

## **ISOTHERMAL CRYSTALLISATION OF PCL STUDIED BY TEMPERATURE MODULATED DYNAMIC MECHANICAL AND TMDSC ANALYSIS**

*A. Wurm, M. Merzlyakov\* and C. Schick\*\**

University of Rostock, Department of Physics, Universitätsplatz 3, D-18051 Rostock, Germany

### **Abstract**

Temperature modulated dynamic mechanical analysis (TMDMA) was performed in the same way as temperature modulated DSC (TMDSC) measurements. As in TMDSC TMDMA allows the investigation of reversible and non-reversible phenomena during crystallisation of polymers. The advantage of TMDMA compared to TMDSC is the high sensitivity for small and slow changes in crystallinity, e.g. during re-crystallisation. The combination of TMDMA and TMDSC yields new information about local processes at the surface of polymer crystallites. It is shown that during and after isothermal crystallisation the surface of the individual crystallites is in equilibrium with the surrounding melt.

**Keywords:** crystallisation, DMA, DSC, PCL, polymer, temperature modulation

### **Introduction**

Temperature modulated DSC (TMDSC) as introduced by Reading [1] enables, under certain conditions, the identification of reversing and non-reversing changes of sample properties. The temperature program normally used consists of an underlying heating or cooling rate superimposed with a periodical temperature perturbation. The concept of dividing the measured signal in an underlying signal and a periodic (reversing) component cannot only be applied to calorimetric measurements but also to thermogravimetric [2], dilatometric [3, 4], dielectric [5], and dynamic mechanical measurements [6].

From the very beginning of TMDSC melting and crystallisation of polymers was considered to be one of the most important applications of this new technique. There was the hope to be able to measure baseline heat capacity in the broad melting region of semi-crystalline polymers. Unfortunately reversing or complex heat capacity obtained from temperature modulated scans in the melting region is not a measure of baseline heat capacity (fast degrees of freedom) rather than a complicated superposition of heat capacity, latent heats, kinetics and last but not least effects related to heat transfer in the sample-calorimeter system [7].

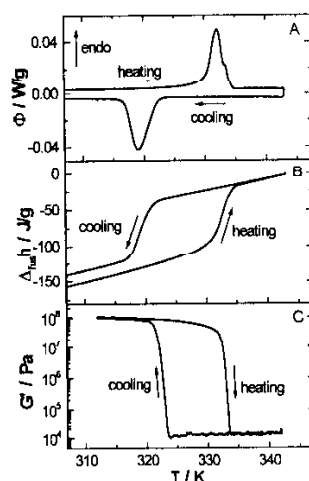
\* On leave from General Physics Institute, Moscow, Russia

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

Because heat capacity of polymer crystals is smaller than that of the melt, one expects during crystallisation a decrease of heat capacity with increasing crystallinity. TMDSC makes the quasi-isothermal determination of heat capacity during crystallisation possible. But as for melting, an excess heat capacity occurs which can be related to reversible melting during and after quasi-isothermal crystallisation [8, 9]. Because crystallisation of polymers is far from being well understood [10] additional information about these processes are needed. To check applicability of TMDMA in this field TMDMA and TMDSC measurements during quasi-isothermal crystallisation of PCL were carried out.

## Experimental

For the TMDMA measurements an Advanced Rheometric Expansion System (ARES) from Rheometric Scientific was used. The Rheotest software, includes a comfortable programming language. With the help of that, it is possible to synthesise any periodic temperature-time-program with or without underlying heating or cooling rate. The same data treatment algorithm as in TMDSC can be used for TMDMA measurements, for details see [11].



**Fig. 1** Heat flow rate,  $\Phi$ , (part A) and enthalpy change,  $\Delta_{\text{fus}}H$ , (part B) from a conventional DSC scan and storage shear modulus,  $G'$ , (part C) from a DMA temperature scan for crystallisation and melting of PCL with cooling and heating rate of  $0.1 \text{ K min}^{-1}$

The period length of the temperature modulation was limited to lower periods by the time constant of the equipment. If one wants to compare the results from TMDMA measurements with that from TMDSC using the same temperature profile high sensitive DSC apparatuses like Perkin Elmer Pyris 1 DSC or Setaram DSC 121 or 141 must be used. For the comparison a careful temperature calibration of both instruments is necessary. The DSCs are calibrated according to the GEFTA recom-

mentation [12]. The calibration was checked in TMDSC mode with the smectic A to nematic transition of 8OCB [13]. The DMA apparatus was temperature calibrated with melting of water, indium, tin, and lead.

The linear aliphatic polylactone polycaprolactone (PCL), with structure  $[(\text{CH}_2)_5\text{COO}]_n$ —used in the experiments is a commercial sample synthesised by Aldrich Chemie with a molecular mass average of  $55\,700\text{ g mol}^{-1}$ . More details about the sample are reported in [14]. In Fig. 1 DSC and DMA scans are shown in the crystallisation and melting range.

## Results

Figure 2, curve a shows the data of the storage modulus for a quasi-isothermal TMDMA crystallisation experiment at 331 K with a temperature amplitude of 0.5 K and a period of 1200 s. The low crystallisation temperature was chosen to be able to follow the whole crystallisation process in one measurement. The total time for this experiment was more than 6 days.

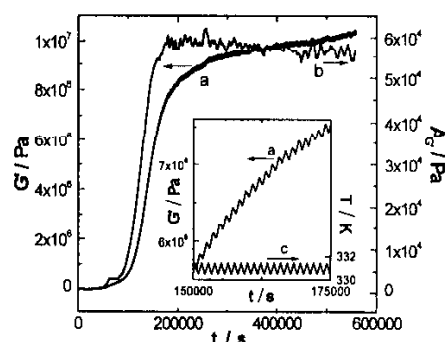


Fig. 2 Time evolution of the storage shear modulus (curve a) during quasi-isothermal crystallisation of PCL at  $T_0=331\text{ K}$ ,  $t_p=1200\text{ s}$ ,  $A_T=0.5\text{ K}$  (curve c). Curve b shows the amplitude of the storage modulus

Crystallisation starts after an induction time due to nucleation. With increasing crystallinity the storage modulus increases, curve a. The relation between the storage modulus and crystallinity is very complicated. A lot of (for the most polymers unknown) sample properties are needed to describe this relation with theories taking into account combinations of amorphous and crystalline parts in the sample. So it is difficult to estimate changes in crystallinity quantitatively from shear modulus measurements. The shape of the modulus curve allows to distinguish between two different crystallisation regimes – until 200 000 s main and up to the end secondary crystallisation.

The insert in Fig. 2 shows a magnified part of the modulus curve at the end of main crystallisation. It is remarkable and unexpected that at the heating segments of the temperature modulation there is always a decrease of the storage modulus. This indicates that parts of the sample melt or undergo a glass transition, probably the

rigid amorphous fraction. Consider the amplitude of the storage modulus (curve b in Fig. 2) one can see an increase during the main crystallisation with a relatively abrupt change to a constant or slowly decreasing value. This is contrary to the behaviour of the storage modulus itself which is related to crystallinity, increasing up to the end of the measurement.

Also with TMDSC it is possible to investigate quasi-isothermal crystallisation if the sensitivity of the instrument is high enough to detect the heat flow rate due to crystallisation and modulation. For TMDMA there are no limitations caused by the rate of changes in crystallinity because shear modulus itself depends on crystallinity. Contrary, the heat flow rate measured in TMDSC depends on the rate of changes and is therefore limited for very slow processes.

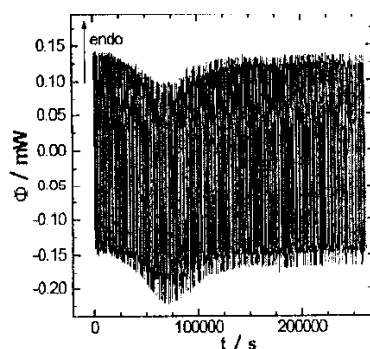


Fig. 3 Time dependence of the heat flow rate during quasi-isothermal crystallisation of PCL at  $T_0=328$  K,  $t_p=1200$  s,  $A_1=0.5$  K

Figure 3 shows the heat flow rate during quasi-isothermal crystallisation at mean temperature of 328 K with a period of 20 min and an amplitude of 0.5 K with the Perkin Elmer Pyris1 DSC. The exothermic crystallisation process has been followed for 3 days. The specific heat capacity was calculated as the ratio of the amplitudes of heat flow rate and heating rate (Fig. 4, curve a). A small decrease with time can be observed but the value is much higher than expected from ATHAS data bank for the semi-crystalline PCL [15].

The degree of crystallinity of the sample was estimated from heat of fusion ( $\Delta_{fus}H=82$  J g<sup>-1</sup>) obtained from a DSC scan from 328 to the melt at 343 K just after quasi-isothermal crystallisation. The ratio between the measured and the heat of fusion for an infinite crystal [15] ( $\Delta_{fus}H^0=156.8$  J g<sup>-1</sup>) yields a crystallinity  $w(cr)=0.5$ . The expected heat capacity  $c_{p, sample}$  for a semi-crystalline sample can be calculated according to

$$c_{p, sample}(T, t) = w(cr)(t)c_{p, crystal}(T) + (1 - w(cr)(t))c_{p, melt}(T) \quad (1)$$

with  $c_{p, crystal}$  specific heat capacity for the crystal and  $c_{p, melt}$  that for the melt, both available from ATHAS data bank [15]. With this data it is possible to calculate the expected phonon heat capacity for the sample with  $w(cr)=0.5$  at 328 K ( $c_{p, semicrystalline}$ ). The heat capacity calculated from the heat flow rate amplitude does not reach this value

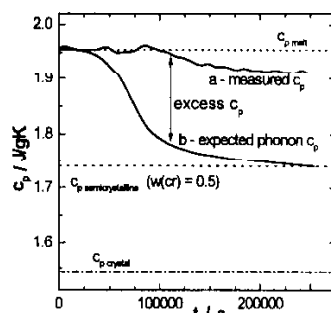


Fig. 4 Comparison of the  $c_p$  value from the measured heat flow rate (curve a) during quasi-isothermal crystallisation at  $T_0=328$  K (see Fig. 3) with expected phonon heat capacity (curve b), see text

at the end of the experiment where crystallinity reaches 0.5. From the difference an excess heat capacity of about  $0.17 \text{ J g}^{-1} \text{ K}^{-1}$  can be obtained. To determine the excess heat capacity during crystallisation as a function of time it is necessary to estimate the curve for the expected phonon heat capacity. This was done with the time dependence of crystallinity and Eq. (1). Crystallinity was estimated from the enthalpy change during crystallisation. The normally used integration of the measured heat flow rate is not appropriate here because the maximum of the exothermic effect is only  $0.05 \text{ mW}$  and the total measuring time was three days. Therefore a sophisticated method to estimate the change in crystallinity from the measured phase angle [16] was used. The result for crystallinity is shown in Fig. 5, curve a and that for expected phonon heat capacity in Fig. 4, curve b. The difference between curves a and b in Fig. 4 represents the excess heat capacity related to a reversible process, present also at the end of crystallisation. The excess heat capacity is shown in curve b in Fig. 5. As for the amplitude of the shear modulus in Fig. 2 it reaches a constant value much faster than crystallinity.

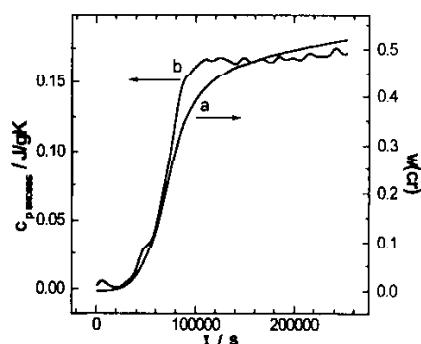


Fig. 5 Comparison of the time evolution of the crystallinity (curve a) and the excess heat capacity (curve b), see text, during quasi-isothermal crystallisation.  $T_0=328$  K (Fig. 3)

## Discussion

Figure 4 shows that the measured heat capacity decreases less than the expected phonon heat capacity with increasing crystallinity. The difference results in an excess heat capacity which stays constant after the end of main crystallisation. It can be related to reversing melting during crystallisation. This excess heat capacity (curve b in Fig. 5) behaves similar to the amplitude of the storage modulus (curve b in Fig. 2). So the same reversible process will be tested with both independent methods. From the excess heat capacity the amount of material taking part in the reversible process was estimated to about 0.2% of the crystalline material.

As shown in Figs 2 and 5 time dependence of the quantities determined from the periodic part of shear modulus and heat flow rate  $A_G$  and  $c_{p, \text{excess}}$ , respectively, are different from that of crystallinity. Therefore the reason for the increase of the amplitude is not the increase of the fraction of crystalline material. One possible explanation is that with the temperature modulation effects on the surface of the crystals are tested.

In Strobl's four-state scheme for polymer crystallisation and melting [10] an equilibrium between the melt and the just developed native crystal is assumed. Consider a polymer molecule of which a fraction is part of the crystal and another fraction is part of the surrounding melt. A small temperature increase will allow to remove another fraction of the molecule from the growth front of the crystal and to attach it again if temperature is decreasing. For such a process no nucleation, also no molecular nucleation [17], is necessary as long as a fraction of the molecule is part of the crystal. During main crystallisation the number of crystals and their surface in growth direction as well as the number of molecules in such a situation is increasing faster than crystallinity. At the end of main crystallisation the whole sample is filled with crystals and remaining amorphous parts in-between. From this time (about 200 000 s in Fig. 2 and 100 000 s in Fig. 5) the number of crystals and their surface remains practically constant. The observed behaviour of amplitudes and crystallinity, Figs 2 and 5, supports such a picture if one consider that reversible melting happens at the surface of all crystals not only at the actual growth front. Consequently all crystals stay during the whole crystallisation process for more than 6 days in a state of something like a 'living' crystal. From temperature modulated experiments it seems to be possible to study such small changes in crystallinity of about 0.2% related to the surface of the crystals.

\* \* \*

This work was financially supported by the European Commission (grant IC15CT96-0821), the German Science Foundation (grant DFG Schi-331/5-1) and the government of Mecklenburg-Vorpommern. The authors would like to thank B. Wunderlich (Oak Ridge National Laboratory) and M. Grehlinger (Rheometric Scientific, Piscataway) for helpful discussions.

## References

- 1 M. Reading, Trends Polym. Sci., 8 (1993) 248.
- 2 R. L. Blaine, Proceedings of the 25<sup>th</sup> NATAS Conference, 1997 p. 485.
- 3 D. M. Price, J. Therm. Anal. Cal., 51 (1998) 231.

- 4 D. M. Price, *Thermochim. Acta*, 315 (1998) 11.
- 5 L. E. Garn and E. J. Sharp, *J. Appl. Phys.*, 53 (1984) 8974.
- 6 A. Wurm, M. Merzlyakov and C. Schick, *Coll. Polym. Sci.*, 276 (1998) 289.
- 7 M. Merzlyakov and C. Schick, *Thermochim. Acta*, 333 (1999).
- 8 A. Toda, C. Tomita, M. Hikosaka and Y. Saruyama, *Polymer*, 38 (1997) 2849.
- 9 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, *Polymer*, 38 (1997) 231.
- 10 G. Strobl, *Acta Polymerica*, 48 (1997) 562.
- 11 A. Wurm, M. Merzlyakov and C. Schick, *Thermochim. Acta*, 333 (1999).
- 12 S. M. Sarge, W. Hemminger, E. Gmelin, G. W. H. Höhne, H. K. Cammenga and W. Eysel, *J. Thermal Anal.*, 49 (1997) 1125.
- 13 A. Hensel and C. Schick, *Thermochim. Acta*, 305 (1997) 229.
- 14 P. Skoglund and A. Fransson, *J. Appl. Polymer Sci.*, 61 (1996) 2455.
- 15 B. Wunderlich, *Pure & Appl. Chem.*, 67 (1995) 1019; see on WWW URL: <http://funnel-web.utec.utk.edu/~athas/databank/intro.html>
- 16 M. Merzlyakov, in preparation.
- 17 B. Wunderlich, *Macromolecular Physics*, Vol. 2, Academic Press, New York 1976.