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Crystallisation kinetics of cyclic and linear poly (butylene terephthalate)

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Abstract:

The isothermal crystallisation kinetics of cyclic poly (butylene terephthalate) (cPBT) were analysed using a primary-limited differential-Avrami analysis and the equilibrium melting point (T_m^o) was determined using the Hoffman-Weeks approach. Further analysis of the kinetic data using the Hoffman-Lauritzen analysis yielded the nucleation constant (K_g) and the end surface free energies ($\sigma\sigma_e$). The kinetic parameters obtained for cPBT were compared with a commercial sample of linear PBT. The K_g values of cPBT and linear PBT were observed to be 5.13 $\pm$ 0.02 x 10^5 K^2 and 4.50 $\pm$ 0.02 x 10^5 K^2, respectively. Meanwhile, the $\sigma\sigma_e$ of cPBT was calculated as 6.44 $\pm$ 0.05 x 10^{-4} J^2m^{-4} and linear PBT was 5.54 $\pm$ 0.05 x 10^{-4} J^2m^{-4}.

Keywords: cyclic (butylene terephthalate) oligomers (CBT), crystallisation kinetics, differential scanning calorimetry (DSC), Avrami analysis, equilibrium melting point, Hoffman–Weeks analysis.

1.0 Introduction

Poly (butylene terephthalate) (PBT) is an engineering polymer that is used in a wide range of application areas including the automotive industry, household electrical appliances, telecommunications, machine components, food packaging and medical applications [1]. Given the increasing need to re-cycle materials in these industries, the process of de-polymerisation as a polymer recycling strategy is of interest [2-4]. In the case of PBT, this process involves the conversion of waste polymer into cyclic oligomers (CEO) through ring-chain equilibration of the polymer in dilute solution (de-polymerisation) with various catalysts [4-7].

Cyclic butylene terephthalate oligomers (CBT) are particularly interesting because they exhibit relatively low melt viscosities ($\approx$ 17 mPa.s, i.e. water-like) and they also undergo rapid isothermal bulk polymerisation to form polymer (PBT), which in turn, exhibits rapid crystallisation and high degrees of crystallinity. Furthermore, there are no significant chemical emissions during processing [8-9].

It has been reported that the polymerisation of CBT oligomers and the crystallisation of the resulting PBT occur simultaneously [4, 10-11]. There have been several attempts to separate the two processes, although these attempts have been hindered by the athermal nature of the polymerisation process [12-14].

Typically, the number average molecular mass (M_n) of cPBT varies between 30000 and 40000 $gmol^{-1}$, and the polydispersity index remains at approximately 2 [11, 15]. It was found that polymer prepared from cyclic oligomers resulted in higher levels of crystallinity than the conventionally prepared polyester [10].

The isothermal crystallisation kinetic studies of PBT produced from its cyclic oligomers have received little attention in the literature. Recently, Lehmann and Karger-Kocsis [16] reported their work on the isothermal and non-isothermal crystallisation kinetics of a linear PBT produced from cyclic oligomers *via* ring opening polymerisation (XB3 and CBT160) and compared the kinetic data to various commercially available linear PBT samples.

The catalyst has been found to control the nature of the polymerisation: the XB3 system yields linear PBT whereas the XB2 system yields cPBT *via* ring expansion polymerisation [4, 8, 10, 16-17]. The isothermal crystallisation of cPBT from a miscible blend of cPBT and SMI has been reported, in this work it was shown that the Avrami crystallisation kinetic parameters of cPBT were strongly influenced by the composition of the blend [18]. Therefore the aim of this work was to compare the crystallisation kinetics of cPBT with those of a commercial sample of linear PBT and thereby complement the two previous studies in the area.

2.0 Experimental

2.1 Materials

The cyclic oligomer of butylene terephthalate (CBT), (XB2-CA4) supplied in powder form, was provided by the Cyclics Corp. (USA). The XB2-CA4 contained a stannoxane catalyst and was termed a one-component CBT, where the resin and catalyst were premixed. The CBT samples were polymerized *in-situ* in the DSC by heating the samples at 100 ^{o}C min^{-1} to 190 ^{o}C and holding at that temperature for 10 min. These conditions have been previously shown to be an optimum for the production of the cyclic polymer (cPBT) [19-20]. The linear polybutylene terephthalate (PBT) (PF100), in pellet form, was purchased from Plastribution Ltd. (UK). These materials were dried in a vacuum oven for about 24 hours at 90 ^{o}C and were

kept in desiccators until required. The molecular weight was characterised by GPC, the number and weight average molecular weights together with the polydispersity of cPBT produced from CBT oligomers and linear PBT are listed in Table 1.

2.2 Differential scanning calorimetry (DSC)

The crystallisation and melting of cPBT and linear PBT were measured using a Perkin–Elmer differential scanning calorimeter (DSC-7, USA). The temperature was calibrated with pure indium and tin standards having melting temperatures (T_m^o) of 156.67 ^oC and 231.97 ^oC, respectively. The enthalpy of fusion of indium (ΔH^o_f), 28.5 Jg^{-1}, was used for power calibration. Experiments were run with sample masses of approximately 20 mg. The DSC head was purged with nitrogen gas with a flow rate of 20 cm^3 min^{-1} to minimise oxidative degradation. Samples were contained in aluminium pans, and an empty pan was used as a reference.

2.2.1 Isothermal crystallisation studies

After *in-situ* polymerisation of CBT oligomers in the DSC, heating was then continued to 10 ^oC above the observed melting point of the cPBT (225 ^oC), the samples were then held at this temperature for 2 min to ensure complete melting. In the case of the linear PBT polymer, samples were also heated to 10 ^oC above the observed melting point and held for 2 min. The subsequent procedures were the same for both materials, i.e., the samples were then cooled to the selected crystallisation temperature at 160 ^oC min^{-1} and held at that temperature until the calorimeter response returned to the baseline. Isothermal melt crystallisations were carried out in the temperature range of 197 to 201 ^oC for cPBT and 209 to 213 ^oC for linear PBT at 1

^{o}C intervals. The crystallisation temperature ranges were selected in accordance with the non-isothermal crystallisation onsets that were observed in Fig. 1.

2.2.2 Determination of the equilibrium melting point

Following of each isothermal crystallisation, the sample was heated at 10 ^{o}C min^{-1} to a temperature 10 ^{o}C above the observed melting point. The melting regions were then analysed using the Hoffman-Weeks approach to yield the equilibrium melting point. According to Hoffman and Weeks [21], the melting point is defined operationally as the temperature where the last detectible trace of crystallinity disappears. Therefore in this study, we defined melting as the temperature at which the last trace of crystallinity was observed.

3.0 Results and Discussion

3.1 Avrami analysis

Polymer crystallisation can be divided into a primary and a secondary stage. Primary crystallisation is characterized by the radial growth of semi-crystalline superstructures (generally spherulites) up to impingement with other growing spherulites; the secondary crystallisation is due to crystallisation of the crystallisable melt which is trapped between the lamellar structures formed during the growth of the spherulites [22]. The processes have been considered to occur consecutively or partially concurrently. The primary stage of crystallisation is often modelled with the Avrami equation [23-24].

Typical crystallisation exotherms for cPBT and conventional linear PBT at the different isothermal crystallisation temperatures (e.g. 200^{o}C for cPBT and 212^{o}C for linear PBT) are shown in Fig. 2. The end of the crystallisation process was taken to be the point where the

isothermal curve converged with the horizontal base line [25] (the data for linear PBT has been truncated to aide comparison).

The relative crystallinity (X_t) for the isothermal crystallisation which developed at time (t) was defined as the ratio of the two areas between the heat flow-time curve and baseline, from t = 0 to t = t and from t = 0 to t = infinity, i.e.; [24, 26]

$$\frac{X_t}{X_\infty} = \frac{\int_0^t \left(dH_t / dt \right) dt}{\int_0^\infty \left(dH_t / dt \right) dt} \qquad (1)$$

The overall development of relative crystallinity with time at the selected crystallisation temperatures of cPBT and linear PBT is illustrated in Figs. 3 and 4. From these figures, a clear temperature dependence of the process was apparent: the time for crystallisation decreased with decreasing crystallisation temperature. The process can be described by the Avrami equation which relates the extent of crystallinity for isothermal melt-crystallisation to time, t, by;

$$1 - \frac{X_t}{X_\infty} = \exp(-Zt^n) \qquad (2)$$

where, Z is a composite rate constant incorporating the nucleation and growth rates, X_t and X_∞ are the volume fractions of crystallized material at time t and at infinity and n is the Avrami exponent, which adopts different values for different mechanisms [24, 26]. In order to limit the Avrami analysis to the primary process, Eq. 2 can be expressed in differential form as shown below,

$$n = -t\left(\frac{dX_t}{dt} \right) \left[\left(1 - \frac{X_t}{X_\infty} \right) \ln\left(1 - \frac{X_t}{X_\infty} \right) \right] \qquad (3)$$

The instantaneous *n* value is diagnostic of the transition between the primary and secondary crystallisation processes and it can be used to determine a value for X_∞ for the primary process in a primary limited conventional double log plot [26]. The mechanistic constant (*n*) and the composite rate constant (*Z*) were determined from the slope and intercept respectively. The half-life ($t_{½}$) of the primary process was determined using the following relationship;

$$Z = \frac{\ln 2}{(t_{1/2})^n} \qquad (4)$$

Example Avrami plots are shown in Fig. 5 (200^{o}C for cPBT and 212^{o}C for linear PBT) yielded kinetic parameters that are listed in Table 2. The *n* values were observed to be in the region of 2.4 to 2.5 for cPBT and 2.8 to 3.0 for linear PBT which suggests the occurrence of heterogeneous nucleation of spherulites [27]. It is instructive to consider the limitations of this presentation of the crystallisation data. For instance, in Fig. 2, it is apparent that the induction times for both exotherms are similar yet the crystallisation $t_{½}$ are measurably different (the $t_{½}$ of cPBT and linear PBT are 10 and 12.5 minutes, respectively). However, to enable comparison of the kinetics of the transformations, the super-cooling (ΔT) must be determined, in which $\Delta T = T_m^o - T_c$, where T_m^o is the equilibrium melting temperature.

3.2 Equilibrium melting point (T_m^o)

According to Hoffman and Weeks [21], the equilibrium melting points (T_m^o) can be determined from a plot of T_m and T_c, where;

$$T_m = T_m^o\left(1 - \frac{1}{2\beta}\right) + \frac{T_c}{2\beta} \qquad (5)$$

in which $\beta = \sigma_e l / \sigma l_e$ and σ is the fold surface free energy, l is the lamellae thickness and the subscript e refers to equilibrium conditions, and $\beta = 1.0$ in the absence of re-crystallisation or annealing during melting. A plot of T_m against T_c should be linear with a slope of 1/2 β. This line intersects to the equilibrium condition of T_m=T_c at T_m^o. The Hoffman and Weeks plots for the cPBT and linear PBT are shown in Fig. 6. The T_m^o of cPBT and linear PBT was determined as 256 ± 1.0 ^{o}C and 266 ± 1.0 ^{o}C respectively. Determination of T_m^o enables the $t_{½}$ to be shown as a function of super-cooling rather than simply the crystallisation temperature. This refinement enables kinetic data for cPBT and linear PBT to be compared under the same thermodynamic driving forces [28-29].

Fig. 7 shows the variation of half-life ($t_{½}$) as a function of degree of super-cooling ($T_m^o - T_c$). The observed temperature dependencies were consistent with what has been observed in many other melt crystallisable polymers: $t_{½}$ increases with increasing T_c (decreasing super-cooling) in the hot-crystallisation region [30-31]. It was apparent that at comparable super-cooling, the crystallisation process of cPBT was slightly slower than the linear PBT. It may be the case that the cyclic nature of the chains imposes restrictions on the transport of crystallisable chains from the melt onto the growth surface. The cyclic nature of the chain may also impose a limiting lamella thickness consistent with the slight reduction in equilibrium melting point for cPBT. However, a confounding factor may be the difference in molecular weight. In terms of M_n, both materials are comparable, but they differ in M_w and it is well known that increasing molecular weight hinders the crystallisation process. Therefore it is likely that there are two factors that are involved in the reduction in crystallisation rate in the materials used in this study; M_w and the cyclic nature of the chains in cPBT.

3.3 Nucleation constant and surface free energy

According to Hoffman and Lauritzen [28, 32] the spherulitic radial growth rate can be expressed as:

$$g = g_o \exp\left(-\frac{U^*}{R(T-T_\infty)}\right)\exp\left(-\frac{K_g}{T\Delta Tf}\right) \qquad (6)$$

where, g is the linear growth rate, g_o is a constant, U^* is the activation energy for viscous flow (where Hoffman and Lauritzen assigned a value of 6300 Jmol^{-1} for this parameter), R is the gas constant, T is the crystallisation temperature and T_∞ is the temperature below which the motions of crystallisable segments to the crystallisation face cease. The T_∞ is usually assumed to be 30K below the glass transition temperature ($T_\infty = T_g - 30$).

With the modification of Eq.6 where the growth rate has been replaced by the reciprocal of the crystallisation half-life, the nucleation constant (K_g) can be determined from the slope of a linear plot of $(\ell n\left(1/t_{1/2}\right) + (U/R(T-T_g+30))$ against $(1/Tf(\Delta T))$ [27]. The K_g values for cPBT and linear PBT (which were determined from the slopes in Fig. 8) were 5.13 ± 0.02 x 10^5 K^2 and 4.50 ± 0.02 x 10^5 K^2, respectively.

If the K_g value is known, the surface free energy product ($\sigma\sigma_e$) can be calculated from this relation;

$$K_g = \frac{nb_o\sigma\sigma_e T_m^o}{\Delta H_f k} \qquad (7)$$

where the n value depends on the regime of crystallisation, i.e., $n = 2$ for regime II and $n = 4$ for regimes I and III. It has been assumed that regime III was applicable for the T_c range adapted in this study, therefore $n = 4$. In order to calculate the $\sigma\sigma_e$, we used 0.580 nm

as the b_o value [1]. Based on previous X-ray analysis, it was reported that the cPBT has the same unit cell as linear PBT [4]. T_m^o and ΔH_f are the equilibrium melting point and enthalpy of fusion per unit volume, respectively while k = 1.38 x 10^{-23} JK^{-1} is the Boltzmann constant. With these values, we found that the surface free energy product ($\sigma\sigma_e$) of cPBT was 6.44 ± 0.05 x 10^{-4} J^2m^{-4} and linear PBT was 5.54 ± 0.05 x 10^{-4} J^2m^{-4}. The difference in surface free energy product is in accordance with the reduction in crystallisation rate observed in cPBT: the elevated surface free energy product retards the crystallisation process (and has been reported previously in PEEK [25]).

4.0 Conclusions

The isothermal crystallisation kinetics of cPBT and linear PBT were analysed using a differential Avrami approach. The crystallisation parameters $t_{½}$, Z, and n, were found to be sensitive to the crystallisation temperatures (T_c) within the range of 197°C to 201°C for cPBT and 209°C to 213°C for linear PBT. The values of the rate constant, Z, decreased with an increase in the temperature. All the crystallisation rate parameters ($t_{½}$, Z, and n) varied predictably with the T_c values. The n values ranged from 2.4 to 2.5 for cPBT and 2.8 to 3.0 for linear PBT, respectively which indicated the occurrence of heterogeneous nucleation of spherulites. This study also found that the crystallisation process of cPBT was slightly slower than that conventional linear PBT for the same degree of super-cooling, the reduction in crystallisation kinetics was attributable to the cyclic nature of the polymer chains in cPBT and a difference in molecular weight (M_w).

5.0 Acknowledgments

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6.0 References

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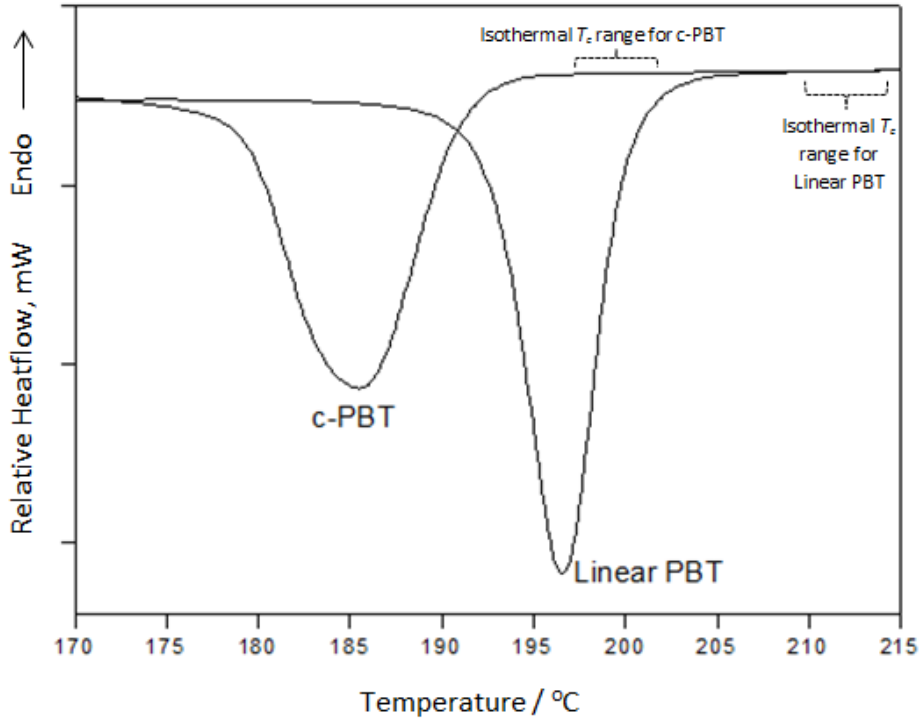

Fig. 1 DSC exotherms of melt crystallisation of cPBT and linear PBT at 10 ^{o}C min^{-1}

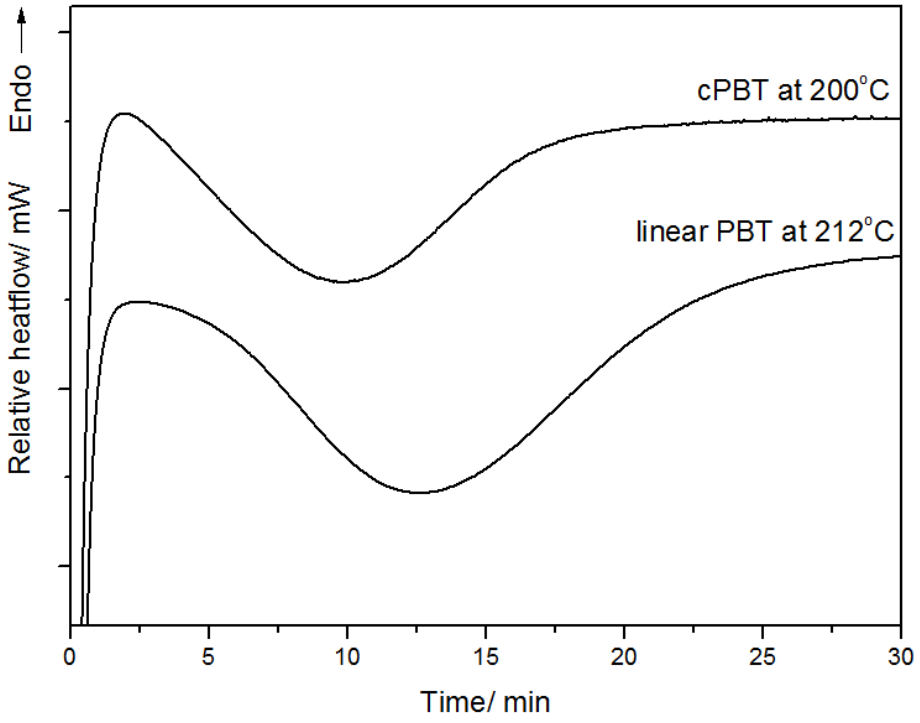

Fig. 2 Typical DSC exotherms of the isothermal crystallisation of cPBT and linear PBT at crystallisation temperatures of 200 ^{o}C and 212 ^{o}C, respectively

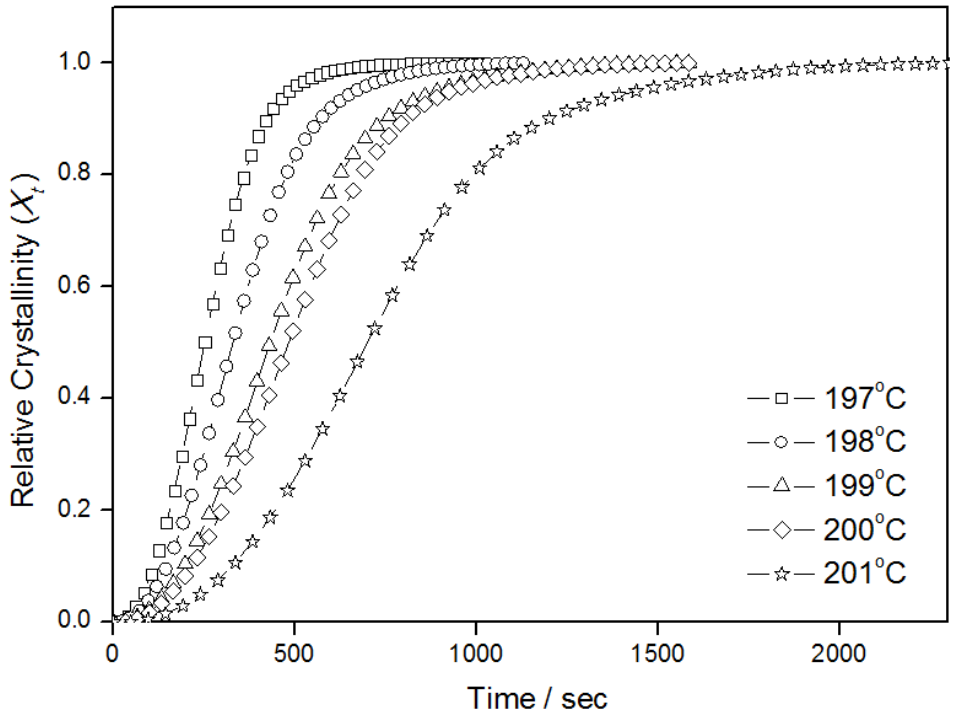

Fig. 3 Development of crystallinity with time for cPBT

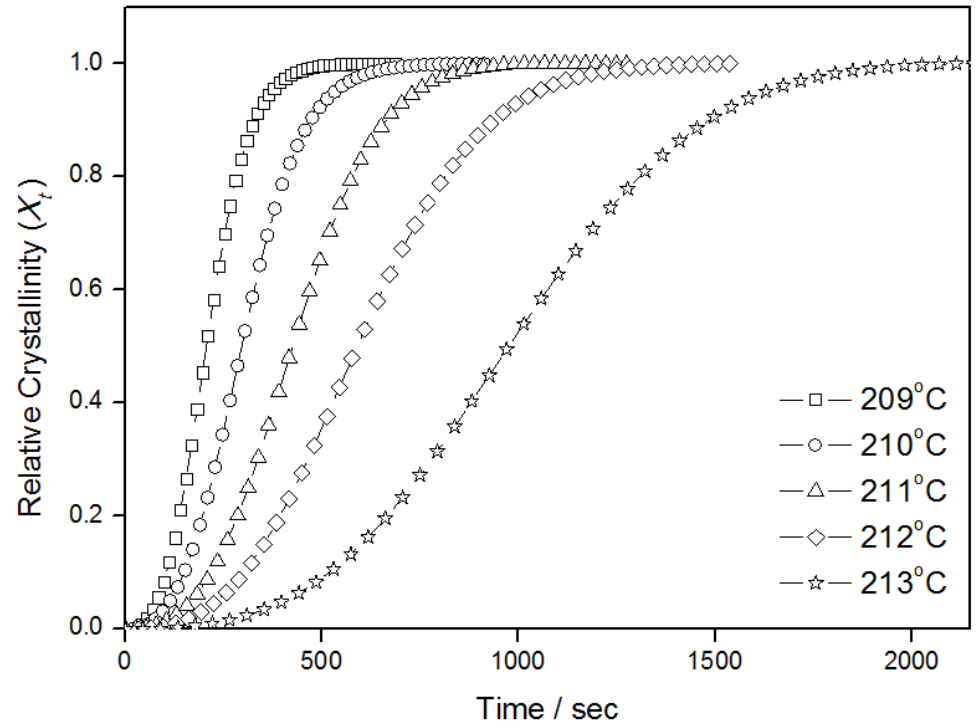

Fig. 4 Development of crystallinity with time for linear PBT

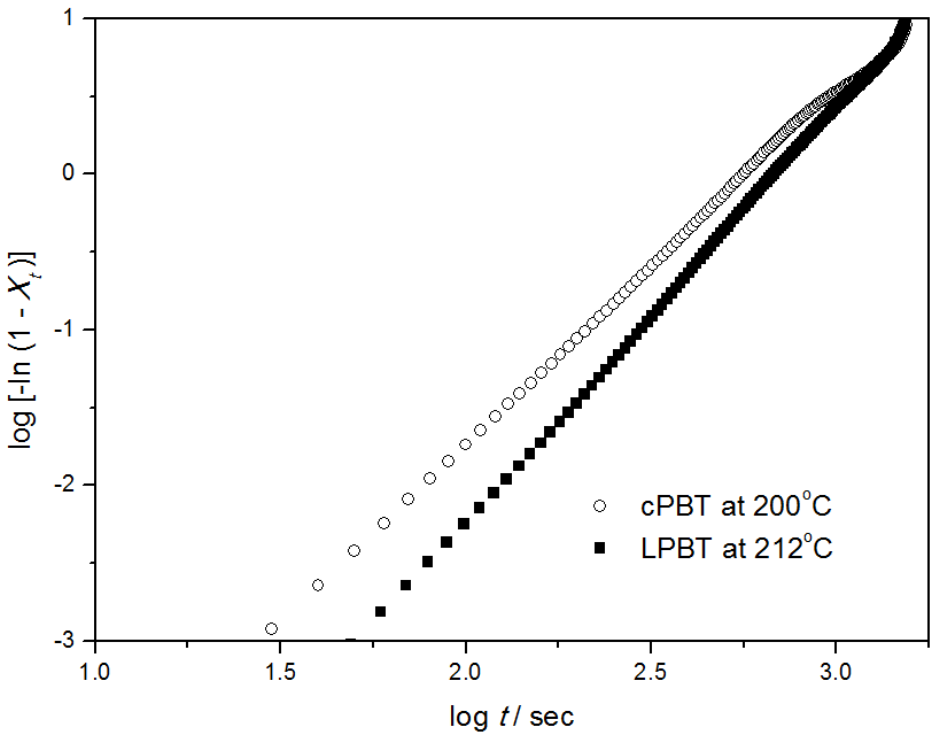

Fig. 5 An Avrami plot of cPBT and linear PBT at 200 °C and 212 °C, respectively

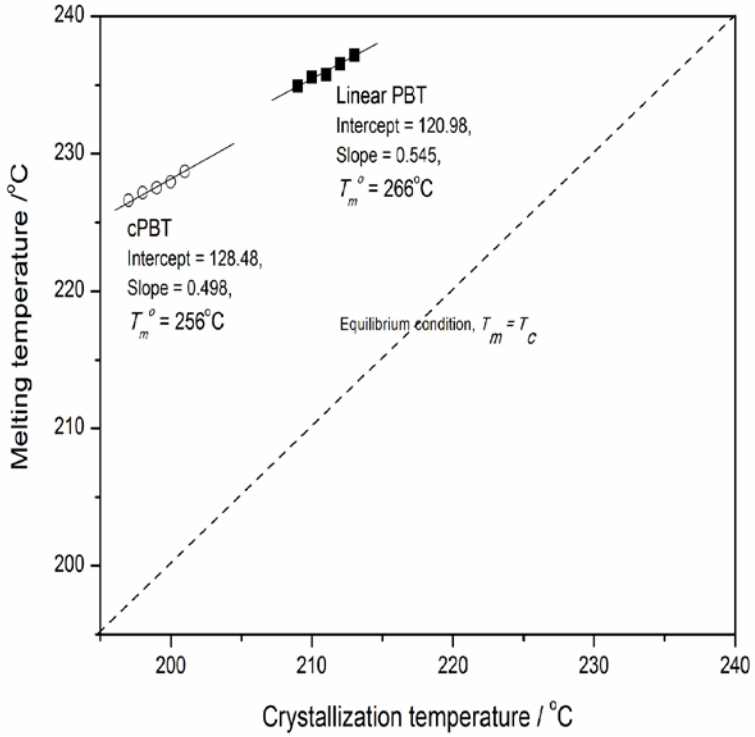

Fig. 6 Hoffman-Weeks plot of observed melting temperature against crystallisation temperature for cPBT and linear PBT

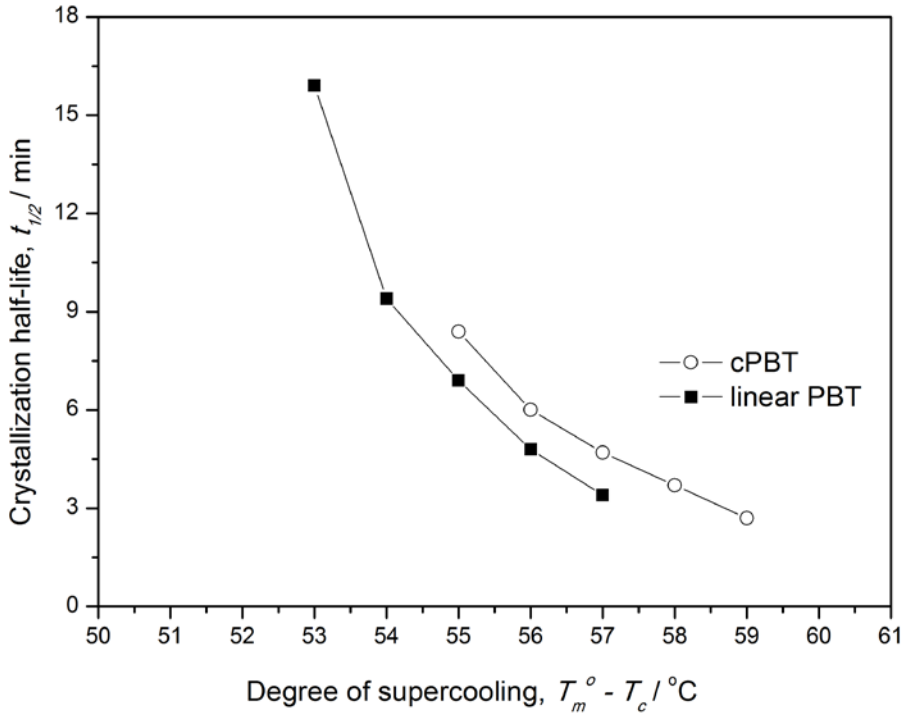

Fig. 7 Variation of half-life ($t_{½}$) as a function of crystallisation temperature (T_c) cPBT and linear PBT

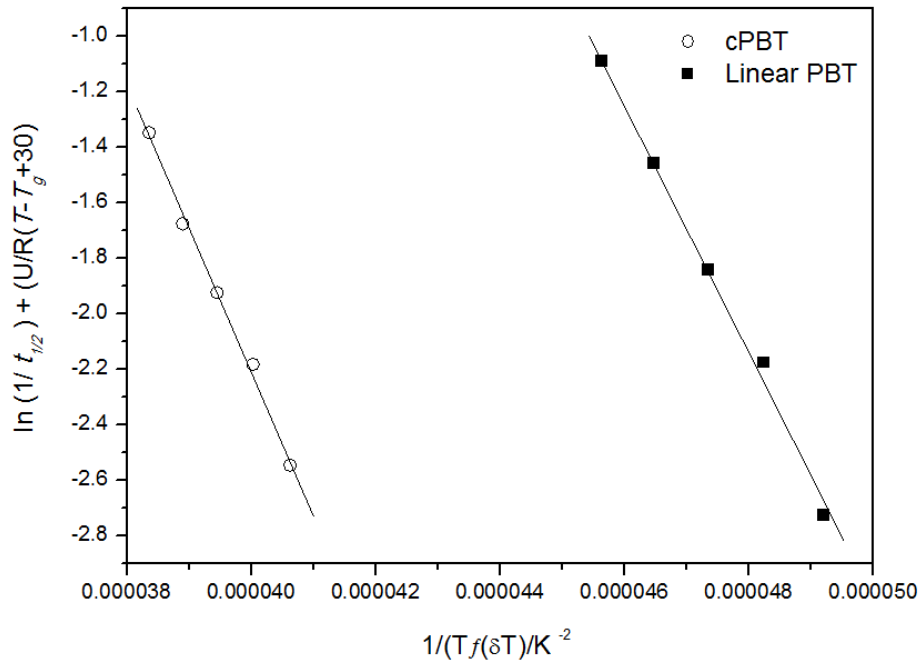

Fig. 8 A Hoffman-Lauritzen plot for cPBT and linear PBT

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Table 1 Average molecular weight and polydispersity of cPBT and linear PBT

Sample	M_w **/gmol^{-1}**	M_n **/gmol^{-1}**	**PDI (Mw/Mn)**
cPBT	94,600	32,500	2.9
Linear PBT	60,997	33,310	1.8

Table 2 The Avrami parameters and melting temperatures for cPBT and linear PBT

Sample	T_c **/ ^{o}C**	n **/± 0.1**	$t_{1/2}$**/ min ± 0.1**	Z **/ min^{-n} (x10^{-4}) ± 0.002**	T_m **/ ^{o}C ± 0.1**
cPBT	197	2.4	2.7	577	226.6
	198	2.4	3.7	269	227.2
	199	2.4	4.7	155	227.5
	200	2.4	6.0	82	227.9
	201	2.5	8.4	25	228.7
Linear PBT	209	2.8	3.4	223	234.9
	210	2.8	4.8	82	235.6
	211	2.9	6.9	26	235.8
	212	2.9	9.4	11	236.5
	213	3.0	15.9	2	237.2