 12 h (Fig. 6 below). Therefore, the results of Fig. 2 constitute an evidence of the extraordinary crystalline memory of BAPC. For instance, all the self-nucleation temperatures greater than 492 K are above any melting signal in the DSC curve of the original SC-BAPC sample, however, there was significant nuclei permanence since the polymer was able to thermally crystallize in 12 h to a measurable extent. At $T_s \geq 508$ K the polymer did not crystallize even in 12 h, nevertheless this does not imply that all the crystalline memory of the material has been erased since amorphous BAPC needs 8 days at 463 K to crystallize thermally and we would have to use longer crystallization times (see below and Fig. 6).

In Fig. 3 a plot of both melting peaks observed in Fig. 2 is made as a function of T_s, while in Fig. 4 the total melting enthalpy is plotted also as a function of T_s. The behaviour previously described in Fig. 2 can be schematically seen in Fig. 3. The peak around 483 K does not change with T_s while the other peak not centred around this temperature is strongly dependent on the value of T_s. At T_s=463 K, only those imperfect and thinner lamellae that melt at temperatures up to the first peak of the original SC-BAPC sample are affected. The ones that are not melted (those with T_m>463 K) anneal in such a way that their endotherm overlaps with the melting peak of those crystals that melt at higher temperatures in the second peak of SC-BAPC (i.e., 483 K). For the crystal population that melts in the second peak of the SC-BAPC, at 483 K, the temperature of T_s=463 K seems to be too low to cause any significant annealing. At higher values of T_s, the crystals that in the original sample (SC-BAPC) melt at 483 K are affected (as already discussed for Fig. 1) and upon annealing their melting temperature increases, forming a new second peak that is highly dependent on T_s. The lower melting endotherm at 483 K that is constant with T_s must reflect the melting of the crystals formed at 463 K during the isothermal crystallization process, since this peak is present in all the samples.

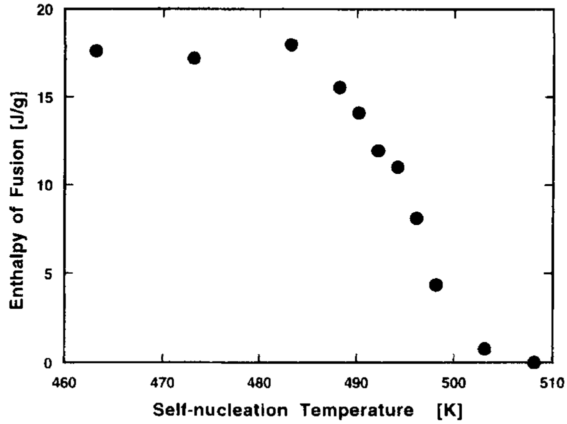

Fig. 4 Melting enthalpies *vs.* self-nucleation temperatures for the samples of Fig. 2

The total melting enthalpy of the original SC-BAPC sample was determined to be 16.6 J g^{-1}. Figure 4 shows that the samples exposed to the lower T_s (463–488 K) were able to gain back during the isothermal crystallization most of the enthalpy lost during the 5 min at T_s (Fig. 1). As expected, the higher the T_s, the lower the final fusion enthalpy since the number of self-nuclei should also be greatly reduced as T_s increases [10]. Once again, it is noteworthy that at temperatures greater than 492 K, substantial crystallinity develops during the isothermal crystallization process as indicated in Fig. 4 due to the remarkable crystalline memory of the material.

The reorganization capability of semi-crystalline BAPC is surprising when compared to the slowness of its crystallization process. In fact, the changes it experiences with self-nucleation and annealing treatment are analogous to those reported in more flexible polymers like poly (ethylene terephthalate) [13–15].

Since the sample annealed at 462 K for 5 min in Fig. 1 has significant differences in its melting endotherm with respect to that of the sample annealed at 463 K in Fig. 2 (a very similar temperature) for 12 h, we decided to study the ef-

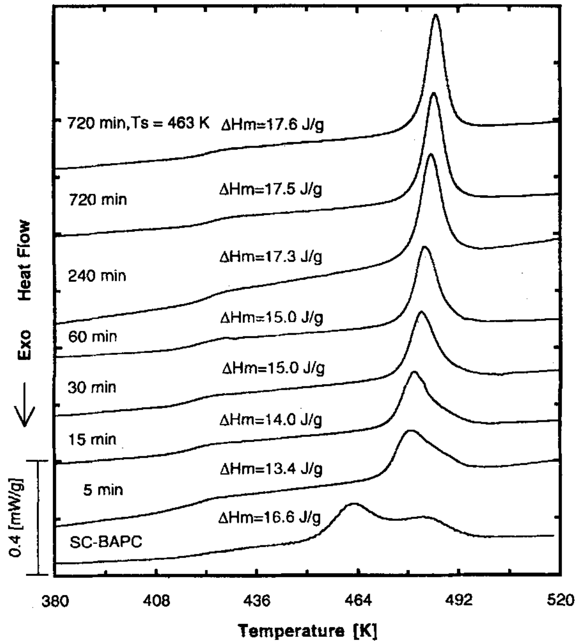

Fig. 5 DSC heating scans of SC-BAPC after annealing at T_a=462 K for the indicated times

fect of annealing as a function of time for a constant temperature. The temperature chosen was 462 K, since it is the temperature of the first melting peak for the original SC-BAPC. The results are shown in Fig. 5. With only 5 min of annealing time the original distribution of melting points is changed since partial melting and annealing have occurred. The fusion enthalpy initially decreases from the value of the SC-BAPC sample to the one annealed for 5 min and then increases steadily with the annealing time. For the sample annealed for 5 min, the first melting peak is shifted to higher temperatures and therefore overlaps the second peak, but still a high temperature shoulder can be observed. With increasing annealing time, the first melting peak shifts further until at 720 min (or 12 h) it completely overlaps the original second melting peak at 483 K. The peak also changed in shape, becoming thinner and taller with increasing annealing time, indicating that thicker and more perfect lamellae with a narrower size distribution are being generated. The melting endotherm in this sample is even higher than in the original SC-BAPC. For comparison, a sample annealed at 463 K for 12 h is also shown in Fig. 5. No substantial differences are observed with respect to the sample annealed for the same time but at 462 K. Figure 5 also constitutes an evidence of how the recrystallization kinetics of the semi-crystalline BAPC is much faster than the thermal crystallization rate of amorphous BAPC.

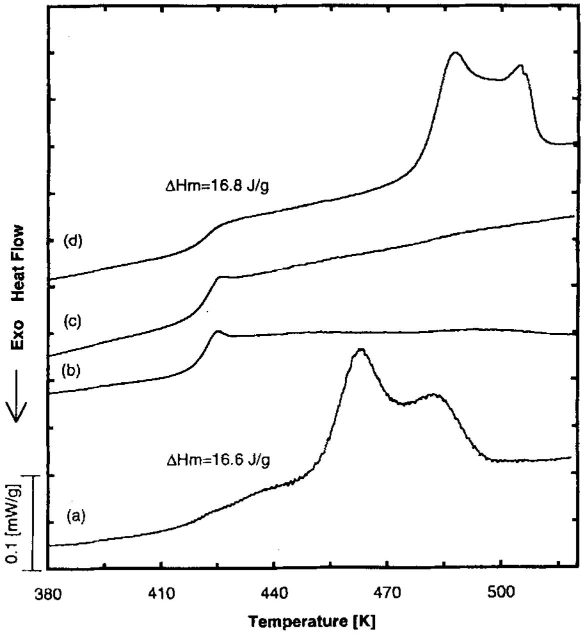

Fig. 6 DSC heating scans for the following samples: (a) original sample (SC-BAPC); (b) amorphous BAPC after 5 min at 508 K and 72 h at 462 K; (c) SC-BAPC after 5 min at 508 K and 12 h at 462 K and (d) SC-BAPC after 5 min at 508 K and 72 h at 462 K

As mentioned above, the fact that in Fig. 2 the sample that was heated up to 508 K was not able to crystallize does not necessarily mean that all crystalline memory was erased, since it is known that the crystalline memory is a phenomenon that depends both on temperature and time. Figure 6 demonstrates this by increasing the crystallization time of the sample to 72 h. For comparison, an amorphous sample of BAPC was subjected to the same treatment applied to the original sample, i.e., 5 min at 508 K and 72 h at 463 K. Figure 6 shows that while the amorphous sample did not develop any crystallinity at all during the 72 h at 463 K, the sample that was semi-crystalline before its melting, was able to recover all of its crystalline content up to 508 K by virtue of its crystalline memory. It is interesting to note that this sample also shows a bimodal distribution of melt temperatures. The first peak corresponds roughly to 483 K, which, according to Fig. 2 would correspond to the melting of the lamellae formed preferentially at 463 K. The second maximum in the melting endotherm would correspond to the second peak shown in Fig. 3, a product of crystal annealing (actually, an extrapolation of the T_m *vs.* T_s line in Fig. 3 yields the observed T_m of the second peak in question).

The remarkable crystalline memory of BAPC must be connected to its rigid backbone structure, a feature that leads to a very high melt viscosity with a weak pseudoplastic flow behaviour [7]. It seems that once the material has undergone all the necessary macroconformational changes to prepare itself for crystallization, its diffusion time back to a statistically random entangled melt is very long. This may explain why, even though it takes 8 days at 463 K for the first crystals to appear (or two hours of exposure to acetone vapours), once the crystals are formed, its seeds do not disappear on heating the material up to 5 min well above its melting point, leading to a much faster recrystallization phenomenon upon cooling to a suitable crystallization temperature.

Conclusions

The annealing experiments performed on semi-crystalline BAPC have demonstrated that this polymer can suffer lamellar thickening processes at very fast rates as compared to its low thermal crystallization rate.

Semi-crystalline BAPC exhibits a remarkable crystalline memory effect. If self-nucleated, the material experiences an acceleration of its thermal crystallization process even if it is melted at temperatures well above its original melting point for 5 min. These results are consistent with the rigid molecular backbone of BAPC and its very high melt viscosity.

In spite of its rigid backbone, if BAPC is crystallized, then it is capable of experiencing reorganization processes during heating in an analogous way to other polyesters with more flexible chains like poly(ethylene terephthalate).

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References

1 H. Schnell, Chemistry and Physics of Polycarbonates, Wiley, New York 1964.
2 B. Von Falkai and W. Rellensmann, Makromol. Chem., 75 (1964) 112.
3 B. Von Falkai and W. Rellensmann, Makromol. Chem., 88 (1965) 38.
4 G. Kämpf, Kolloid Z., 50 (1960) 1972.
5 J. P. Mercier, G. Groeninckx and M. Lesne, J. Polym. Sci., Part C, 16 (1967) 2059.
6 A. J. Müller and E. Paredes, Latin Amer. J. Metallurgy and Materials, 5 (1985) 130.
7 G. Di Filippo, M. González, M. Gasiba, A. J. Müller, J. Appl. Polym. Sci., 34 (1987) 1959.
8 F. Gallez, R. Legras and J. P. Mercier, Polym. Eng. Sci., 16 (1976) 276.
9 F. Gallez, R. Legras and J. Mercier, J. Polym. Sci.: Phys. Ed., 14 (1976) 1367.
10 B. Fillon, J. C. Wittman, B. Lotz and A. Thierry, J. Polym. Sci., Polym.: Phys. Ed., 31 (1993) 1383.
11 R. P. Kambour, F. E. Karasz and J. H. Daane, J. Polym. Sci., Part A-2, 4 (1966) 327.
12 P. H. Hermans and A. Weidinger, Makromol. Chem., 64 (1963) 135.
13 L. Shaow and J. Koenig, J. Polym. Sci.: Polym. Symp., 71 (1984) 121.
14 G. Alfonso, E. Pedemonte and L. Ponzetti, Polymer, 20 (1979) 104.
15 R. Seguela, Polymer, 34 (1993) 1761.