Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 549–555

CRYSTALLIZATION AND MELTING OF POLYCARBONATE STUDIED BY TEMPERATURE-MODULATED DSC (TMDSC)

C. Schick[1]*, *A. Wurm*[1]*, M. Merzlyakov*[1]*, A. Minakov*[2] *and H. Marand*[3]

[1]University of Rostock, Department of Physics, Universitätsplatz 3, 18051 Rostock, Germany
[2]General Physics Institute, RAS, Vavilov st. 38, 117942 Moscow, Russia
[3]VPI & SU, Department of Chemistry, Blacksburg, VA 24061-0212, USA

Abstract

Temperature-modulated DSC (TMDSC) measurements at reasonably high frequencies allow for the determination of base-line heat capacity. In this particular case vitrification and devitrification of the rigid amorphous fraction (RAF) can be directly observed. 0.01 Hz seems to be a reasonably high frequency for bisphenol-A polycarbonate (PC). The RAF of PC is established during isothermal crystallization. Devitrification of the RAF seems to be related to the lowest endotherm. For PC the melting of small crystals between the lamellae is expected to yield the lowest endotherm.

Keywords: rigid amorphous fraction, semi-crystalline polymers, TMDSC, vitrification

Introduction

From glass transition it is well known and generally accepted that heat capacity can be described by complex numbers. The typical frequency dependence like for other relaxation processes can be observed – a sigmoid step in real and a peak in imaginary part of heat capacity [1–3]. At a given temperature the peak frequency can be related to the mean relaxation time τ according to $\omega\tau=1$.

Recent measurements also indicate a frequency dependence of the heat capacity of semi-crystalline polymers outside the glass transition range [4, 5]. These observations are related to the occurrence of an excess heat capacity that can often be seen in a rather wide temperature range between the glass transition and the melting temperature. The origin of this excess heat capacity and its frequency dependence is not yet understood. Probably the molecular processes involved are related to the surface of the polymer crystallites and often the term reversing melting [6] is used. For polymers showing a sliding diffusion (α relaxation) in the crystallites, large contributions to reversing melting are probably due to surface melting [7]. For other semi-crys-

---

* Author for correspondence: E-mail: christoph.schick@physik.uni-rostock.de

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

talline polymers we do not know which surfaces, growth or fold, are responsible for the process of reversing melting and the corresponding excess heat capacity.

In order to obtain information about the characteristic time scale of the molecular processes related to excess heat capacity we have studied the frequency dependence of complex heat capacity during quasi-isothermal crystallization. To extend the frequency range available with TMDSC (10^{-5}–10^{-1} Hz) AC calorimetric measurements were performed at frequency 1 Hz. A mean relaxation time in the order of seconds can be estimated for the process at 328 K for PCL. As can be seen from Fig. 1 the frequency range available is still not broad enough for a detailed discussion of the curve shape. From this curve one expects for frequencies higher than about 100 Hz to measure base-line heat capacity without contributions due to reversing melting. Base-line heat capacity corresponds to the heat necessary to increase the temperature of the sample without changing crystallinity. In other words it is the heat capacity without any contribution from latent heat. In this paper we will focus on base-line heat capacity which can be measured as the asymptotic value of heat capacity at high frequencies, Fig. 1. In this case vitrification and devitrification of the rigid amorphous fraction (RAF) of semi-crystalline polymers can be studied.

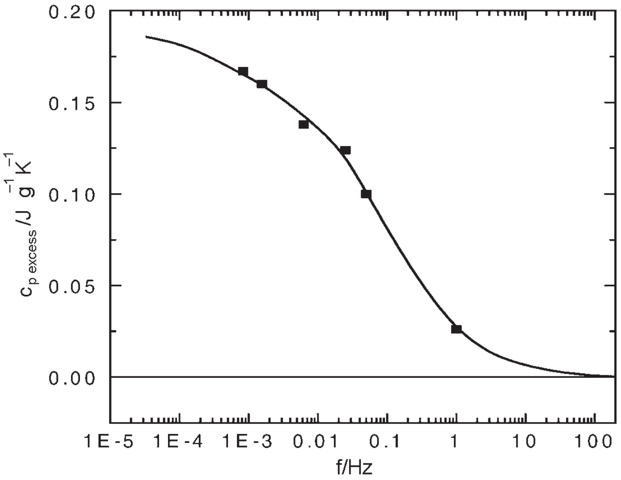

Fig. 1 Excess heat capacity of PCL after 2000 min crystallization at 328 K as a function of modulation frequency [4]. Perkin Elmer Pyris 1 DSC and AC calorimeter [8]

There are two possible paths to reach this goal: To extend the frequency range of heat capacity measurements or to study a polymer with very slow dynamics of the reversing melting so that the high frequency limit is reached at standard frequencies of temperature modulated DSC (TMDSC). For PCL, as an example, frequencies above 100 Hz are necessary to measure base-line heat capacity. This is far above the TMDSC high frequency limit of 0.1 Hz. A chance to reach such a high frequency for heat capacity measurements is given with recent developments of AC calorimetry [8] rather than by the 3ω-method [2] where it seems to be difficult to distinguish between heat capacity and thermal conductivity contributions. In this paper we followed the second approach and have studied bisphenol-A polycarbonate (PC). PC was chosen for this study because of its very slow crystallization behavior [9].

Experimental

TMDSC, a technique described for the first time in 1971 by Gobrecht *et al.* [1], and the necessary data treatments are described elsewhere [1, 10–14]. If one wants to perform TMDSC measurements in a broad frequency range high sensitive DSC apparatuses with different time constants like Perkin Elmer Pyris 1 DSC, DSC-2 and Setaram DSC 121 must be used, for details see [15]. For measurements at a fixed frequency of 0.01 Hz a TA Instruments DSC 2920CE was used. For the comparison of various experimental data sets a careful temperature calibration of all instruments is necessary. The DSC are calibrated at zero heating rate according to the GEFTA recommendation [16]. The calibration was checked in TMDSC mode with the smectic A to nematic transition of 8OCB [17, 18].

The polycaprolactone (PCL) is a commercial sample synthesized by Aldrich Chemie with a molecular mass average M_W=55700 g mol^{-1}. More details about the sample are reported in [19]. The bisphenol-A polycarbonate was obtained from General Electric (tradename LEXAN^{TM}) and was purified by dissolution in chloroform, filtering and precipitation in methanol [20, 21]. The weight average molar mass and polydispersity index for the polycarbonate were obtained by Gel Permeation Chromatography in chloroform (M_w=28400 g mol^{-1} and M_w/M_n=2.04). The heat capacity data for these polymers in the liquid and the solid state are available from ATHAS data bank [22].

Results and discussion

In a first approximation the expected base-line heat capacity c_{pb} for the semi-crystalline sample can be calculated using a simple two-phase-model according to

$$c_{pb}(T,t)=\chi_c(T,t)\,c_{p\ \mathrm{crystal}}(T)+(1-\chi_c(T,t))\,c_{p\ \mathrm{melt}}(T) \qquad (1)$$

with $c_{p\ \mathrm{crystal}}$ specific heat capacity for the crystal, $c_{p\ \mathrm{melt}}$ that for the melt and χ_c degree of crystallinity. For most polymers deviations from such a simple two-phase-model are observed [23, 24]. Introducing a rigid amorphous fraction the base-line heat capacity can be obtained from

$$c_{pb}(T,t)=\chi_r(T,t)\,c_{p\ \mathrm{rigid}}(T)+(1-\chi_r(T,t))\,c_{p\ \mathrm{melt}}(T) \qquad (2)$$

with $c_{p\ \mathrm{rigid}}$ specific heat capacity of the rigid fraction that contains crystalline and rigid (immobilized, vitrified) amorphous material (RAF). For most polymers $c_{p\ \mathrm{rigid}}$ equals $c_{p\ \mathrm{crystal}}$ and is available from [22]. $\chi_r(T,t)$ is the rigid fraction. At the glass transition temperature $\chi_r(T_g)$ can be obtained from the step of heat capacity at T_g.

$$\chi_r = 1 - \frac{\Delta c_p}{\Delta c_{pa}} \tag{3}$$

where Δc_p is the heat capacity step of the semi-crystalline sample while Δc_{pa} is that of the totally amorphous sample. To obtain the exact base-line heat capacity in the temperature range between glass transition and melt iterative procedures are necessary [25, 26].

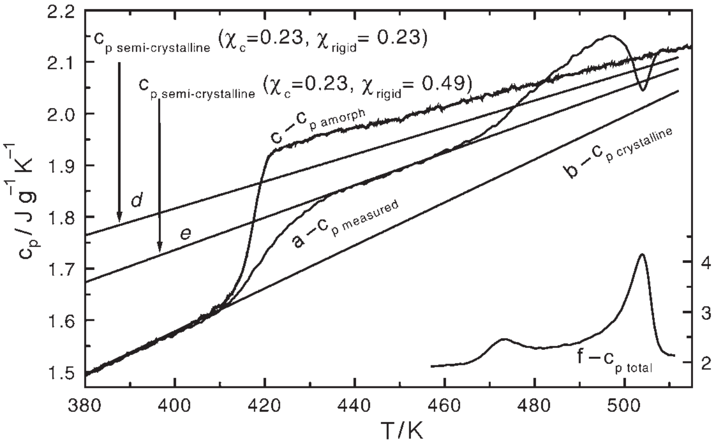

Fig. 2 TMDSC scan measurement of semi-crystalline (curve a) and amorphous (curve c) PC at underlying heating rate 0.5 K min^{-1}, temperature amplitude 0.5 K and period 100 s. Curve b correspond to the heat capacity for crystalline PC. Curve d was estimated from a two-phase-model, Eq. (1) and curve e from a three-phase-model, Eq. (2) using data from T_g. Curve f shows the total heat capacity in the melting region

The modulus of complex heat capacity and the total heat flow from TMDSC heating scans of PC are shown in Fig. 2. Curve e in Fig. 2 was estimated, Eq. (2), from the data obtained at the glass transition Eq. (3). Outside the melting region this can be used as the base-line heat capacity. For PC this is approximately true above glass transition and below 460 K. Measured heat capacity equals this value as can be seen in Fig. 2. This shows that there is no reversing melting and no excess heat capacity on the time scale of 100 s.

Because the maximum crystallization rate of PC is observed at ca 460 K there is a chance to study crystallization of PC without any excess heat capacity at 0.01 Hz.

In Fig. 3 the time evolution of heat capacity during isothermal crystallization of PC at 456.8 K is shown. Measured heat capacity becomes smaller than base-line heat capacity obtained from Eq. (1), curve d, – indicating the occurrence of a significant RAF during the crystallization process. After 10^6 s (ca 11 days) the heat capacity equals base-line heat capacity according to Eq. (3), curve e, using the data for the RAF from the step of heat capacity at the glass transition at 420 K. From this observation we can conclude that the total RAF of PC is established (vitrified) during the isothermal crystallization and no additional vitrification occurs during cooling to the glass transition temperature. To draw further conclusions from this measurement seems to be difficult. At present we are not able to answer the question at what stage of crystallization, main or secondary, the RAF vitrifies. After 200 000 s (Fig 3), heat capacity is below line d, indicating some RAF. Also secondary crystallization dominates crystallization at longer times, this does not mean that the corresponding small crystals are not formed before. If we assume that these small crystals are formed just after the formation of the dominating lamellae the RAF would be vitrified during main crystallization by the mechanism resulting in secondary crystallization at long times.

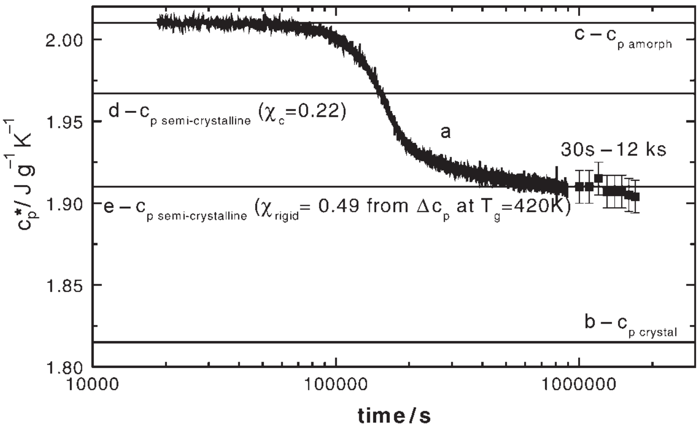

Fig. 3 Time evolution of heat capacity during quasi-isothermal crystallization of PC at 456.8 K, curve a. Curves b and c correspond to crystalline and liquid heat capacities, respectively. Curve d was estimated from a two-phase-model, Eq. (1) and curve e from a three-phase-model, Eq. (2)

Next, the question arises at what temperature the RAF devitrifies on heating – before the crystals melt or is devitrification of the RAF part of the main melting. The heat capacity measured at scanning through the melting region of PC, Fig. 2 curve a, shows some excess heat capacity in the temperature range 460–510 K due to reorganization on slow heating (0.5 K $\mathrm{min^{-1}}$). To measure heat capacity without large contributions from reorganization quasi-isothermal TMDSC measurements at stepwise increasing temperatures were performed. The results in the temperature range above glass transition (Fig. 2), are shown in Fig. 4.

From about 470 K changes in heat capacity during the quasi-isothermal measurements can be seen. The difference between squares and triangles corresponds to 10 h. After 10 h the sample has re-crystallized, except in the temperature range 495–505 K where the sample finally melts. Let us focus on the region of the lowest endotherm between 460–485 K. A step-like increase of heat capacity can be observed. The heat capacity starts to deviate from the base-line heat capacity obtained from a three-phase-model including RAF, Eq. (2) curve e, and at about 480 K it crosses the base-line heat capacity obtained from a two-phase-model, Eq. (1) curve d. In Eq. (1) only crystalline and mobile amorphous material are taken into account. At higher temperatures, during main melting, some excess heat capacity can be observed. In this region also the heat capacity obtained after 10 h annealing at each temperature increases and finally reach the liquid heat capacity, curve c. The occurrence of an excess heat capacity in this region is also supported by the increasing heat capacity at decreasing frequency of 0.001 Hz.

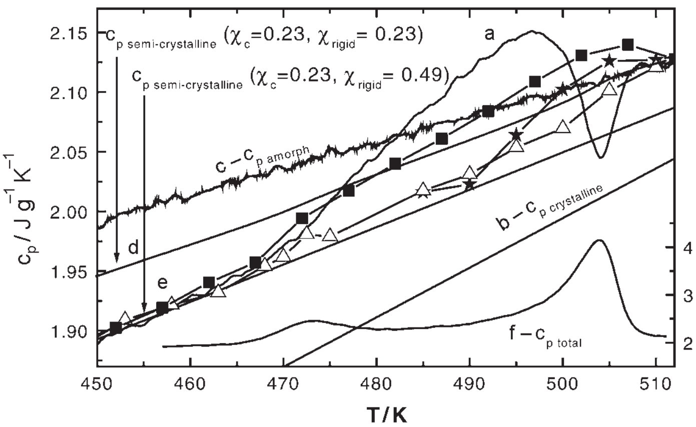

Fig. 4 Magnified part of Fig. 2 in the melting region of PC. Curves as in Fig. 1 except curve d where now the changes in crystallinity in the main melting region are taken into account. The triangles show the heat capacities from quasi-isothermal TMDSC measurements on stepwise increasing temperatures. The data were taken for frequency 0.01 Hz after 15 min, squares, and after 10 h, open triangles, while stars present data at 0.001 Hz after 10 h

Conclusions

TMDSC heat capacity measurements of the asymptotic value of heat capacity at high frequencies allow to measure base-line heat capacity as shown on the example of PC. For PC the RAF is established during isothermal crystallization as can be seen from Fig. 3. Devitrification of the RAF seems to be related to the lowest endotherm (annealing peak) (Fig. 4). For PC the melting of small crystals between the lamellae yield the lowest endotherm [9, 20, 21, 27]. The immobilization of the amorphous material around these small crystals, which are formed during isothermal crystallization [27] and which can be reestablished by annealing for 10 h after melting, results in the vitrification of the RAF during crystallization and in its devitrification during melting. The asymptotic value of heat capacity at low frequencies is the sum of base-line heat capacity and excess heat capacity due to reversing melting. This will be studied in detail in future.

This research was supported by the European Commission (Grant IC15CT96-0821), the German Science Foundation (grant DFG Schi-331/5-1) and the government of Mecklenburg-Vorpommern. Support by Perkin Elmer Instruments and TA Instruments is acknowledged.

References

1 H. Gobrecht, K. Hamann and G. Willers, J. Phys. E: Scientific Instruments, 4 (1971) 21.
2 N. O. Birge and S. R. Nagel, Phys. Rev. Lett., 54 (1985) 2674.
3 S. Weyer, A. Hensel and C. Schick, Thermochim. Acta, 304/305 (1997) 251.
4 C. Schick, M. Merzlyakov, A. Minakov and A. Wurm, J. Therm. Anal. Cal., 59 (2000) 279.
5 Y. Saruyama, Thermochim. Acta, 330 (1999) 101.
6 I. Okazaki and B. Wunderlich, Macromol., 30 (1997) 1758.
7 W. Hu, T. Albrecht and G. Strobl, Macromol., 32 (1999) 7548.
8 A. A. Minakov, Yu. Bugoslavsky and C. Schick, Thermochim. Acta, 317 (1998) 117.
9 S. Sohn, 'Crystallization Behavior of Bisphenol A Polycarbonate: Effect of Time, Temperature and Molar Mass', Ph.D. Thesis, Virginia Polytechnic and State University, April 2000
10 B. Wunderlich, Y. M. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
11 M. Reading, Trends Polym. Sci., 8 (1993) 248.
12 J. E. K. Schawe, Thermochim. Acta, 260 (1995) 1.
13 M. Merzlyakov and C. Schick, Thermochim. Acta, 330 (1999) 55 and 65.
14 S. Weyer, A. Hensel and C. Schick, Thermochim. Acta, 304/305 (1997) 267.
15 M. Merzlyakov, A. Wurm, M. Zorzut and C. Schick, J. Macromol. Sci.– Phys., 38 (1999) 1045.
16 S. M. Sarge, W. Hemminger, E. Gmelin, G. W. H. Höhne, H. K. Cammenga and W. Eysel, J. Thermal Anal., 49 (1997) 1125.
17 A. Hensel and C. Schick, Thermochim. Acta, 304/305 (1997) 229.
18 C. Schick, U. Jonsson, T. Vassiliev, A. Minakov, J. Schawe, R. Scherrenberg and D. Lörinczy, Thermochim. Acta, 347 (2000) 53.
19 P. Skoglund and A. Fransson, J. Appl. Polym. Sci., 61 (1996) 2455.
20 S. Sohn, A. Alizadeh and H. Marand, Polymer, 41 (2000) 8879.
21 A. Alizadeh, S. Sohn, J. Quinn, H. Marand, L. Shank and H. D. Iler, Macromol., submitted (May 2000).
22 B. Wunderlich, Pure & Appl. Chem., 67 (1995) 1019; see on WWW URL: http://web.utk.edu/~athas/databank/intro.html.
23 Y. Ishida, K. Yamafuji, H. Ito and M. Takayanagi, Kolloid-Z. & Z. Polym., 184 (1962) 97.
24 H. Suzuki, J. Grebowicz and B. Wunderlich, Makromol. Chem., 186 (1985) 1109.
25 V. B. F. Mathot, Ch. 5: 'Thermal Characterization of States of Matter' in 'Calorimetry and Thermal Analysis of Polymers', V. B. F. Mathot (Ed.); Hanser Publishers, München 1994.
26 M. Alsleben and C. Schick, Thermochim. Acta, 238 (1994) 203.
27 H. Marand, A. Alizadeh, R. Farmer, R. Desai and V. Velikov, Macromol., 33 (2000) 3392.