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High pressure differential scanning calorimetry on polymers

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Abstract

With the aid of a home-made high-pressure measuring cell, connected to a commercial power compensated DSC, it is possible to investigate the melting and crystallization behaviour of polymeric materials as functions of pressure (up to 500 MPa). Results from poly-4-methylpentene-1, syndiotactic polystyrene, and different types of polyethylene are presented and discussed. In addition the melting behaviour of alkanes and alkane mixtures has been investigated, and a thermodynamic description is given. These results are helpful for better understanding of phase transition behaviour under pressure. High pressure DSC is a powerful method which gives additional insight into polymer systems. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Poly-4-methylpentene-1 (P4MP1); High pressure differential scanning calorimetry (HPDSC); Conformational disordered (CONDIS); Polyethylene

1. Introduction

High pressure differential scanning calorimetry (HPDSC) is not widely used in polymer research. There are two main reasons for this: high pressures, up to 500 MPa or even more, are not easy to handle and need special equipment and some experience in their use because of the danger. In addition, no commercial HPDSC is currently available, so that potential workers in this field must construct their own. However, introducing pressure as another variable in the thermal analysis of polymers gives additional insight into the behaviour of such systems and, in particular, a better understanding of their thermodynamics.

This paper reviews the advantages, possibilities and limits of HPDSC on the basis of published results from this laboratory.

Different research groups, have solved the several problems of HPDSC in different ways [1–7]. We chose to use a commercial DSC (Perkin-Elmer DSC 7) and make a new measuring head only, rather than to build a complete new high pressure DSC. We initially used the original platinum furnaces and put them into an autoclave constructed specially for this purpose [8]. The advantage of this construction is that it can be used with every Perkin-Elmer DSC by plugging in the new measuring unit instead of the normal measuring head. We used oil as the pressure medium, this has the advantage of ease of handling and safety measures are not as demanding as for high pressure equipment using a gas as the pressure transmitting medium. There are, however, serious disadvantages: the oil may decompose at higher temperatures (especially if in contact with the platinum wires of the heater in the furnaces), react with the sample, solidify or even crystallize at higher pressures and will not easily fill unavoidable small cavities homogeneously. Fortunately the implied disadvantage of restricted temperature range is not so serious for polymers where an

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upper temperature limit of 350°C is generally sufficient. We found a silicone oil of medium viscosity and containing a few percent of branched chains (to impede crystallization) to be a good compromise. Fortunately this oil has a rather low thermal conductivity and heat losses by convection could be reduced by careful design. Nevertheless the "heat leakage" of the high pressure measuring head is much larger than that of a normal DSC. The very large heat capacity of the pressure medium naturally requires additional heating power and makes high demands on the symmetry of the system.

Experience with this first version led us to reconstruct the original furnaces. To increase the thermal conductivity between heater and sample we used silver instead of platinum for the furnace and wrapped the platinum wires of the thermometer and heater directly on the furnaces (after isolating them by a thin layer of aluminium oxide). Heat transfer to the oil was reduced by a layer of ceramic glue which simultaneously prevented the catalytic decomposition which occurred on direct contact with the hot platinum wire. The sample, which in every case was sealed hermetically in aluminium pans (avoiding any cavity), was mechanically pressed against the bottom of the furnace. Again the arrangement of sample and reference furnace had to be as symmetric as possible for both the heat transfer characteristics and the volume (heat capacity) of the surrounding oil.

The HPDSC constructed this way had the following properties: pressure and temperature ranges from 0.1 to 500 MPa and from ambient to 600 K respectively; thermal noise was 50 to 100 μW (10 times larger than normal DSC) with a peak detection limit of 5 mJ (i.e. 1 J g^{-1}). The baseline repeatability is poor (2–3 mW!) because of unavoidable differences in oil volume on remounting a new sample. This makes any measurements in the so-called c_p-mode (i.e. subtracting a zeroline before evaluation) impossible, a serious disadvantage for the thermal analysis of polymers. Examples of typical curves showing baseline quality and noise are given in Figs. 2, 3 and 12.

2. Results

In the following we show some results, obtained using the HPDSC described above, which demonstrate the potential of the technique. We start with some phase diagrams, which could, in principle, have been measured with simpler high pressure DTA equipment (see [1,9–11]) and then proceed to more sophisticated measurements and evaluations of different polyethylenes and some of their oligomers, the alkanes.

2.1. Phase diagrams

The phase transition behaviour of partially crystalline poly-4-methylpentene-1 (P4MP1) has already been investigated by high pressure DTA [12–14]. It is unusual in so far as the melting point first increases with pressure, goes through a maximum and then, above 150 MPa, decreases with pressure. X-ray studies [15,16] showed a rather complex phase behaviour including an amorphization on pressure rise at room temperature and reversible crystallization at temperature rise at constant pressure above 200 MPa. This strange behaviour caused us to investigate P4MP1 in our HPDSC. The results are shown in Fig. 1. The results from X-ray measurements were completely confirmed. In addition it was found that the amorphization on raising the pressure at 300 K (pathway 1) produced a very weak ($\Delta Q = -0.7$ J g^{-1}) but clearly visible exothermic peak in the HPDSC (Fig. 2) proving something like an "inverse melting" with decreasing entropy on amorphization. Even the endothermic (reversible) crystallization on temperature rise at

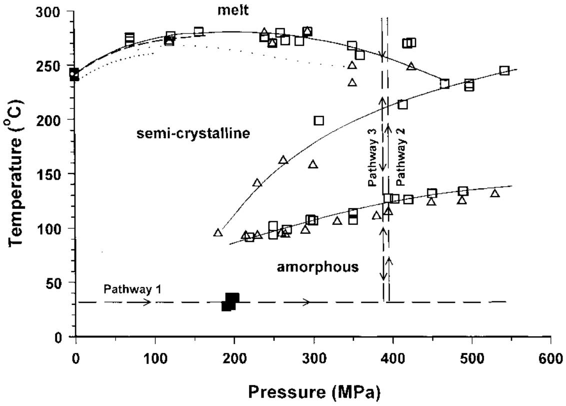

Fig. 1. Phase diagram of P4MP1 as measured in the HPDSC. Mass: 5–10 mg, heating rate: 20 K min^{-1}, (□) 1st run after crystallization at ambient pressure, (△) 2nd and further runs, solid symbols: exothermic (pathway 1), open symbols: endothermic (pathway 2). Literature results: · · · [14], – – – [12], • • • [13].

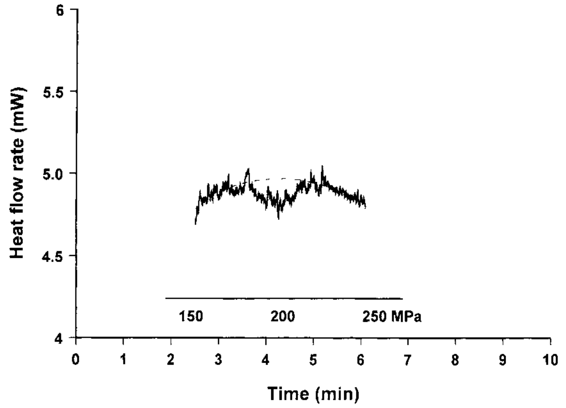

Fig. 2. HPDSC curve (mass: 7 mg, heating rate: 20 K min^{-1}) of exothermic event at 200 MPa on isothermal pressure rise (pathway 1 in Fig. 1).

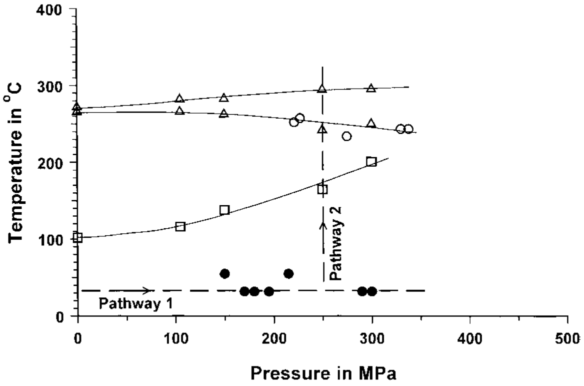

Fig. 4. Phase diagram of s-PS as measured in the HPDSC. Mass: 8–11 mg, heating rate: 10 K min^{-1}, (△) melting on isobaric heating (pathway 2), (○) phase transition on isothermal pressure rise (pathway 1), (□) glass transition, solid symbol: exothermic, open symbol: endothermic.

constant pressure above 200 MPa (Fig. 1, pathway 2) could be found as a small peak (ΔQ=1.5 J g^{-1}, Fig. 3) which could be reproduced in several cycles at constant pressure (Fig. 1, pathway 3) even though it could not be found on cooling probably because of a too slow transition rate. For a detailed discussion of the phase transition behaviour of P4MP1 from the thermodynamic point of view see [15,17].

Another partially crystalline polymer with an interesting phase diagram is syndiotactic polystyrene (s-PS). The crystals exist in two modifications [18]. The stable α phase shows a normal behaviour of the melting point with pressure whereas that of the metastable β phase decreases with pressure (Fig. 4). Obviously the β phase becomes more and more unstable at higher pressure. This is supported by the observation that the β phase is not formed on cooling at pressures above ambient but only in the totally decompressed state. The phase diagram (Fig. 4) also contains the glass transition temperature of the amorphous phase and this increases considerably with pressure. Again there is an amorphization process of the crystalline phase with increase in pressure below the glass transition temperature [18] (Fig. 4, pathway 1) which seems to be combined with a very small exothermic event found with the HPDSC.

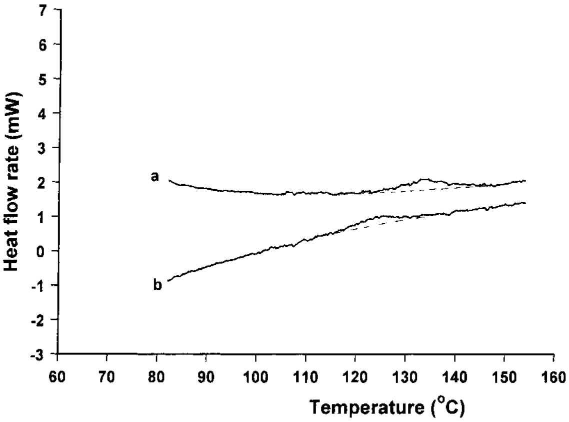

Fig. 3. HPDSC curves (mass: 7 mg, heating rate: 20 K min^{-1}) of endothermic "crystallization" on isobaric heating (pathway 2); (a) 1st run (b) rerun (pathway 3).

2.2. Alkanes

Alkanes have long been used to model the behaviour of polyethylene. The basis of this idea is the identity of the monomer units in the chains and the similar crystal structure (mostly orthorhombic lamellae crystals). More quantitatively, the thermodynamic quantities inside the crystals are thought to be almost the same in all cases which implies that the molar quantities can be calculated in an incremental way using the number of CH_2 groups of the respective chain as a parameter, surface contributions appear as an additive excess quantity. In this way the molar enthalpy and entropy of alkanes with *n* C-atoms follow as:

$$\Delta H^n_{\mathrm{mol}} = n \cdot \Delta H^\infty_{\mathrm{CH_2}} + 2H_\mathrm{e} \tag{1}$$

$$\Delta S^n_{\mathrm{mol}} = n \cdot \Delta S^\infty_{\mathrm{CH_2}} + 2S_\mathrm{e}. \tag{2}$$

For an equilibrium phase transition the Gibbs free enthalpy change is zero and we get:

$$\frac{\Delta S^n_{\mathrm{mol}}}{\Delta H^n_{\mathrm{mol}}} = \frac{1}{T^n_{\mathrm{fus}}} = \frac{\Delta S^\infty_{\mathrm{CH_2}} + 2(S_\mathrm{e}/n)}{\Delta H^\infty_{\mathrm{CH_2}} + 2(H_\mathrm{e}/n)} \tag{3}$$

which connects the fusion temperature with the enthalpy and entropy of fusion. Eq. (3) can be expanded as a Taylor series of powers of $1/n$. The linear part reads

$$\frac{1}{T^n_{\mathrm{fus}}} \approx \frac{1}{T^\infty_{\mathrm{fus}}}\left(1 + 2\frac{T^\infty_{\mathrm{fus}}S_\mathrm{e} - H_\mathrm{e}}{\Delta H^\infty_{\mathrm{CH_2}}} \cdot \frac{1}{n}\right) \tag{4}$$

the well known Thomson–Gibbs equation, which has been proven valid for *n*-alkanes with a chain length $n>10$ and for cyclic alkanes with $n>20$. In both cases the incremental fusion enthalpy of a CH_2-group has almost the same value, whereas the excess enthalpy is clearly different because of the different surface structure (CH_3-groups or narrow folded back chains).

With this background we investigated the pressure behaviour of the phase transitions of pure *n*-alkanes (with even *n*) as well as of binary mixtures in the HPDSC. The results, together with those of other groups [10,19–21] should help to clarify the behaviour of polyethylenes.

The pressure dependence of the melting temperature and of the enthalpy of fusion are presented in Figs. 5 and 6, respectively. All curves are parallel and this behaviour supports the approach of incremental thermodynamic quantities and the validity of Eqs. (1)–(4). This becomes even clearer if we plot the reciprocal melting temperatures against $1/n$ at different pressure (Fig. 7). This confirms the linear dependence expected from Eq. (4). Extrapolation to the ordinate gives the melting temperature of an alkane of infinite chain length (which is almost that of an chain-extended polyethylene crystal) as a function of pressure. To a good approximation this can be represented by a parabola [22]

$$T^\infty_{\mathrm{fus}}(p) = 414.8 + 0.2503p - 1.348 \times 10^{-4}p^2. \tag{5}$$

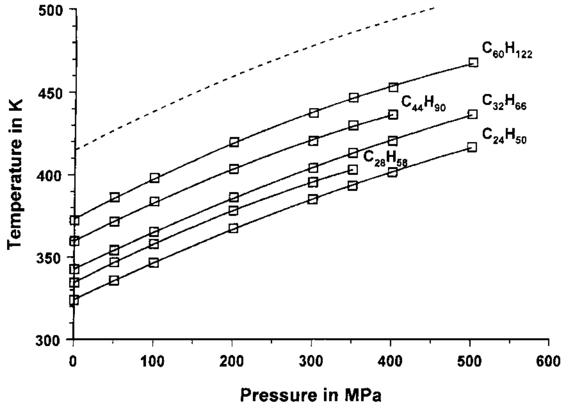

Fig. 5. Pressure dependence of the melting temperature of *n*-alkanes. Mass: 2–7 mg, heating rate 10 K min^{-1}. The dashed line characterizes the extrapolated melting temperature for infinite *n*.

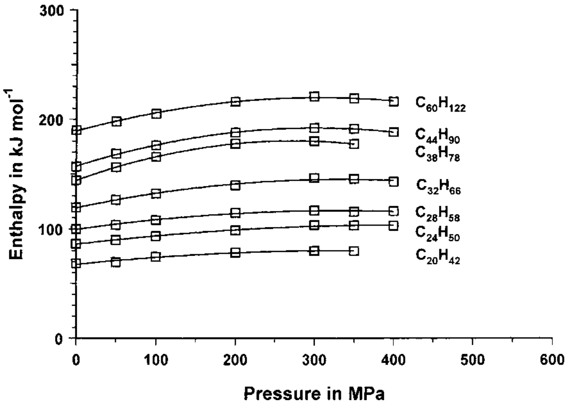

Fig. 6. Total transition enthalpy of *n*-alkanes.

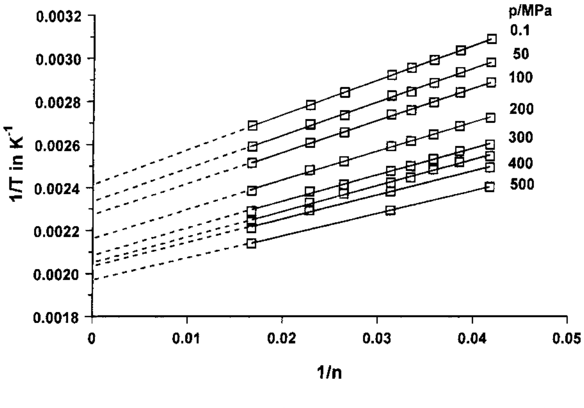

Fig. 7. Thomson–Gibbs plot of the melting temperatures of *n*-alkanes at different pressure.

This important quantity is shown as a dashed line in Fig. 5 and in later figures.

The enthalpy of fusion of n-alkanes has only a very small pressure dependence with a weak maximum around 300 MPa (see Fig. 6). This is also the case for polyethylenes and may be described starting with the Clausius–Clapeyron equation:

$$\frac{dT_{tr}}{dp} = \frac{\Delta_{tr}V}{\Delta_{tr}S} = T_{tr}\frac{\Delta_{tr}V}{\Delta_{tr}H}. \qquad (6)$$

From this the slope of the $T_{tr}(p)$ curve (Fig. 5) should be almost the same as the product of the transition temperature T_{tr} and the change of the molar volume $\Delta_{tr}V$. In other words the volume change of transition must decrease with pressure, which was indeed found by dilatometric measurements [23]. The same is true for the entropy change of transition.

Similar measurements have been made for two cyclic alkanes (Fig. 8). The phase diagram of $(CH_2)_{28}$ looks like that of linear polyethylene (see Figs. 10 and 11) and indeed this and other cyclic alkanes pass through an intermediate conformational disordered (CONDIS) phase [24] as polyethylene does. It is very interesting that the transition temperature of the other cyclic alkane $(CH_2)_{96}$ has a slope which is different from that of linear alkanes (dashed line) but parallel to the transition temperature of the CONDIS phase of the smaller cyclic alkane – this alkane already appears to be in the CONDIS phase at ambient pressure. From Eq. (6), the larger slope comes from either a larger volume change (which is unlikely) or from a smaller entropy change which is true for CONDIS melting (see Section 2.4). Another possibility is that the surface excess quantities change very much with pressure and in this case we must add an additional term, containing this quantity, to the Gibbs function and to modify the Clausius–Clapeyron Eq. (6) properly.

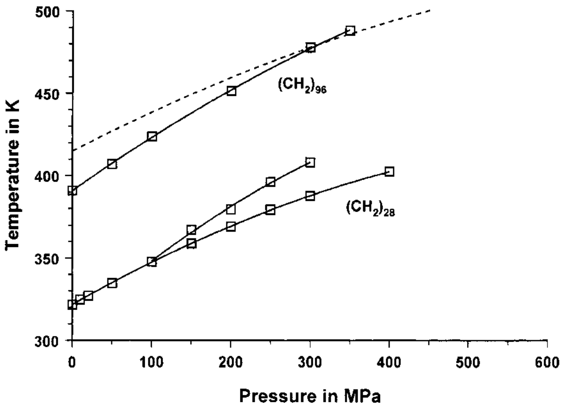

Fig. 8. Pressure dependence of the melting temperature of two cyclic alkanes. Mass: 2–4 mg, heating rate 10 K min^{-1}. Dashed line as in [5].

2.3. n-Alkane mixtures

Binary mixtures of n-alkanes (with even n) have been investigated by HPDSC to learn something of their mixing behaviour under pressure. This was done by determining the phase diagram (the dependence of the transition temperature on composition) for various binary mixtures under different pressures. The mixing behaviour changes from total miscibility in the solid and liquid states via eutectoid to eutectic, depending on the difference in n. The measured phase diagrams could be described quantitatively by using the one parameter Porter statement from the thermodynamics of mixtures. Details have been published elsewhere [22,25], and only a summary follows.

Regardless of the type of mixing behaviour, miscibility decreases with increasing pressure. This is valid for miscibility in both solid and liquid states and can be followed in the phase diagrams which change, say, from a cigar shaped (miscible) system to a eutectic one. More quantitatively, the slope of the liquidus or solidus line increases with pressure which is equivalent to an increasing Porter parameter, corresponding to Flory's χ-parameter.

Furthermore it could be shown, that the excess volume of mixing is positive and increases with pressure. For mixed crystals of n-alkanes this is understandable, because of the different length of the chains incorporated into the lamellae, but it turns out to be true even for liquid mixtures at pressures above about 30 MPa. Obviously the alkane chain structure in the liquid mixture changes from random coil to more bundle-like, this saves free volume, which is very expensive under pressure, but results in a positive excess volume of mixing. The tendency to phase separation (de-mixing), even in the liquid state, increases with pressure for the same reason. There is an upper critical temperature of de-mixing which increases with pressure and seems to cross the melting

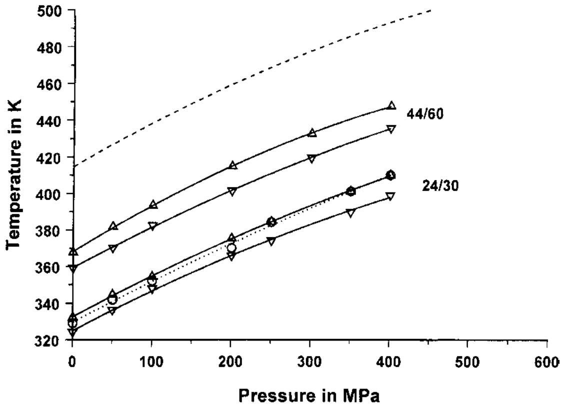

Fig. 9. Pressure dependence of the melting region of two *n*-alkane mixtures. Mass: 2–5 mg, heating rate 10 K min^{-1}. (▽) onset of the melting, (△) end of melting, (○) melting maximum. The melting region increases with pressure. Dashed line as in [5].

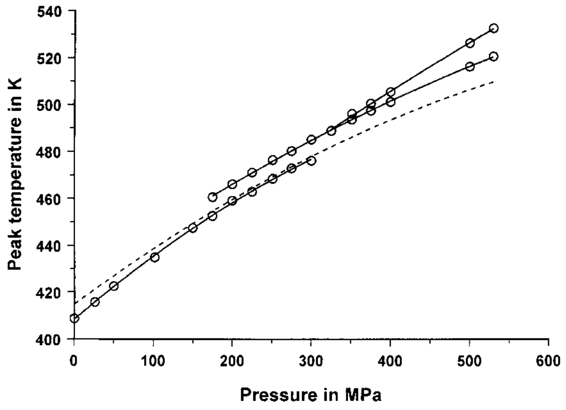

Fig. 10. Peak maximum temperatures of HDPE (GUR, M_w: 4000 kg mol^{-1}, M_w/M_n: 6.5). Mass: 7–12 mg, heating rate: 10 K min^{-1}. Dashed line as in [5].

temperature entering the liquid region at pressures of 700 to 1000 MPa, although not be proved because of the pressure limit of our HPDSC.

It follows from this thermodynamic behaviour, that the melting region of a given mixture of alkanes (the melting peak) should become broader and more asymmetric with increasing pressure and that the maximum should shift somewhat to higher temperatures, reaching the melting temperature of the larger component when the system behaves as an eutectic (Fig. 9). In other words, looking at the pressure dependence of the melting temperature curve, that for a mixture should start at lower temperatures, rise more steeply and approximate the slope of the respective curve of the pure alkane at higher pressure. The approach to such behaviour can be seen in Fig. 9. Similar effects should be found for mixtures of polyethylene and *n*-alkanes.

2.4. Polyethylenes

Figs. 10–15 show the phase diagrams of different polyethylenes (PE) and one melting curve. Again most of these results have been published before [26] and we restrict ourselves to some general remarks.

The ability of linear PE (HDPE) (Figs. 10 and 11) to form a special intermediate hexagonal, conformational disordered (CONDIS) phase at pressures above 300 MPa is well known [11,27–30]. A characteristic of the transitions (see Fig. 12) is that most of the total enthalpy and entropy change occurs at the lower temperature transition, the higher temperature event appears to be Λ-shaped suggesting an order-disorder transition. It is interesting to recognize that the same behaviour is found at ambient pressure for cyclic alkanes with n=22 and 24 [24] and above 100 MPa for n=28 (Fig. 8). Even the slope of the respective transition curves of the CONDIS phase in the phase diagrams seems to be the same in both cases. The CONDIS phase is not found for either (branched) low density polyethylene (LDPE, Fig. 13) or a low molecular weight mixture of linear PEs (Fig. 14) as is the case for linear alkanes. Obviously the special helical

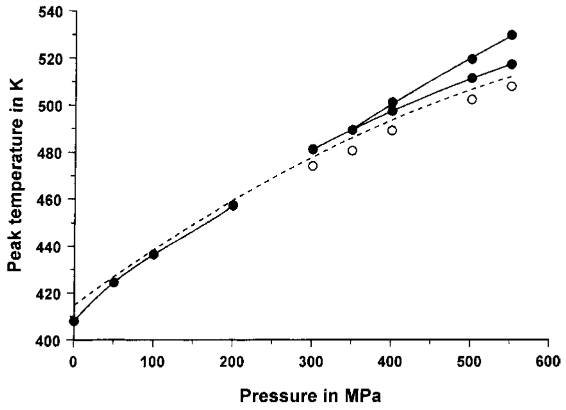

Fig. 11. Peak maximum temperatures of HDPE (Lupolen 6011, M_w: 63 kg mol^{-1}, M_w/M_n: 2). Mass: 7–12 mg, heating rate: 10 K min^{-1}. The open symbols at higher pressure mark a small pre-peak (phase separation?). Dashed line as in [5].

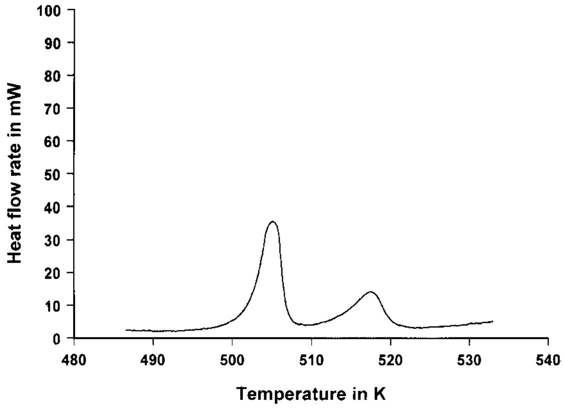

Fig. 12. HPDSC curve of HDPE at 530 MPa. Mass: 7 mg, heating rate: 10 K min^{-1}.

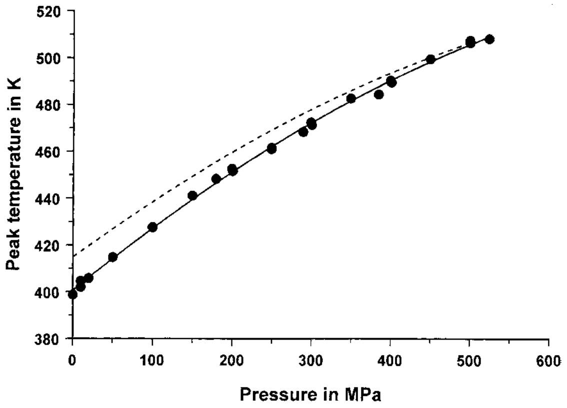

Fig. 14. Peak maximum temperatures of PE wax (PE130, M_w: 4.6 kg mol^{-1}, M_w/M_n: 3.6). Mass: 7–10 mg, heating rate: 10 K min^{-1}. Dashed line as in [5].

structure of the chains in the CONDIS phase can only exist if the lamella is thick enough – which is the case for chain-extended high molecular weight LDPE – or if the conformations are hindered in moving out of the lamella by the narrow folding back in the surface of, for instance, cyclic alkane crystals.

Another observation is that the slope of the transition (melting) of the orthorhombic phase of HDPE (Figs. 10 and 11) and LDPE (Fig. 13) equals that (dashed line) of *n*-alkanes (Fig. 5) at higher pressure. HDPE forms folded chain lamellae crystals at lower pressures, these change to extended chain crystals above 200 MPa. In the region between 200 and 300 MPa both forms of crystals coexist but with continuously changing fractions. The step-like change of the respective melting temperatures is clearly visible in Fig. 10. (It should be born in mind, that for broadly melting polymers only the peak maximum temperature can be evaluated from DSC curves, these always give systematically high temperatures because of thermal lag). In the region below 100 MPa the slope is somewhat larger than that of the dashed line. The increased slope is due to lamellae thickening with increasing pressure, as found by X-ray measurements

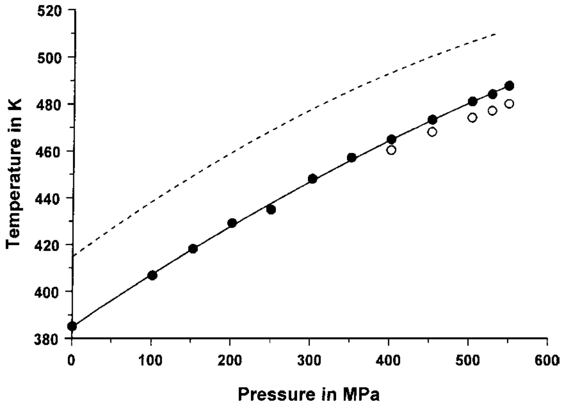

Fig. 13. Peak maximum temperatures of LDPE (1840D, M_w: unknown, SCB: 25 per 1000 C-atoms). Mass: 10 mg, heating rate: 10 K min^{-1}. The open symbols at higher pressure mark another small peak which may be due to some phase separation. Dashed line as in [5].

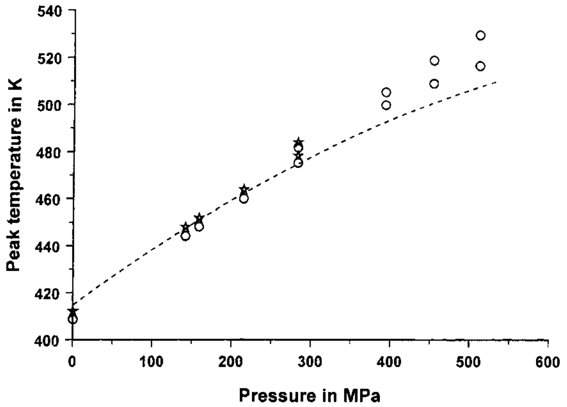

Fig. 15. Peak maximum temperatures of gel crystallized UHMWPE. Mass: 10–11 mg, heating rate: 10 K min^{-1}, (☆) 1st run of the virgin material, (○) rerun after crystallization at the respective pressure. Dashed line as in [5].

[30]. This behaviour does not occur with LDPE (Fig. 13), where the lamellar thickness is fixed by the main chain length between side chains and cannot be changed by pressure. The approach discussed in Section 2.2 can be used to describe the thermodynamics of melting of polyethylene.

In this context the special melting behaviour of gel crystallized ultra high molecular weight PE (UHMWPE) in the HPDSC should be discussed (Fig. 15). Though the lamellar thickness of this material is smaller than that of melt crystallized UHMWPE, the fusion temperature is somewhat higher (see Fig. 15). Although at first sight strange, this may be understood by looking at the fusion temperatures of cyclic alkanes [31,32] which are always higher than those of linear alkanes forming lamellae crystals of *same thickness*. They are, however, the same if we compare linear and cyclic alkanes having the *same number* of CH_2-groups in the crystal. The approach of Section 2.2 is again valid and gel crystallized PE contains a lot of narrow chain folds in the surface, behaving as cyclic alkane in this context, and gives a higher melting temperature for this type of lamellae compared with those with looser folds (i.e. those formed on cooling from the random coiled melt).

Finally, we will discuss the phase diagram of the low molecular weight PE mixture (PE-wax, Fig. 14). As already mentioned, there is now a CONDIS phase visible and the melting temperature is always lower than that of HDPE samples and even lower than it should be looking at the mean molecular mass M_w=4.6 kg mol^{-1} and the expected lamellar thickness. This material must be discussed as a multicomponent mixture which behaves generally as an alkane mixture discussed in Section 2.3. Indeed, the larger slope of the curve in Fig. 14 and the lower temperature of fusion can easily be understood if we take it as an eutectic mixture which shows increasing phase separation with increase of pressure, resulting in a broadening of the melting region and a shift of the maximum to higher temperatures.

3. Conclusions

Our results show that the additional variable available through HPDSC measurements leads to a better understanding of the melting behaviour of polymers. Currently, however, high pressure DSC measurements are only rarely found in polymer research because no commercial equipment is available and in-house construction needs experience both in high pressure technology and in DSC design. In addition, high pressures are dangerous and appropriate safety precautions must always be taken. Nevertheless, HPDSC is a powerful tool giving valuable additional information for polymer systems. Investigation of oligomer systems, if available for the polymer in question, gives a more quantitative description of the overall thermodynamics.

We strongly encourage the scientific community, as well as commercial manufacturers, to construct more HPDSC. Many difficult questions, could be solved by high pressure thermal analysis, especially HPDSC.

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References

[1] C. Schmidt, M. Rittmeier-Kettner, H. Becker, J. Ellert, R. Krombach, G.M. Schneider, Thermochim. Acta 238 (1994) 321–336.

[2] H. Arntz, Rev. Sci. Instrum. 51(7) (1980) 965–967.

[3] M. Kamphausen, Rev. Sci. Instrum. 46(6) (1975) 668–669.

[4] R. Sandrock, Rev. Sci. Instrum. 53(7) (1982) 1079–1081.

[5] A. Eichler, W. Gey, Rev. Sci. Instrum. 50(11) (1979) 1445–1452.

[6] B.-E. Mellander, High pressure studies of silver iodide and related compounds, Dissertation, University of Göteborg, 1981.

[7] S.L. Randzio, J. Phys. E: Sci. Instrum. 16 (1983) 691–694.

[8] K. Blankenhorn, G.W.H. Höhne, Thermochim. Acta 187 (1991) 219–224.

[9] A.I. Shulgin, Y.K. Godovsky, J. Thermal Anal. 38 (1992) 1243–1250.

[10] C. Nakafuku, T. Sugiuchi, Polymer 34(23) (1996) 4945–4952.

[11] C. Nakafuku, Polymer 27(9) (1995) 917–927.
[12] A.K. Jain, B. Wunderlich, J. Polym. Phys. Ed. 15 (1977) 2271–2275.
[13] S. Okumura, H. Miyaji, K. Izumi, A. Toda, Y. Miyamoto, Polymer 37(11) (1996) 2285–2287.
[14] P. Zoller, J.H.W. Starkweather, G.A. Jones, J. Polym. Sci.: Polym. Phys. 24 (1986) 1451–1458.
[15] S. Rastogi, M. Newman, A. Keller, J. Pol. Sci. B 31 (1993) 125–139.
[16] S. Rastogi, M. Newman, A. Keller, Nature 353 (1991).
[17] S. Rastogi, G.W.H. Höhne, A. Keller, Macromolecules (1999) in press.
[18] S. Rastogi, Personal communication (1998).
[19] A. Würflinger, G.M. Schneider, Ber. Bunsen-Ges. Phys. Chem. 77(2) (1973) 121–128.
[20] G. Ungar, Macromolecules 19 (1986) 1317–1324.
[21] T. Ohta, Thermochim. Acta 230 (1993) 1–13.
[22] G.W.H. Höhne, K. Blankenhorn, Thermochim. Acta 238 (1994) 351–370.
[23] W. Dollhopf, Druckdilatometrie an einigen n-Alkanen und Polymeren, Dissertation, Universität Ulm, 1979.
[24] H.-P. Grossmann, Polymer Bull. 5 (1981) 137–144.
[25] K. Blankenhorn, Differenzkalorimetrie (DSC) bei hohen Drücken, Untersuchungen zur Druckabhängigkeit des Mischungsverhaltens von n-Alkanen und Polyethylenen, Dissertation, 1993.
[26] G.W.H. Höhne, J.E.K. Schawe, A.I. Shulgin, Thermochim. Acta 296 (1997) 1–10.
[27] M. Yasuniwa, C. Nakafuku, T. Takemura, Polym. J. 4(5) (1973) 526–533.
[28] D.C. Basset, Polymer 17 (1976) 460.
[29] A.I. Shulgin, V.A. Aulov, Polym. Sci. USSR 33(7) (1991) 1466–1473.
[30] M. Hikosaka, S. Rastogi, A. Keller, H. Kawataba, J. Macromol. Sci. B 31(1) (1994) 87–131.
[31] B. Wunderlich, M. Möller, J. Grebowicz, H. Baur, Conformational Motion and Disorder in Low and High Molecular Mass Crystals, vol. 87, Springer, Berlin, 1988.
[32] H. Drotloff, D. Emeis, R.F. Waldron, M. Möller, Polymer 28 (1987) 1200–1206.