

Correlation between Polymerization of Cyclic Butylene Terephthalate (CBT) and Crystallization of Polymerized CBT*

Jian-qiang Zhang^{a**}, Zhi-fang Li^a, Zheng Zhang^a, Hui-xia Feng^a, Zong-bao Wang^b, Ya Li^c,
Peng Chen^d and Qun Gu^{c**}

^a School of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, China

^b Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

^c Institute of Material Engineering, Ningbo University of Technology, Ningbo 315016, China

^d Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

Abstract The correlation between ring-opening polymerization (ROP) of cyclic butylene terephthalate (CBT) and crystallization of polymerized CBT (pCBT) strongly affected the final properties of pCBT and its composites. The major objective of this contribution is to pinpoint the threshold temperature between them and the interrelation is successfully disclosed. That is, crystallization during polymerization occurs below 204 °C and the crystallization properties of pCBT are determined by this isothermal ROP stage; polymerization and crystallization are gradually separated with the increase of temperature of ROP (T_p) from 204 °C, and the crystallization properties of pCBT are dominated by cooling stage; only polymerization is performed above 212 °C. Moreover, quantitative analysis suggests that uniform crystal size distributions and thicker lamellar crystals derive from the stage of crystallization during polymerization. On the contrary, the crystal size distributions become wider above 204 °C of T_p and lead to obvious double melting peaks during heating scan. These efforts provide a very useful guide for the related investigation and application of CBT.

Keywords: Ring-opening polymerization; Crystallization; Cyclic butylene terephthalate.

INTRODUCTION

Cyclic butylene terephthalate (CBT) is a kind of solid mixture composed of different crystalline cyclic oligomers. CBT can be synthesized into high-molecular-weight poly(butylene terephthalate) (PBT) by ring-opening polymerization (ROP) in the presence of appropriate tin or titanate catalysts^[1–5]. During the past few years, studies about CBT mainly focus on the following three aspects. Firstly, due to the thermal stability and compatibility in combination with numerous fillers, CBT is favorable to well disperse fillers for composites preparation including clay^[6], silica^[7], carbon nanotubes^[8], polyhedral oligomeric silsesquioxane (POSS)^[9] and graphene^[10]. Also, CBT can be used as masterbatch^[6, 9], lubricant^[11] or blending compatilizer^[3, 12] *etc.* Secondly, ultra-low viscosity (~30 mPa·s, 190 °C)^[1–5] allows CBT to impregnate many kinds of dense fibrous reinforcements easily, thus, the thermosetting composites manufacturing technologies can be employed in the thermoplastic fields directly, such as typical resin transfer molding (RTM), casting and rotational molding^[13, 14]. Thirdly, toughening by *in situ* copolymerization is another important field^[15–17]. In addition, the thermoneutral

* This work was financially supported by the National Natural Science Foundation of China (No. 21364004), Gansu Province University Fundamental Research Funds and Doctor Research Fund of Lanzhou University of Technology, China.

** Corresponding authors: Jian-qiang Zhang (张建强), E-mail: zhangjq@lut.cn

Qun Gu (顾群), E-mail: guqun@nimte.ac.cn

Received November 22, 2014; Revised January 30, 2015; Accepted February 7, 2015

doi: 10.1007/s10118-015-1662-7

ROP of CBT can be quickly performed within several or tens of minutes without evolution of low-molecular-weight byproducts^[1–5]. ROP is often performed below the melting temperature (225 °C) of polymerized CBT (pCBT) and the solidified product can be removed from the mold without cooling. This meets the manufacturing requirements which need the thermal cycling time and expenses as low as possible^[18]. Therefore, CBT has become a promising “green material” for fabricating the recyclable thermoplastic composites.

With regard to PBT, it is usually produced by polycondensation and its properties are strongly dependent on the degree of crystallization, processing condition^[19] and the resulting spherulite morphology^[20–26]. As for pCBT, the polymerization methods, *i.e.* RTM, vacuum-assisted RTM, hot plate press^[13–17] and the correlative parameters, such as polymerization temperature (T_p), reaction time, heating or cooling rates and catalyst types are involved in the performance of the final matrix, not only in pure pCBT but also in its composites^[5, 13, 14]. Though PBT and pCBT have the same chemical structure, however, the researchers and engineers are always suffered from a key problem that pCBT and the composites prepared by CBT are much more brittle than PBT^[1–5]. Some researchers ascribed the brittleness to higher crystallinity and more perfect crystal structure of pCBT than PBT^[1–5, 13, 14]. Parton *et al.*^[13, 14] demonstrated that the pCBT was brittle when polymerization and crystallization occurred simultaneously at 190 °C, but the brittleness was improved when polymerization was proceeded at 230 °C and then isothermal crystallization at 190 °C. They also found that the multiple melting peaks resulting from the melting and recrystallization of imperfect crystals, indicated poor crystal quality in the composites part. Moreover, Tripathy^[5] declared that crystallization of pCBT at relatively low temperature (lower than 190 °C) resulted in “unusual” type spherulites, but above 195 °C, “usual” type ones were observed. Wu^[27] displayed the similar morphologies of pCBT under different crystallization temperatures (T_c). Importantly, Moginger *et al.*^[28] studied the amount of different type spherulites of PBT in injection moulded samples and found an increase in amount of “usual” type spherulites when the cooling rate decreased and the melt temperature increased. Together with the increasing amount of “usual” type spherulites, PBT became more brittle.

Therefore, it is the most important question to clarify the interrelation between polymerization and crystallization for effective monitoring and process controlling in industrial production. Hakmé *et al.*^[29] monitored electrical properties during polymerization of CBT by dielectric sensor. Although they declared that the polymerization and crystallization occurs simultaneously below 200 °C according to the study of four T_p (190, 200, 210 and 220 °C), but the sensor could not distinguish the distinctness between polymerization and crystallization when T_p was below 210 °C. Similarly, Archer *et al.*^[30] used the dielectric analysis (DEA) to correlate conversion rate and curing state (crystallization of pCBT) during the preparation of fiber reinforced composites for wind energy and they found an inverse relationship between cure time and molecular weight.

Among all the techniques, differential scanning calorimetry (DSC) is proven to be a simple and convenient choice and has been used in almost all related research works about CBT. Typically, Lehmann^[31] studied the polymerization of CBT at 250 °C for 0 and 15 min and examined the isothermal and non-isothermal crystallization kinetics of pCBT at T_c from 190 to 195 °C with 1 K intervals. Wu^[27] studied the ROP of CBT at 230 °C for 30 min and investigated crystallization kinetics, crystallization morphologies and melting behaviors from 190 °C to 205 °C at 2–5 K intervals. Lanciano^[32] studied the effects of thermal history of ROP at 220, 240 °C for 10 min and the mixtures of CBT with montmorillonite on the crystallization of the resulting pCBT. Tripathy^[5] employed DSC to characterize the different catalyst's effect on the ROP and monomer conversion at 185–205 °C with 5 K intervals. But they all did not discuss the occurrence order between polymerization and crystallization which is an important factor for the mechanical properties' definition of pCBT.

Despite the considerable efforts paid to the research about CBT, however, the key issue of correlation between ROP of CBT and crystallization of pCBT is uncertain up till now. Therefore, the aim of this work is to systematically investigate and pinpoint the threshold temperature between polymerization of CBT and crystallization of pCBT and further elucidate the differences of crystallization during polymerization or crystallization from melt (polymerization followed by crystallization) and finally disclose the instructive variation laws for the further investigation of CBT.

EXPERIMENTAL

Materials

CBT[®]100 pellets were purchased from Cyclics Corporation. Butyltin chloride dihydroxide catalyst (Fascats[®]4101) was commercially available from Sigma-Aldrich. CBT and catalyst were dried at 105 °C overnight under vacuum before using. Trichloromethane (CHCl₃) was procured from Sinopharm Chemical Reagent, China and used as received. CBT and catalyst were pre-mixed in CHCl₃ at room temperature and the blends were named as catalyzed CBT. After solvent evaporated, it was dried at 105 °C for 12 h in a vacuum oven. For all of our experiments and measurements, the catalyst content to the neat CBT was fixed at 0.45 wt%.

Characterization

Differential scanning calorimetry (Mettler Toledo DSC I) was calibrated with an indium standard and employed to characterize the melting point and record heat flow during polymerization and crystallization. Sample mass of ~5 mg was adopted in 40 μ L standard aluminum crucibles for all experiments. Heating rate is 10 K/min for CBT. For catalyzed CBT, the thermal circle procedure is follows: first quick heating to T_p at a heating rate of 100 K/min, hold for 30 min to finish polymerization, cooling to room temperature; second heating to 250 °C, hold for 5 min to erase heat history, and followed by second cooling and third heating at a rate of 10 K/min. Note that the heat flow of every DSC curve was normalized by sample mass in our study. A nitrogen purge gas (flow rate: 50 mL/min) was used to minimize thermal degradation. Thermogravimetric analysis (TGA) was performed with about 5 mg sample in nitrogen atmosphere (flow rate: 50 mL/min) at a heating rate of 10 K/min from 50 °C to 600 °C by a Mettler Toledo-TGA/DSC I instrument.

RESULTS AND DISCUSSION

As a mixture, the CBT's component distribution varies from two to seven, which results in a melting range from 115 °C to 200 °C^[1]. In Fig. 1, the DSC curve shows the melting behavior of CBT used in the following studies and four endothermic peaks (115, 140, 155 and 185 °C) can be observed obviously. These peaks correspond to the melting point of the oligomers with different distributions in CBT^[1, 33, 34].

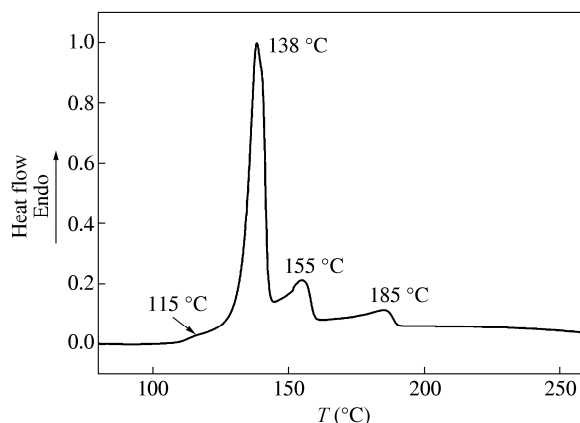


Fig. 1 DSC curve of neat CBT with heating rate of 10 K/min

Due to the final performance of pCBT are determined by polymerization and the first cooling stage in practical application. Unlike the laboratory method of quenching reaction system by ice-water or liquid nitrogen^[1], very fast cooling rate is difficult to achieve in industrial community, especially for the composites fabrication, so an appropriate cooling rate of 10 K/min is chosen in all measurements. And the time window at isothermal stage for ROP is fixed for 30 min in the following studies to correspond to the industrial practice requirements, as well as to enhance the comparability. What is more, it is well known that catalyst is introduced into the end of ring-opened cyclic molecules during ROP^[1-5], and it has been proven to be an important factor

connected with properties of pCBT^[5]. In Fig. 2(a), the TGA curve shows about 5 wt% and 10 wt% mass losses at 220 °C and 250 °C respectively. Unlike cyclic stannoxane catalyst with melting point of 230 °C^[5], the melting point of tin-based catalyst used in this study are 134 °C (Fig. 2b) which are very close to the main melting point of CBT. That is, it may immediately initiate ROP once CBT melted at about 115 °C. Therefore, the highest T_p is set 230 °C to avoid the thermal decomposition of catalyst.

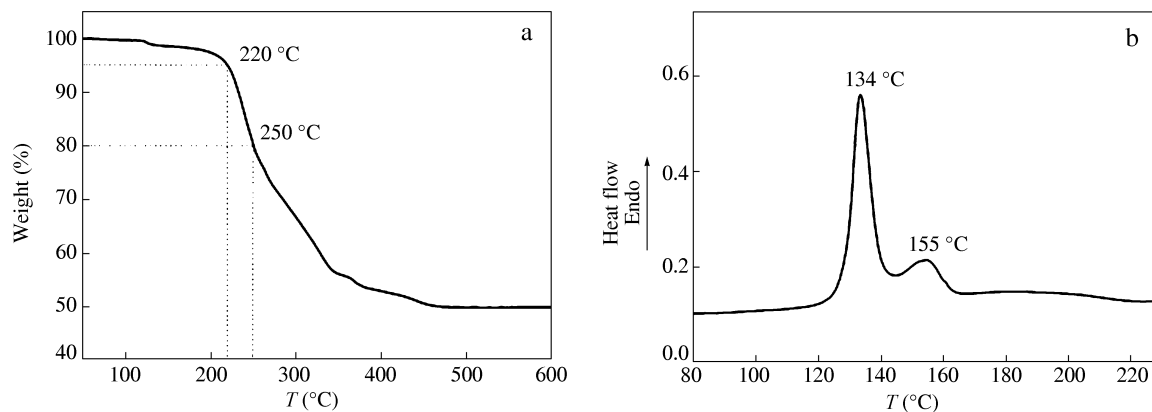


Fig. 2 Thermal analysis of catalyst: (a) TGA and (b) DSC

Subsequently, ROP of catalyzed CBT is performed in DSC at 190 °C for 30 min with different heating rates in order to disclose the influences of heating rate. According to the literature^[1–5, 34], entropy-driven ROP of CBT is a thermal neutral process. Therefore, exothermic peaks observed in Fig. 3 must derive from the crystallization of pCBT. Also, the time to peak in Fig. 3 indirectly indicates the crystallization induction time of pCBT during isothermal stage^[5]. In addition, the peak position shifts to longer time with the increase of heating rate. Because CBT can melt gradually from 115 °C (Fig. 1), this kind of difference of peak location indicates that the melted CBT can be firstly initiated to build up molecular weight. Once the chain propagation meets the primary demand of crystallization, these macromolecules will crystallize preferentially^[35]. Therefore, it is very important that the high heating rate should be chosen to perform ROP, namely, the heating rate of 100 K/min is set for the following DSC study.

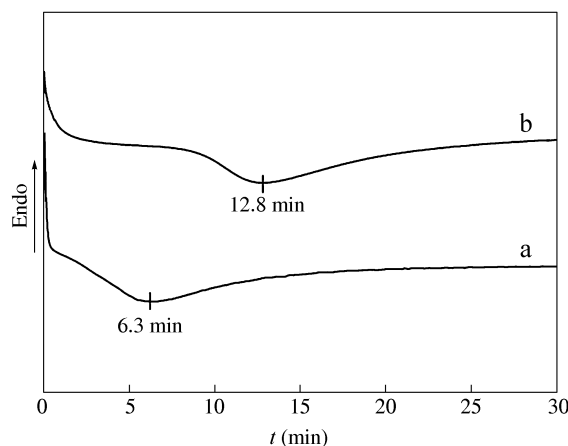


Fig. 3 DSC curves of catalyzed CBT at 190 °C for 30 min with heating rates of 10 K/min (a) and 100 K/min (b)

Based on the former results, the systematic results for T_p from 190 °C to 230 °C are displayed in Fig. 4, in which 5 K intervals of T_p (190–200 °C and 220–230 °C) and 2 K increments (200–220 °C) were chosen. As shown in Fig. 4(a) (ROP at T_p for 30 min), all the exothermic peaks originated from the crystallization of pCBT

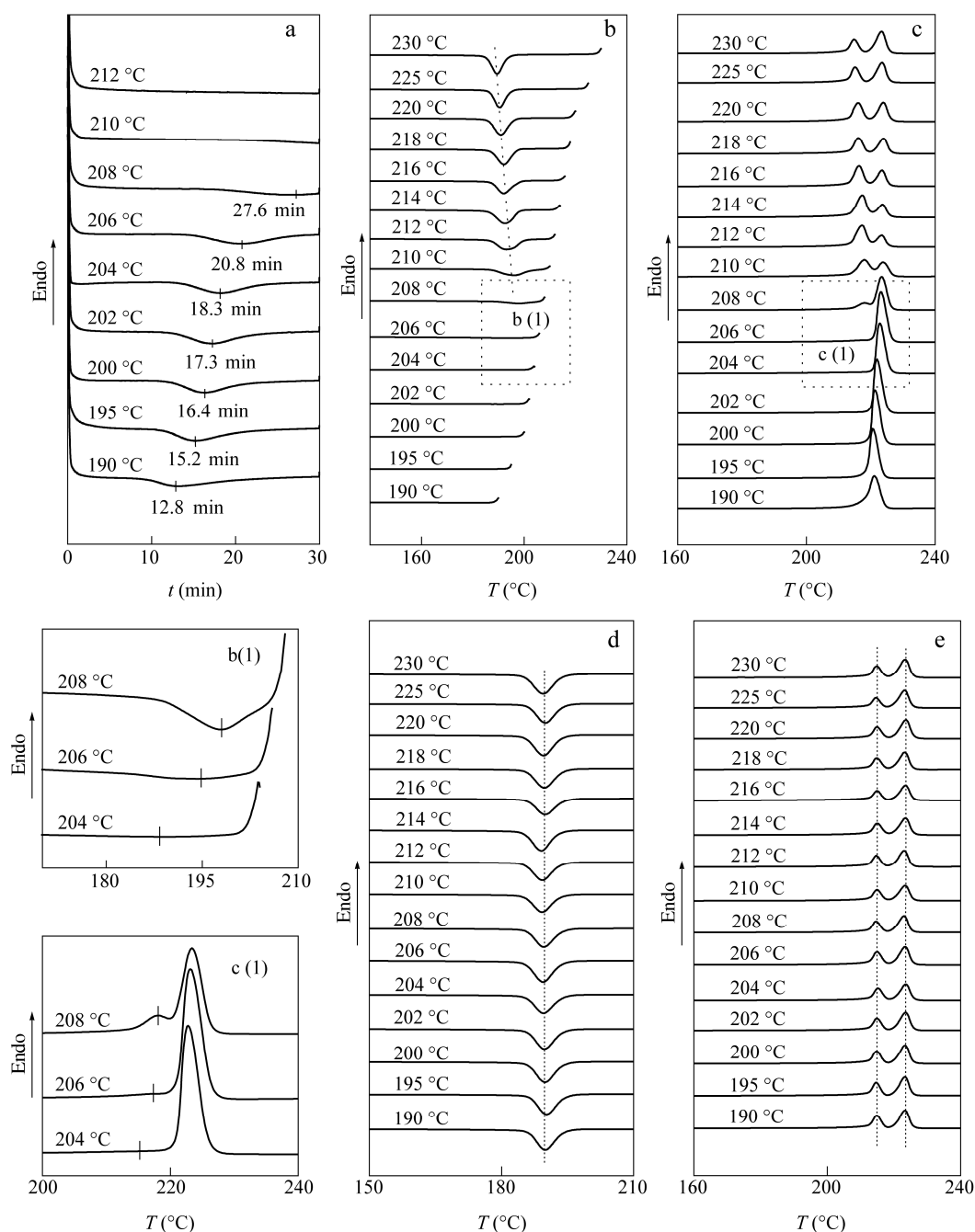


Fig. 4 DSC thermograms of catalyzed CBT during thermal circles: (a) Holding at T_p for 30 min to finish ROP; (b) First cooling from T_p to room temperature; (c) Second heating to 250 °C to erase heat history; (d) Second cooling; (e) Third heating. Each curve is labeled with T_p above it. The steps (a) and (b) are decisive for the final properties of pCBT. b(1) and c(1) represent the enlarged views of rectangular regions marked with dashed lines in (b) and (c), respectively.

due to no reaction heat of ROP. The peak positions shift to longer time with the increasing of T_p which is just right equal to the T_c of pCBT. This is a common phenomenon of semi-crystalline polymers, namely, crystallization is postponed when T_c increase. When the T_p is below or equal to 206 °C, the integral shape of crystallization peak can be seen (Fig. 4a). However, the crystallization can not completely finish from 206 °C to

212 °C and only a straight line is shown above 212 °C, so the curves from 214 °C–230 °C are not displayed. In Fig. 4(b) (cooling from T_p), the heat release of cooling crystallization can not be detected below 204 °C. This indicates that the main crystallization of pCBT has finished (during isothermal ROP stage within 30 min). But above 204 °C, exothermic peaks become more and more remarkable and the peak temperature show an obvious decreasing trend labeled with a dotted line. When the T_p is set above 220 °C, the curves are almost the same.

In addition, under the cooperation of enlarged view (Fig. 4b(1)), a slight heat liberation labeled with 204 °C and 206 °C can be seen and there exist a transition point from 204 °C to 206 °C. Also, the other obvious transition point appears between 210 °C to 212 °C. Based on results of Hakmé^[29], the former threshold temperature (204–206 °C) must demonstrate that polymerization and crystallization occur simultaneously below 204 °C within 30 min, namely crystallization during polymerization. The second threshold temperature (210–212 °C) may indicate that polymerization and crystallization are separated. Namely, polymerization of CBT is followed by crystallization of pCBT when the T_p is beyond 210 °C, and only polymerization occurs beyond 220 °C of T_p . In other words, the crystallization properties of pCBT are determined by isothermal stage when T_p is below 204 °C where the main crystallization of pCBT has finished, on the contrary, when T_p is above 204 °C, crystallization of pCBT occurs mainly in the cooling stage.

It is well known that the crystal size is proportional to the polymer's melting point (T_m)^[36], and Parton^[13, 14] demonstrated that the more perfect lamellae were observed in pCBT than in PBT. Figure 4(c) displays the heating stage which can disclose the crystallization behavior determined by the ROP and the cooling stage from T_p . Accordingly, single exothermic peaks (corresponding to the T_p : 190–204 °C) suggest a relatively perfect crystals of pCBT^[13, 14]. On the contrary, from 204 °C to 230 °C of T_p , the double melting peaks can be distinguished obviously. The multiple melting behavior of PBT has been investigated intensively^[37–47]. The appearance of multiple melting peaks is nowadays most attributed to the melting and recrystallization during the heating scan^[13, 14, 46, 48, 49]. Therefore, according to Figs. 4(c), 4(d) and 4(e), it can be concluded that the crystal size of samples derived from crystallization during polymerization (ROP below 204 °C) is larger than that when polymerization and crystallization are separated (ROP above 204 °C). That is to say, the smaller crystals will melt firstly and show up the low temperature melting peak (T_L), then the melting/recrystallization occurs during heating scan of DSC and leads to the high temperature melting peak (T_H).

Furthermore, a small peak can be seen after second heating in Fig. 4c(1) marked with a short line, which matches the temperature of first appearance of T_L of double melting peaks in Fig. 4(c). This further confirms the threshold temperature of 204 °C. Here, though the spherulite morphology study is beyond this work, it should be noted that ROP, crystallization during polymerization or reaction-induced crystallization can result in complex molecular weight architecture process^[50] or crystallization morphology^[51]. And Lorenzo and Righetti^[25] concluded that an “unusual” type spherulite of PBT would change to mixed-type at $T_c = 204$ °C and the II-III regime transition^[52, 53] occurred around 210–212 °C, accompanied by the change in crystal morphology. These transition points agree well with our two threshold temperatures (204–206 °C and 210–212 °C). Therefore, the T_p is an immediate and fundamental reason not only for the crystallization of pCBT but for the different spherulite morphologies of pCBT. Moreover, double melting peaks become more and more prominent with the increase of T_p , but only single melting peak can be found below 204 °C which further demonstrates that the uniform distribution of crystals size is obtained for T_p below 204 °C, on the contrary, double melting peaks, T_L and T_H , appear dominantly when polymerization is performed above 204 °C. However, it is obvious that the results are completely different to each other in twice cooling (Figs. 4b and 4d), and twice heating (Figs. 4c and 4e), respectively. That is, the interrelation between ROP and crystallization has a strong impact on crystallization behavior of pCBT.

Thus, quantitative analysis of the second heating has been made. As shown in Fig. 5, the second heating curve of the sample obtained from polymerization at 210 °C is set as an example to explain the change of double melting peaks in which melting enthalpy (ΔH_L and ΔH_H) are calculated according to the method in literature^[54, 55]. Detailed data are summarized into Table 1. It should be noted that the peaks of samples polymerized at 204 and 206 °C are too small for calculating the related enthalpy (Fig. 4b(1)), the effective data, therefore, are recorded for T_p of 208 °C to 230 °C.

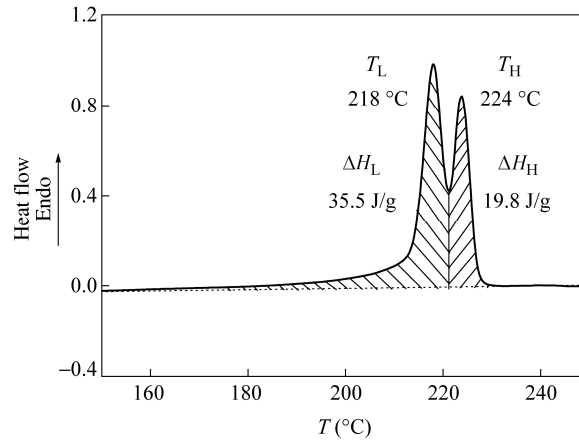


Fig. 5 Quantitative analysis of double melting peak in second heating for the sample after ROP at 210 °C

Table 1. Comparison of thermal parameters of the second heating

T_P (°C)	Peak L^a		Peak H^b	
	T_L (°C)	ΔH_L (J/g)	T_H (°C)	ΔH_H (J/g)
190	—	—	220.6	64.5
195	—	—	220.6	65.7
200	—	—	221.4	67.0
202	—	—	222.0	66.7
204	—	—	222.8	65.1
206	—	—	223.2	62.9
208	218.2	16.4	223.4	44.0
210	218.0	35.5	223.9	14.0
212	217.2	38.5	223.3	14.4
214	217.4	42.2	223.5	26.2
216	216.0	27.0	224.0	20.0
218	216.3	34.0	223.4	20.3
220	216.0	31.7	223.9	25.4
225	215.1	24.0	223.5	26.6
230	215.0	24.2	223.5	21.5

^a low temperature melting peak; ^b high temperature melting peak; T_L and T_H : temperature of low and high temperature peaks; ΔH_L and ΔH_H : melting enthalpy of low and high temperature peaks

On the basis of the former discussion, it is necessary to elucidate the change connected with T_P because the final properties of pCBT are significantly affected by this stage. According to the method of Gupta^[56], the second cooling curve labeled with 210 °C is used as an example (Fig. 6), the cross-point of baseline and two tangents on cooling curve determine the crystallization start temperature (T_{onset}) and end temperature (T_{endset}). Also, the peak temperature is obtained by the intersection of the two tangents. The value of ΔT ($T_{onset} - T_{peak}$) represents the difference of overall crystallization rate. Here, ΔT and crystallization rate possesses inverse changing relationship, in other words, when the value of ΔT is smaller, crystallization rate will be quicker. The ΔW , in Fig. 6, indicates the width at half-height of the cooling crystallization peak and can be used to explain the distributions of crystal size. When ΔW is larger, crystals size distribution is wider. Finally, the detailed data, obtained from the method in Fig. 6, are listed in Table 2.

Regarding the rate of crystallization at cooling stages, the first cooling stage shows that the crystallization rate becomes quicker with the decrease of the value of ΔT as given in column four in Table 2. On the other hand, when the T_P is below the melting point of pCBT (225 °C), partially crystallized pCBT, however, left seeds which can act as centers for further growth on subsequent cooling^[57]. With the increase of T_P , of course, the portion of crystallized pCBT becomes smaller and its effect on cooling stage will become weak and the overall

crystallization rates should be dominated by supercooling. This is also confirmed by the data of second cooling stage in Table 2, which display the almost same thermal and crystallization behaviors after the heat history is eliminated at 250 °C. Concerning the distributions of crystal size (ΔW), the single endothermic peaks of second heating stage below 204 °C of T_p indicate the relatively uniform crystal sizes. But above 208 °C, ΔW becomes more and more smaller with the increase of T_p as given in column five in Table 2, which is supported by the results of Fig. 4(c). When the T_p is above 220 °C, the data in Table 2 are almost the same for the first and second coolings, which demonstrates that the crystallization (first cooling stage) occurs from the melt of pCBT during cooling to the room temperature, just like the crystallization from 250 °C.

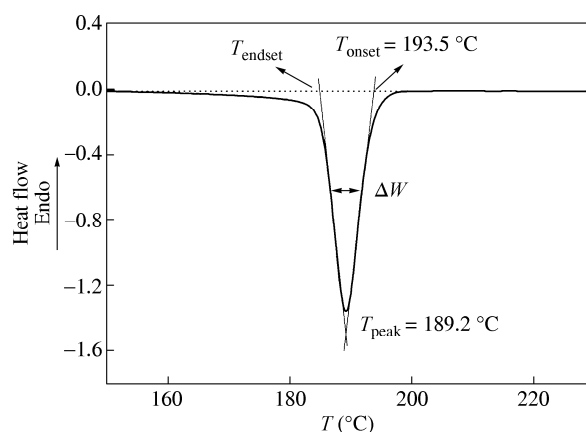


Fig. 6 Quantitative analysis of the second cooling stage for the sample after ROP at 210 °C

Table 2. Comparison of crystallization parameters of first and second cooling stages

T_p (°C)	First cooling stage (Fig. 4b)				Second cooling stage (Fig. 4d)			
	T_{onset} (°C)	T_{peak} (°C)	ΔT (°C)	ΔW (°C)	T_{onset} (°C)	T_{peak} (°C)	ΔT (°C)	ΔW (°C)
190	—	—	—	—	194.2	190.0	4.2	4.8
195	—	—	—	—	194.5	190.2	4.3	4.8
200	—	—	—	—	194.1	190.0	4.1	4.8
202	—	—	—	—	194.1	190.0	4.1	4.8
204	—	—	—	—	194.0	190.0	4.0	4.9
206	—	—	—	—	194.0	189.4	4.6	4.9
208	206.2	197.9	8.3	10.8	194.0	189.7	4.3	4.9
210	203.5	196.0	7.5	10.2	193.5	189.2	4.3	4.8
212	200.1	193.2	6.9	8.6	193.5	189.3	4.2	4.8
214	198.2	192.6	5.6	7.4	193.1	189.0	4.1	4.7
216	197.9	192.0	5.9	6.2	194.0	190.0	4.0	5.0
218	197.2	192.0	5.2	6.0	194.0	190.0	4.0	5.0
220	196.0	191.0	5.0	5.9	194.0	189.5	4.5	4.9
225	194.7	190.5	4.2	4.8	194.0	190.0	4.0	4.8
230	193.7	189.5	4.2	4.8	194.0	189.5	4.5	4.8

$\Delta T = T_{onset} - T_{peak}$; ΔW : Peak width at half-height

To further disclose the effect of crystallization during ROP, in a new test programme (Fig. 7a), the second heating scan is started from T_p directly, and only one endothermic peak is displayed for every curve (Fig. 7b). Combining these results with the discussion of Fig. 4(c) indicates that uniform size distribution of crystals is formed during isothermal stage, and further demonstrates that the double melting behaviors of pCBT result from the melting/recrystallization during heating scan. Moreover, it is well known that the molecular weight increases faster with the increase of T_p ^[13, 14]. Therefore, with the increase of T_p (below 210 °C), relatively, the propagated chains will obtain more annealing time and show the slight increase of melting temperatures (Fig. 7b) related to

the lamellae thickening^[36]. Finally, combined with Figs. 4(b), 4(c) and 7(b), the accurate separation temperature between ROP of CBT and crystallization of pCBT is pinpointed, namely, 212 °C.

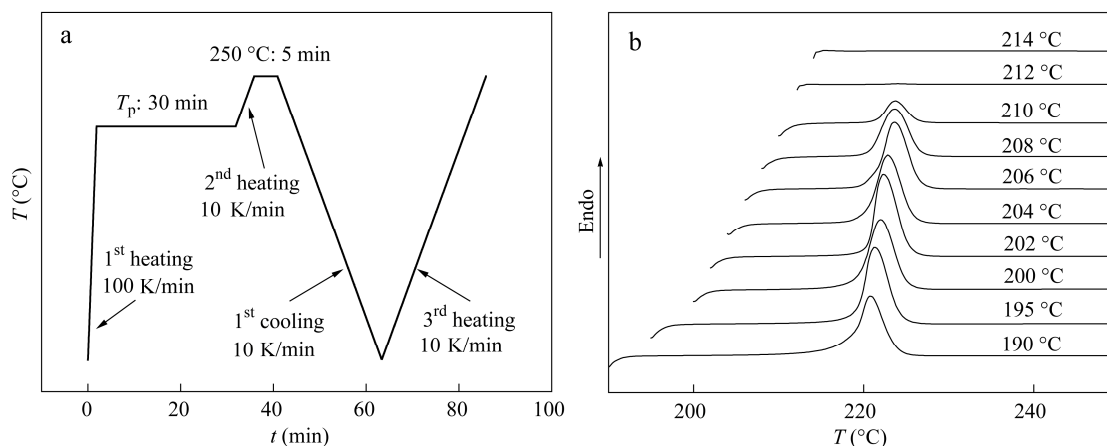


Fig. 7 (a) DSC testing procedure; (b) Second heating curves corresponding to (a)

CONCLUSIONS

Based on the careful investigation between ROP of CBT and crystallization of pCBT, their correlation is clearly disclosed for the first time. Namely, the crystallization during polymerization occurs when T_p is below 204 °C; polymerization and crystallization are gradually separated with the increase of T_p from 204 °C; only polymerization is performed beyond 212 °C. Furthermore, the quantitative analysis about the related thermal results demonstrates that the uniform distributions of crystals size are formed when polymerization and crystallization occur simultaneously below 204 °C. With the increase of T_p above 204 °C, crystal size distributions become wider and lead to more and more obvious double melting peaks during second heating scan. Finally, the crystallization properties of pCBT are determined by the isothermal stage when T_p is below 204 °C, and mainly dominated by cooling stage when T_p is above 204 °C. In summary, these efforts are helpful to processing, morphology, structure controlling and brittleness mechanism investigation of pCBT and contribute to the industrial practice for fabrication of composites with CBT or tailoring their properties.

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