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A MODULATED DSC STUDY ON THE IN SITU POLYMERIZATION OF CYCLIC BUTYLENE TEREPHTHALATE OLIGOMERS

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The polymerization of a cyclic butylene terephthalate (CBT) oligomer was studied as a function of temperature (T=200 and 260°C, respectively) by modulated DSC (MDSC). The first heating was followed by cooling after various holding times (5, 15 and 30 min) prior to the second heating which ended always at T=260°C. This allowed us to study the crystallization and melting behavior of the resulting polybutylene terephthalate (PBT), as well. In contrary to the usual belief, the CBT polymerization is exothermic and the related process is superimposed to that of the CBT melting. The melting behavior of the PBT was affected by the polymerization mode (performed below or above the melting temperature of the PBT product) of the CBT. Annealing above the melting temperature of PBT yielded a product featuring double melting. This was attributed to the presence of crystallites with different degrees of perfection. The crystals perfection which occurred via recrystallization/remelting was manifested by a pronounced exothermic peak in the non-reversing trace.

Keywords: *crystallization, cyclic butylene terephthalate (CBT), melting, modulated DSC, polybutylene terephthalate (PBT), ring-opening polymerization*

Introduction

Researchers, fascinated by the in-situ polymerization, try to adopt this technique for novel monomers and oligomers. Suitable reactive cyclic oligomers such as carbonates, phthalates and carboxylates [1–3] may be polymerized into engineering and advanced thermoplastics. The major benefit of the polymerization of cyclic compounds is related with their low melt viscosities which can be as low as 0.02 Pa s [4]. This allows us to use liquid resin composite molding techniques such as resin transfer molding (RTM) and reinforced reaction injection molding (RRIM) which are not available for conventionally produced thermoplastics. One recent and commercially relevant development focuses on the preparation and polymerization of cyclic butylene terephthalate (CBT) oligomers. Albeit the related patents have been filed in the 90 s, CBT compounds became commercially available only very recently [5].

It is often stated in the literatures that the polymerization of CBT to polybutylene terephthalate (PBT) is an athermic process being an entropically-driven ring-opening process [6, 7]. CBT polymerization can be performed below and above the melting temperature of the resulting PBT. The outcome is practically the same: number average molecular mass (M_n) varies between 30 000 and 40 000 g mol^{-1}, and the polydispersity index remains at approximately 2 [8]. The residual oligomer content lies between 3–5 mass%. The industry prefers the isothermal polymerization below the melting of the PBT as it is accompanied with crystallization. This will help the producer to remove the ‘solidified’ parts from the mold without subsequent cooling. DSC studies on the polymerization of CBT have been published and information on the crystallization and melting behavior of the resulting PBT is also available [2, 9, 10]. Interestingly, the modulated DSC (MDSC) technique has not been yet adopted for that purpose although the MDSC is predestinated to study the polymerization of CBT, including the crystallization and melting of the PBT end product. This is due to the fact that some overlapping effects (polymerization/crystallization, recrystallization/melting) can be separated by using MDSC (e.g. [11–13]). This issue was the objective of this paper.

Experimental

CBT powder (Grade: XB3-CA4) purchased from Cyclics Co. (Schenectady, NY, USA) was used throughout this study. This CBT contains the catalyst (butyltin chloride dihydroxide) and was termed as one-component CBT. MDSC investigations were performed on a TA Instruments-Waters LLC Thermal Advantage for Q-Series equipped with a Q1000

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auto-Modulated Differential Scanning Calorimeter, connected to a liquid nitrogen cooling system (LNCS). Scans were recorded from 0 to 200°C and 0 to 260°C, respectively. The samples (ca. 6 mg) were held at the upper threshold temperature for 5, 15 and 30 min, respectively. This was followed by cooling and then by a second heating, however, in that case the measurement ended always at *T*=260°C. Both cooling and second heating were performed under the same MDSC conditions as the first heating. The following scanning parameters were set: heating rate of 5°C min^{-1} with a modulation of ±0.531°C min^{-1} and a frequency of 40 s under helium flow. The data were analyzed by the Universal Analysis 2000 software package of TA Instruments, Version 4.1D. It has to be emphasized that no efforts were made to study the effects of modulation amplitude, modulation period and heating rate although they affect the MDSC response considerably.

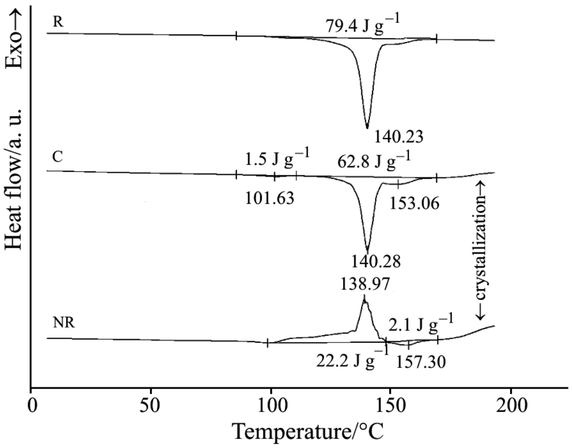

Fig. 1 Characteristic *R*, *C* and *NR* traces recorded during the first heating of CBT ending at *T*=200ºC

Results and discussion

Polymerization below the melting of PBT

Figure 1 shows the deconvoluted conventional (*C*), reversing (*R*) and non-reversing (*NR*) DSC traces taken during the first heating from the CBT. The C trace displays two melting peaks: a small one at *T*≈100°C (~1.5 J g^{-1}) and the major one at *T*=140°C (~62.8 J g^{-1}). The latter is likely composed of two endotherms. The enthalpy value of this peak is closely matched with literature data [2]. This peak is usually attributed to that of the melting of the CBT which already started at *T*≈100°C. In the non-reversing (*NR*) component, a broad exothermic (*T*≈139°C, 22.2 J g^{-1}) and one small endothermic peak (*T*≈158°C, 2.1 J g^{-1}) can be resolved. The reversing (*R*) component shows a broad endotherm with a peak at *T*≈140°C (79.4 J g^{-1}). It is worth of noting that the above enthalpy values, summarized also in Table 1, proved to be very well reproducible. The most interesting finding is the relative broad exothermic peak with quite high enthalpy value in the *NR* trace. According to this the polymerization is not athermic or thermoneutral when this peak can be unequivocally assigned to the polymerization. This is, however, not an easy task. Note that the various CBT oligomers (dimers, trimers, etc.) started to melt at *T*≈100°C – cf. *C* and *R* traces in Fig. 1. This is superimposed to exothermic changes owing to catalyst activation and/or polymerization (the shape of the *NR* curve suggests a combined action). If polymerization runs, however, more or less parallel with the CBT melting, then PBT could be produced even at *T*≈140°C. Rheological measurements under this isothermal condition indicated a strong viscosity increase after long holding time [14]. As a consequence, the exothermic peak at *T*≈140°C on the *NR* trace should be linked with the polymerization process. One can thus quote that the polymerization (or initiation) reaction of CBT is, indeed, of exothermic character. However, this process is superimposed to that of the melting of the CBT oligomers. So, the apparent 'athermic' reaction is just interplay between polymerization-dependent exothermic and melting-related endothermic effects.

In the subsequent cooling MDSC traces (cf. Fig. 2) the T_g step at *T*≈40°C is obvious – cf. *R* component. The exotherms in the *C* and *NR* traces at *T*≈170°C are ascribed to crystallization. Note that this has been started during the first MDSC run (cf. Fig. 1). The assignment to crystallization is supported by the fact that this peak disappears with increasing holding time at *T*=200°C.

Table 1 MDSC data on CBT samples heated to/hold at *T*=200°C

	MDSC trace	Temperature/ºC, Enthalpy/J g^{-1}
	R	≈140/–78.6
First heat	*C*	≈102/–1.5 ;≈140/–62.3
	NR	≈139/+22.2;≈157/–2.1
	R	≈226/–22.8 (5 min); –23.8 (15 min); –20.1 (30 min)
Second heat	*C*	≈225/–64.4 (5 min); –69.0 (15 min); –68.3 (30 min)
	NR	≈225/–41.7 (5 min); –45.7 (15 min); –48.3 (30 min)

Endotherms and exotherms are indicated by – and + signs, respectively. Change due to the holding time is indicated for the second heat. First heat data are mean values from 3 parallel measurements

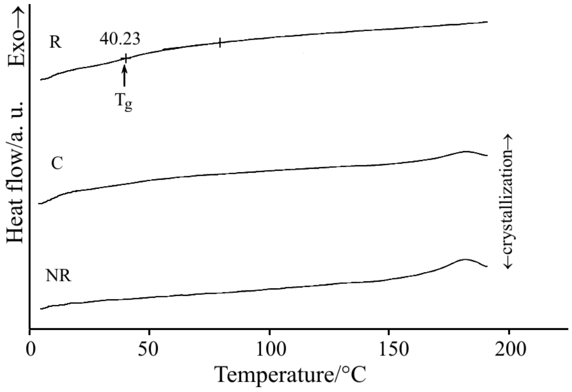

Fig. 2 *R*, *C* and *NR* traces recorded during cooling from T=200ºC after 15 min holding time

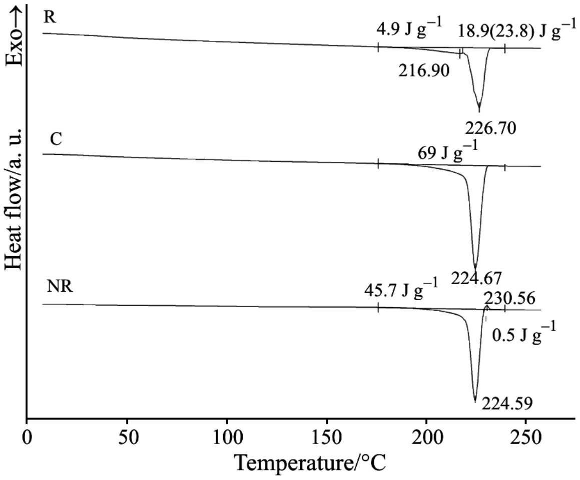

Fig. 3 Characteristic *R*, *C* and *NR* traces recorded during the second heating which ended at T=260ºC

The MDSC traces registered during the second heating are shown in Fig. 3. Note that all traces show endotherm peaks in the same temperature range (except a negligible exothermic peak in the *NR* trace just above the melting temperature of the PBT– T≈225°C; 0.5 J g^{-1}). The appearance of both *R* and *NR* melting indicates that the population of PBT crystals formed differs in their degree of perfection. The *NR* contribution increases whereas the R-type melting decreases at least above t≥15 min (– cf. Table 1) as a function of the holding time at T=200°C. This can be attributed to the development of more, however, less perfect PBT crystals. This is intuitive as in an already crystallized solid only imperfect crystals may form additionally.

Polymerization above the melting of PBT

The MDSC traces registered in the first heating up to T=260°C (cf. Fig. 4) show two additional features to those measured up to T=200°C (cf. Fig. 1). First an exothermic peak appears at T=198°C which represents the crystallization – cf. *C* and *NR* traces in Fig. 4. Note that this process was broken during the test series ending at T=200ºC. On the other hand, the *C* and *NR* traces in Fig. 4 corroborate our assignment in respect to crystallization in Fig. 1. Second, this peak is followed by an endothermic one at T=225ºC which represents the melting of the crystalline PBT – cf. *C* and *NR* traces in Fig. 4. Note that the crystallization and melt enthalpies are practically the same (*C* trace in Fig. 4, and also data in Table 2) which is in concert with the expectation. One can also recognize that the crystallization is a completely *NR* process which is again in line with the MDSC fundamentals. On the other hand, melting is a combined *R*+*NR* process which likely reflects the simultaneous presence of more and less perfect PBT crystals, respectively.

Figure 5 shows the MDSC traces taken during cooling. In the *R* trace, the T_g step is obvious at T=43°C. The physical meaning, if any, of the peculiar signal at T=200°C in the *R* trace (marked by a question mark) is unknown. The crystallization of the molten PBT at T≈198°C in the *C* and *NR* traces is well resolved (cf. Fig. 5). Note that this process should completely be a *NR* type. The MDSC traces of the second melting show an endothermic double peak (T=216 and 223°C) in the *R* and *C* responses, and the related melting process is associated with a pronounced heat release (cf. Fig. 6).

Before discussing the possible reason of the doubling in the melting peak, it is straightforward to check how the melting behavior was influenced by the holding time during the first run. This is shown in Fig. 7, and summarized in Table 3. Note that for the splitting of the double melting peak the integration,

Table 2 MDSC data on CBT samples heated to/hold at T=260°C

	MDSC trace	Temperature/ºC, Enthalpy/J g^{-1}
First heat	*R*	≈140/–78.6; ≈225/–9.6
	C	≈101/–1.4; ≈140/–63.1; ≈198/+24.2; ≈225/–26.4
	NR	≈140/+22.6; ≈156/–1.2; ≈198/+27.3; ≈225/–17.4
Cooling	*R*	(T_g≈43ºC)
	C	≈198/+47.4
	NR	≈198/+44.4

The effect of holding time on the results of cooling was negligible and thus not indicated separately. For other notes those of Table 1 are applicable

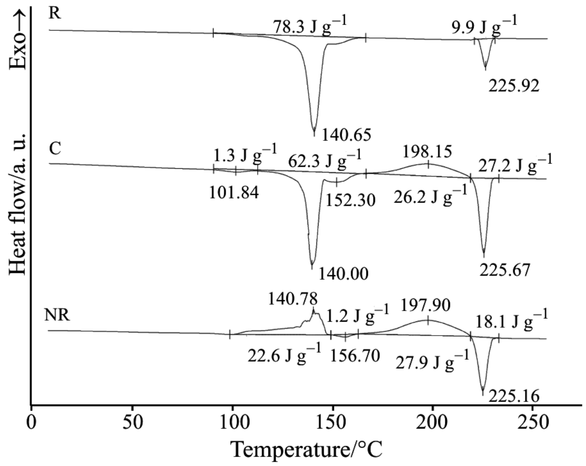

Fig. 4 Characteristic *R*, *C* and *NR* traces recorded during the first heating of CBT ending at *T*=260ºC

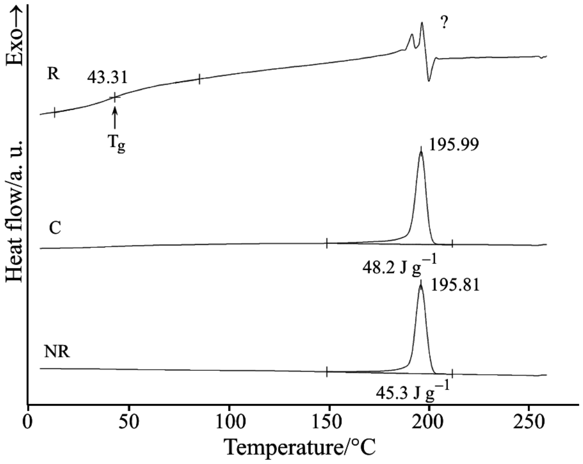

Fig. 5 *R*, *C* and *NR* traces monitored during cooling from *T*=260ºC after 5 min holding time. Note: Authors are not aware of the meaning of the signal with question mark in the *R* trace

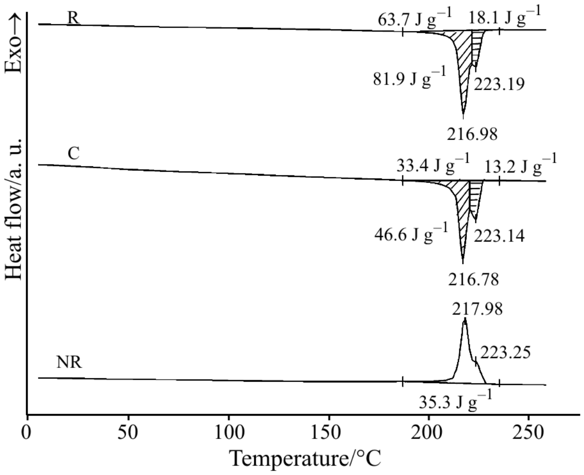

Fig. 6 *R*, *C* and *NR* traces monitored during the second heating up to *T*=260ºC. Notes: This sample was hold for 5 min at *T*=260ºC during the first heating. This figure also shows how the double melting peak has been split for the enthalpy determination

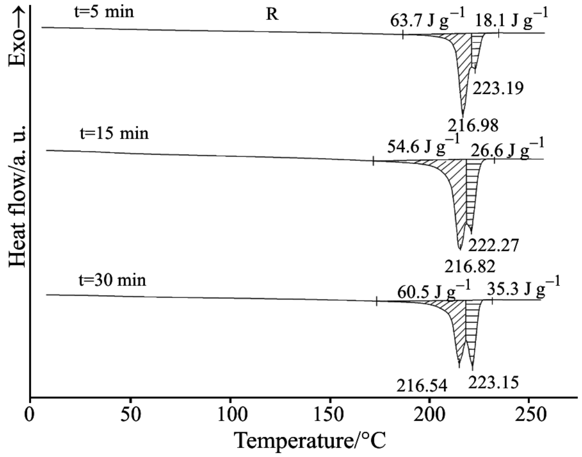

Fig. 7 Change in the reversing (*R*) double melting feature of the PBT as a function of the holding time (*t*) at *T*=260ºC during the first heating

Table 3 Effect of holding time at *T*=260°C for the MDSC data derived from the second heating

	Holding time/min	Enthalpy/J g^{-1}		
		endotherm		exotherm
		T=217ºC	*T*=223ºC	*T*=218ºC
Reversing	5	–63.7	–18.1	–
	15	–54.6	–26.6	–
	30	–60.4	–40.5	–
Conventional	5	–33.4	–13.2	–
	15	–25.4	–46.1	–
	30	–23.4	–23.9	–
Non reversing	5	–	–	+35.3
	15	–	–	+35.1
	30	–	–	+53.6

demonstrated in Figs 6 and 7 (cf. traces *R* and *C*), was followed. The tendencies which can be derived from Fig. 7 and Table 3 are as follows: the relative enthalpy of the higher to the lower melting peak increases (based on the *R* and *C* traces) and this goes parallel with an increase in the exothermic peak of the *NR* response. This suggests that the double melting, often observed for PBT [15], is caused by remelting/recrystallization processes. This is obviously affected by the melt annealing at T=260°C. On the other hand, the large exothermic peak behind this crystal perfection procedure (*NR* traces; 35–50 J g^{-1}) is unusually high. This should be linked with the peculiarities of the PBT produced from CBT.

Note that the above treatise disregarded any changes in the CBT conversion and in the molecular mass (distribution) of the resulting PBT. Our preliminary studies showed that those aspects can be neglected in the first approximation, in fact, owing to the fast conversion of CBT. Further, it was found that polymerization below and above the melting temperature of PBT affects mostly the average molecular mass, M_n and less the polydispersity (the latter remains at ca. 2.6). The molecular mass is lower when CBT is polymerized above the PBT melting. With increasing melt annealing M_n reduces further. This should result in higher crystallinity and more perfect crystals compared to the low temperature polymerization route. Recall that the latter route will produce solidified PBT via crystallization. Comparing the *R* melting enthalpies of the second heating run for low (cf. Table 1) and high polymerization temperature (cf. Table 3) the above speculation seems to be verified.

Conclusions

Based on this study devoted to investigate the polymerization, crystallization and melting behavior of one-component cyclic butylene terephthalate (CBT) oligomers via modulated DSC technique, the following conclusions can be drawn:

- The polymerization of CBT is non athermic. The heat of polymerization derived from the *NR* trace is ca. 22 J g^{-1}. Its development overlaps, however, with that of the CBT melting at T=140°C.
- The crystallization and especially the melting behavior of the resulting PBT depend on whether the polymerization was performed below or above the PBT melting. The later method results in PBT showing double melting characteristics. Double melting feature was assigned to crystal perfection owing to remelting/recrystallization process. It was speculated that the onset of double melting is influenced by the mean molecular mass of the resulting PBT which is changing as a function of polymerization conditions (performed below or above of the PBT melting).

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References

1 X. Huang, S. Lewis and W. J. Brittain, Macromol., 33 (2000) 2000.
2 D. J. Brunelle, J. E. Bradt, J. S. Guzzo, T. Takekoshi, T. L. Evans, E. J. Pearce and P. R. Wilson, Macromol., 31 (1998) 4782.
3 J. H. Youk, R. P Kambour and W. J. MacKnight, Macromol., 33 (2000) 3606.
4 D. J. Brunelle and J. S. Guzzo, U. S. Patent 5,661,214 (1997).
5 R. H. J. Eder, in 'Flüssigimprägnierung mit Duro- und Thermoplasten' IVW-Berichte, Band 25, Ed.: M. Neitzel, Universität Kaiserslautern, 2001, p. 33.
6 Y. F. Wang, U. S. Patent, 6,420,048 (2002).
7 A. R. Tripathy, A. Elmoumni, H. H. Winter and W. J. MacKnight, Macromol., 38 (2005) 709.
8 N. Lotti, L. Finelli, V. Siracusa, A. Munari and M. Gazzano, Polymer, 43 (2002) 4355.
9 H. Parton and I. Verpoest, Polym. Comp., 26 (2005) 60.
10 A. R. Tripathy, W. J. MacKnight and S. N. Kukureka, Macromol., 37 (2004) 6793.
11 B. Wunderlich, Thermochim. Acta, 355 (2000) 43.
12 M. Reading, J. Therm. Anal. Cal., 64 (2001) 7.
13 A. Genovese and R. A. Shanks, J. Therm. Anal. Cal., 75 (2004) 233.
14 Z. A. Mohd Ishak, K. G. Gatos and J. Karger-Kocsis, Polym. Eng. Sci., 46 (2006), in press.
15 H.-J. Radusch in 'Handbook of Thermoplastic Polyesters', Ed.: S. Fakirov, Wiley-VCH, Weinheim 2002, Vol. 1, p. 389.

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