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Melting point of polymers under high pressure
Part I: Influence of the polymer properties

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Abstract

The pressure dependence of the melting point of various polymers including homo- and copolymers (HDPE, LDPE, PP and ethylene vinyl acetate copolymers (EVA)) was investigated under nitrogen atmosphere up to 330 MPa within a high pressure differential thermal analysis cell designed by our group. The properties of the polymers (vinylacetate content, melt flow index, molecular weight, isotactic index, crystallinity, density, and frequency of branching) have been correlated with the change of the melting point under pressure ($\mathrm{d}T_\mathrm{m}/\mathrm{d}p$). It could be shown that the melting point always increases linearly with pressure up to 330 MPa. The pressure dependence was found to be in the range of 11–17 K/(100 MPa). From these results it is possible to approximate $\mathrm{d}T_\mathrm{m}/\mathrm{d}p$ using the enthalpy of fusion of the polymers at ambient pressure.

Keywords: Polymer; Melting point; DTA; High pressure; EVA

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1. Introduction

The investigation of the melting and crystallization behavior of polymers under high pressure is on the one hand of fundamental interest for the understanding of the polymer structure and on the other hand of practical importance for various industrial processes. The pressure dependence of the melting point is of great interest for processes which are carried out under pressures up to 500 MPa. These processes involve the melting of polymers under high pressure (i.e. high pressure injection molding, particle formation processes, extrusion and film calandration) [1–3].

During the production of polymers (up to 300 MPa) the deposition of a thin layer of polymer on the cooler wall of the reactor is possible. This can be a serious safety concern, due to the fact that the cooling of the reactor is reduced. A thermal runaway of the polymerization can occur under these conditions. Therefore the melting point of the polymer under process conditions needs to be known in order to regulate the temperature of the wall to an appropriate level [4].

This paper presents the melting points of several homo- and copolymers under nitrogen pressures up to 330 MPa. Our main interest was devoted to the dependence of the melting point in relation to the polymer properties. Commercially DTA-cells are not available in the investigated range of pressure of up to 300 MPa. Therefore a high pressure cell designed by our group was used for the DTA experiments.

Although DTA-cells are described at length in the literature [5–8], there are some differences to the cell designed by our group. The sample is pressurized with a gas atmosphere, hence there is no need to encapsulate the sample. It is possible to investigate solids as well as liquids. The sample and the reference compartment are separated inside the pressure cell. The cell design allows a high amount of flexibility in relation to reaction conditions and the nature of the investigated sample.

2. Experimental

2.1. Apparatus

All measurements were made in a high pressure DTA cell which is shown in Fig. 1. It is designed for pressures

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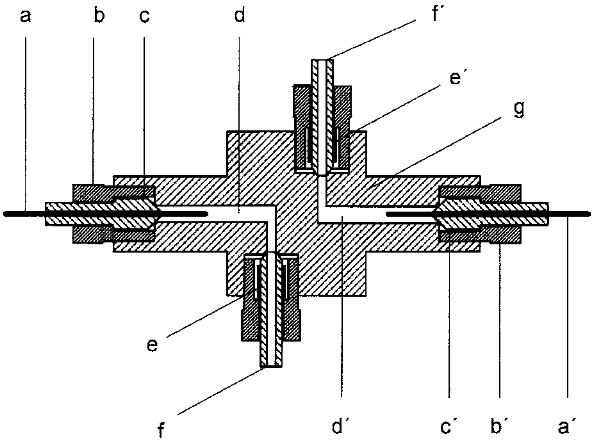

Fig. 1. DTA-cell: (a) thermocouple; (b) high pressure plug; (c) metal packing; (d) sample cell; (e) pressure ring; (f) gas feed; (g) body; (′) reference cell; without index, sample cell.

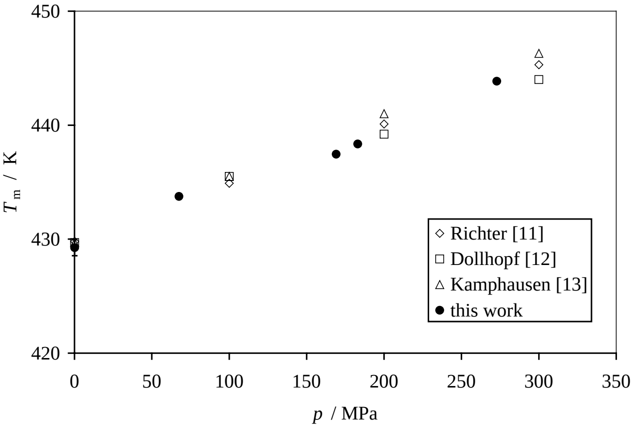

Fig. 2. The pressure dependence of the melting point of indium.

up to 350 MPa and temperatures to 573 K. The sample and the reference cell (d and d′) were fabricated by drilling two symmetrical holes of 5 mm diameter in a cylindrical block of steel alloy of high strength (German standard number 1.7707). The volume of each cell is 0.7 ml. Furthermore the steel cylinder contains two ports (f) for the supply with compressed gas. NiCr–Ni thermocouples (type K) (a) of 1 mm diameter are used for the temperature measurement. The thermal emf of this type of thermocouples is nearly independent of pressure in the range of 0.1–330 MPa [9]. After Rittmeier–Kettner the influence of pressure on the emf should be smaller than 0.2 K up to 1000 MPa [10]. Furthermore the thermo wires are not in direct contact with the pressurized gas but are shielded with an inconel mantle also reducing the effect of pressure. To verify that the emf is practically independent of pressure up to 300 MPa, the melting point of indium was measured and compared with melting point data of the literature [11–13]. The values obtained in this work show good agreement with those measured in three other laboratories (Fig. 2). For temperature calibration the following substances where used: Indium (427.8 K), benzoic acid (395.6 K), azobenzene (341.2 °C). The dependence of the emf on temperature was assumed to be linear. The standard deviation after repeated determination of the melting point of indium was found to be ±0.7 K.

In Fig. 3 a scheme of the complete setup is shown. Sample and reference cell are placed in an oven (a). The cell is placed in the center of the oven. The position is stabilized by a mounting support. The heating source is mounted in the walls of the oven. A fan ensures a gradient free temperature field inside the furnace. There is no direct contact between the heating device and the cell (Fig. 4).

The heating source of the oven is regulated with a PID-controller in order to produce a linear increase of the temperature in the cell. The nitrogen is taken from gas cylinders (d) and compressed with a membrane compressor (b).

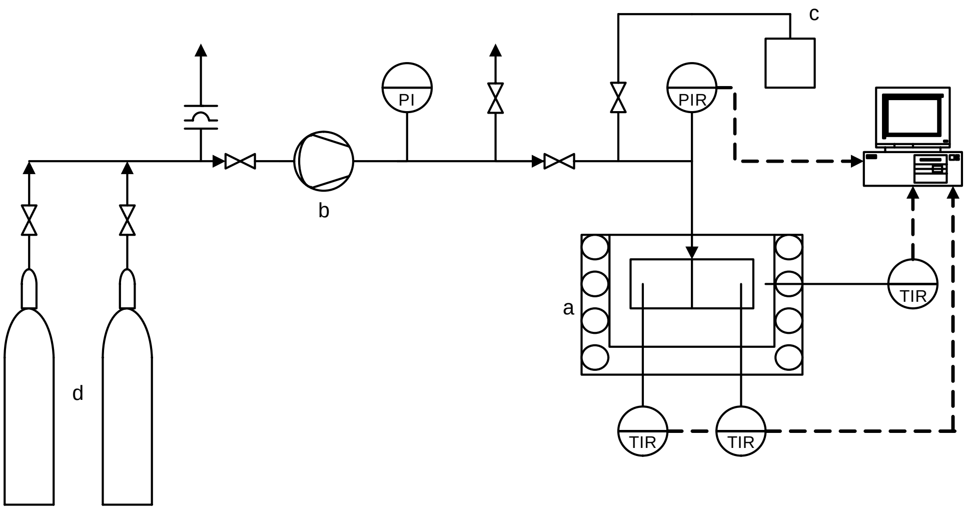

Fig. 3. Scheme of the installation: (a) cell and oven; (b) diaphragm compressor; (c) pressure compensation vessel; (d) gas bottles.

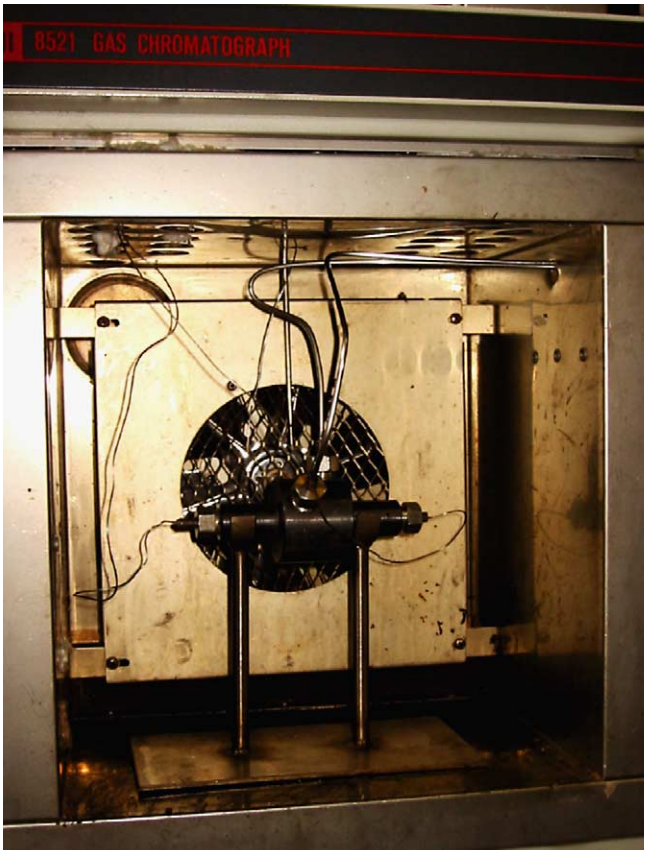

Fig. 4. Furnace with DTA-cell.

A pressure compensation vessel (c) is available for isobaric measurements. The sample and the reference cell are heated with 2 K/min. The temperature difference between the sample and the reference is continuously recorded. The reference cell was left empty. The sample cell was completely filled with grounded polymer. Then the thermocouple was placed perpendicular to the center of the abutting faces of the cylindrical sample cell (Fig. 1). So the contact between the sample and the thermocouple is rather loose and the amount of the polymer fill near to the thermocouple will contribute most to the DTA-signal. Due to this fact the calculation of the enthalpy of fusion is difficult because the thermal conductivity of the polymer fill needs to be known. Nevertheless this should not affect the precision of the determination of the melting point.

2.2. Samples

Ethylene vinyl acetate copolymers (EVA) whose melting behavior under pressure was unknown up to now, as well as ethylene low density (LDPE), high density homopolymers (HDPE) and polypropylene (PP) as a reference were used. Their data are listed in Table 1. The EVA- and LDPE-samples are industrial (Exxon Mobile) polymers manufactured by high pressure radical polymerization. HP 1 and HP 2 (HDPE) were prepared under medium pressure (7 MPa) with a metallocene catalyst. The PP-sample PP 1635 is a metallocene based (Exxon Mobile) grade. The polymers were used as received for the DTA-experiments

Table 1
Polymer data

Polymer	VA (wt.%)	M_w (10^5 g/mol)	$D = M_w/M_n$	ρ (g/ml)	T_M (at 0.1 Mpa) (K)	C (%)	MFI (g/10 min)	N_B ((10^3 C-atoms)$^{-1}$)	I_{II} (%)	(dT_m/dp) (K/100 MPa^{-1})	ΔH_m (J/g)
EVA											
FL 00328	27.0	1.77	3.17	0.952	346.0	–	3	1.89	–	12.2	76.9
UL 15028	27.5	0.91	3.01	0.926	347.1	–	145	1.93	–	11.7	95
UL 15019	19.0	0.92	3.35	0.928	354.1	–	150	1.33	–	12.3	92.3
UL 00018	17.5	2.58	4.24	0.933	363.9	–	0.37	1.23	–	13.8	104.4
LD 369 BW	9.7	3.56	7.04	0.909	369.5	–	0.41	0.68	–	14.1	153.6
LDPE											
LD 655	0	2.37	9.04	0.907	374.5	42.6	155	2.11	–	13.6	123.6
LD 165	0	4.25	5.74	0.912	383.9	54.5	0.33	1.38	–	14.6	158
LD 151	0	1.73	3.71	0.920	388.9	54.1	3	0.86	–	15.8	157
HDPE											
HYA 600	0	2.86	5.46	0.954	401.3	68.8	0.3	0	–	16	202.5
HMA 014	0	2.12	3.03	0.960	403.2	58.7	4	0.73	–	16.5	218.8
HP 1[a]	0	0.68	2.89	0.983	401.1	77.9	124	0.17	–	16.9	225.8
HP 2[a]	0	6.03	7.01	0.981	403.8	74.1	0.06	0.09	–	15.7	215
PP											
PP 45379	0	1.56	3.44	0.899	429.0	43.9	150	–	98	11.9	83.4
PP 400	0	1.96	2.89		437.0	45.6	52	–	97	12	86.7
PP 4062	0	4.72	6.05	0.899	439.1	49.6	1.3	–	95	11.3	94.2
PP 1040	0	1.84	3.36	0.910	439.9	56.7	8.3	–	93	11.7	107.7
PP 1635[a]	0	2.54	1.72	0.899	424.6	42.4	12.2	–	98	13.1	80.5

[a] Metallocene based.

and always only the first run of the heating-up was evaluated, because the cooling rate could not be regulated. All the polymer samples were characterized by means of the weight average molecular weight M_W, polydispersity D, crystallinity C, melt flow index MFI as well as the structural parameters tacticity I_{II} and degree of branching N_B. Before the DTA measurements all polymers were cooled with liquid nitrogen and then ground in a mill.

2.3. Analytical work

The DSC-measurements for the determination of the melting point and the melting enthalpy under ambient pressure were carried out on a differential scanning calorimeter (Perkin Elmer DSC 6). The crystallinity was calculated from the enthalpy of fusion as guidelines for the thermal analysis the codes DIN 53756 [14] and ASTM D3418 [15] were used.

The determination of the melt flow index was done according to DIN 53735 [16] resp. ASTM D 1238 [17] with a melt flow indexer (Göttfert 011), at 463 K and 2.16 kg load.

The distribution of the molecular weight was determined by means of high temperature gel-permeation chromatography (Waters 150 C-plus). A column (PSS Polefin Linear XL) packed with a highly networked plasma-modified styrene-divinyle-benzene copolymer was used. 1,2,4-Trichlorbenzene was used as the solvent at 413 K.

The density of the polymer samples was measured according to DIN 53479 [18].

Crystallinity and degree of branching of the homo polymers were determined by means of IR spectroscopy according to ASTM D2238-92 [19]. The IR data were obtained on a Bruker IFS 48 fast-Fourier-transform-infrared spectrometer (400–4000 cm^{-1}). For the measurements polymer films were prepared in a high pressure compactor (400 MPa and 500 K). Because of signal overlapping in the IR spectra the determination of degree of branching of the EVAs was not possible. Therefore ^{1}H-NMR spectroscopy was applied.

A fast-Fourier-transform-NMR spectrometer (Bruker ARX 300, 300 MHz) was used. The polymer samples were dissolved in chloroform-d (approximately 0.5 wt.%). The spectral assignment was done in accordance with the work of Keller [20–21].

The isotactic index II was quantified according to ISO 9113 by extraction with boiling n-heptane [22].

3. Results

For the determination of the melting point the temperature difference between the sample and the reference was plotted against the sample temperature (T_s). As an example a series of thermograms for LDPE and EVA measured at three different pressure levels are shown in Fig. 5. As usual the melting point was defined as the absolute minimum of the melting curve [14–15]. The melting peaks of the homopolymers (HDPE, LDPE, and PP) are sharp while the EVAs show very broad peaks. The copolymers show no easily identifiable single peak. Sometimes more than one peak maximum was observed. In this case the upper minimum of the curve was used for the determination of the melting point [23]. The melting point of the investigated polymers always increases with pressure.

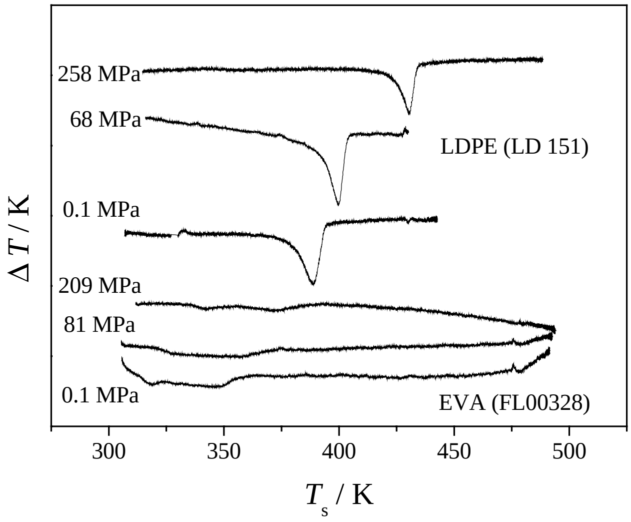

Fig. 5. DTA melting curves.

The change of the melting points with pressure of the EVA-copolymers is compared to those of LDPE in Fig. 6. The melting points increase linearly with pressure. The slope dT_m/dp of the melting curves is given in Table 1.

If the pressure dependence of the melting point of the homopolymers and the copolymers is compared it becomes obvious that the melting point of the high density polyethylene shows the highest dependence on the pressure. The influence of pressure on the melting point is lower for low density polyethylene. Polypropylene shows the lowest

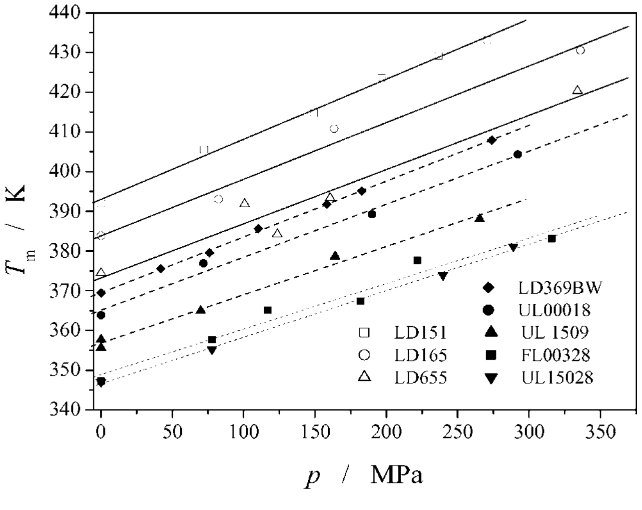

Fig. 6. Pressure dependence of the melting point.

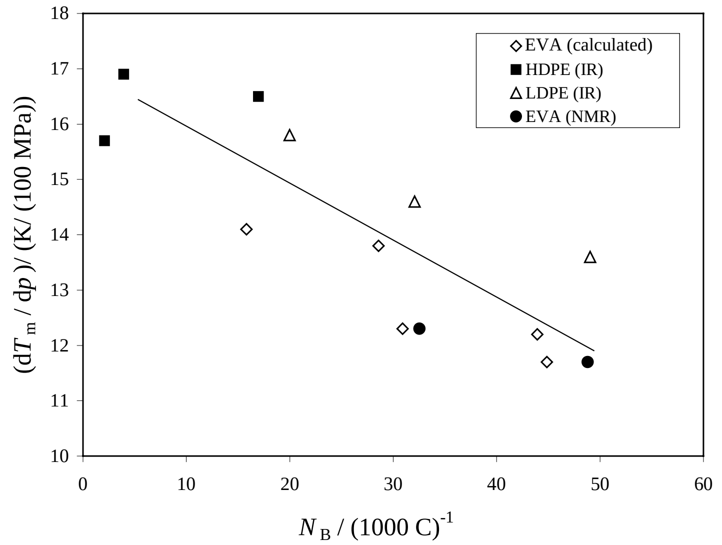

Fig. 7. Influence of the degree of branchings.

dependence. EVA lays in between LDPE and PP. With rising MFI (at constant VA content) and rising vinyl acetate content (at constant MFI) the pressure dependence of the melting point decreases (Table 1).

As the pressure dependence of the melting point decreases with increasing VA content it can be assumed that dT_m/dp decreases with a rising degree of branching N_B. An estimation of the degree of branching can be made under the assumption that every VA molecule in the copolymer results in a branching point and that there are no other branches formed.

It becomes obvious from a comparison of the ^{1}H-NMR measurements of the overall degree of branching that N_B is dominated mainly by the content of VA. The values from the ^{1}H-NMR measurements are a little higher (<10%) than the calculated values.

In general the dT_m/dp values decrease with an increasing degree of branching (Fig. 7).

In case of polypropylene, dT_m/dp is also influenced by the tacticity of the polymer. The isotactic index of the investigated PPs increases with increasing dT_m/dp (Table 1).

Finally the DTA-measurements indicate that a significant correlation between the enthalpy of fusion, measured at ambient pressure (DSC) and the rise of the melting point with increasing pressure exists (Fig. 8). The measured enthalpies are ranging from 77 to 226 J/g, whereas the polypropylenes have the lowest and the polyethylenes the highest values. LDPE is located in-between. The enthalpy of the EVAs

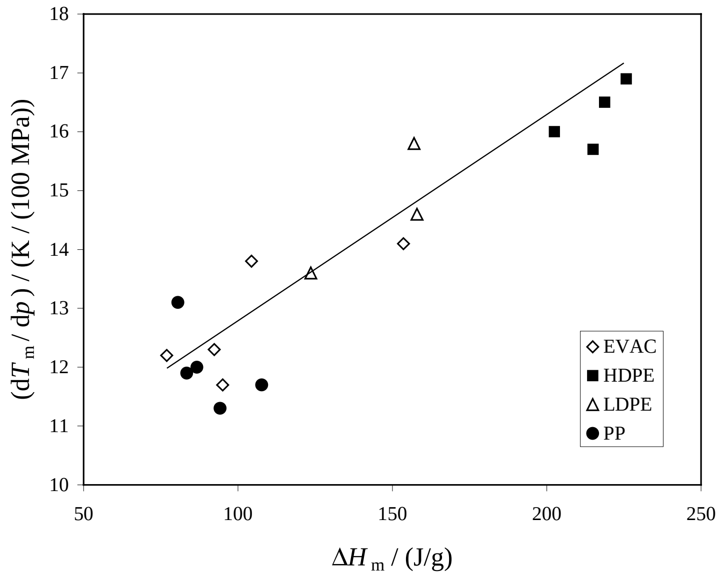

Fig. 8. Correlation between dT_m/dp and the melting enthalpy measured at 0.1 MPa.

Table 2
Comparison

Polymer	T_m (at 0.1 MPa)(K)	$(dT_m/dp)^a$ (K/(100 MPa))	Comment	Source
HDPE	410.0	24.8		[25]
	406.5	24.0		[26]
	405.7	24.5		[27]
	409.0	27.0		[28]
	410.3	24.8		[29]
	–	23.6		[30]
	411	25.4		[31]
	407.0	(a) 16.7	Under pressurized nitrogen (a) FCC	[32]
	415.6	(b) 23.5	(b) ECC	
	404	22.5		[33]
	409–410	23		[34]
	383–403	22–25		[35]
	–	23		[36]
	409	23.2		[37]
	401–408	23–25.6		[38]
	401–404	15.7–16.9		This work
UHMWPE	408	22	Ultra high molecular weight PE $M_w = 2.7 \cdot 10^6$ g/mol	[39]
LDPE	385	20		[34]
	390	26.9		[31]
	374–389	13.6–15.8		This work
PP	442	33.8		[40]
	445	37		[41]
	437	26	α-PP (monocline)	[42]
	425–440	11.3–13.1		This work
LLDPE	401	16.6	Ethylene-1-butene copolymer	[32]
PTFE	–	140	Polytetrafluorethylene	[43]
PCTFE	488	65	Polychlortrifluorethylene	[43]
EVA	347–369	11.7–14.1		This work

[a] Obtained by linear regression up to 300 MPa.

ranges from medium to low values of dT_m/dp, with increasing VA-content. It is obvious that the enthalpies of fusion are very low. This can be explained by the low degree of crystallinity of the polymers (Table 1). During the industrial manufacturing process the polymers are fused at ambient pressure and then extruded into a water bath. Due to the high cooling rate the amount of regular folded chain crystals (FCC) should be rather low and no extended chain crystals (ECC) should be present, because they will only be formed when the polymer is crystallized at high pressure (above 300 MPa for HDPE) [24].

In Table 2 the dT_m/dp values measured in this work are listed together with data of the literature. In order to be able to compare our measured values of dT_m/dp with those from other laboratories, the literature values were fitted linear in the relevant range of 0.1–300 MPa. The values obtained by linear regression are always smaller than the often stated (dT_m/dp)-value in the literature at 1 bar, because the investigators usually used a quadratic equation to fit their data, which was not used in this work.

Obviously, dT_m/dp for polyethylene and polypropylene in this work is mostly lower than in the literature. Only the data of Davidson and Wunderlich [32] are similar to ours. It seems to be reasonable that the large deviations (up to 10 K/(100 MPa)) are caused by the influence of the gas, because only Davidson and Wunderlich also used nitrogen for pressurization. All the other authors used oil for pressure transmission and performed their experiments with encapsulated samples. The influence of the gas is the topic of running investigations [44]. In order to affirm this hypothesis a sample of the HDPE (HMA 014) was measured at another laboratory by a high pressure DSC (HPDSC) [30].

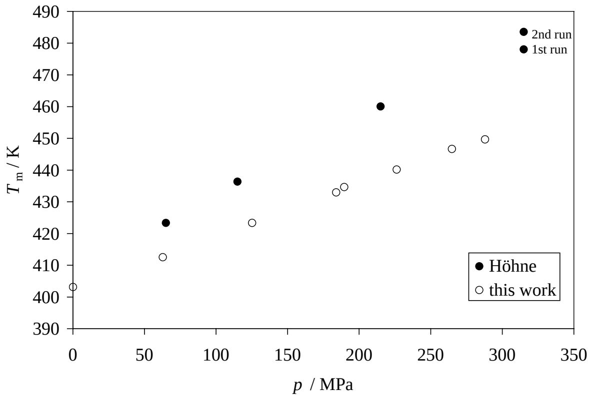

Fig. 9. Peak maximum temperatures for HDPE (HMA 014) measured by high pressure DSC by Höhne [30] (filled circles) and by high pressure DTA under nitrogen atmosphere used in this work (empty circles).

For the measurements the samples (mass: 5 mg) were hermetically sealed in aluminum pans to avoid direct contact with the pressure medium. For a detailed description of this DSC see Ref. [45]. The result is shown in Fig. 9. The peak temperatures measured in the HPDSC do not change much between the first and the second run up to 300 MPa. Above 320 MPa peak separation occurs, because of the now formed extended chain crystals and the hexagonal CONDIS phase [46]. Nevertheless the values for the peak temperatures of the first run are apparently higher than our values measured under nitrogen atmosphere.

4. Conclusions

From our results it can be concluded that higher values of VA content, MFI and degree of branching decrease the dependency of the melting temperature on the pressure dT_m/dp of the EVA-copolymers. dT_m/dp of the polypropylene increases with higher tacticity. The values of dT_m/dp for the LDPEs are rising strongly with increasing density. Generally dT_m/dp of the investigated polymers rises with the melting enthalpy measured at 0.1 MPa.

The results obtained in this work are in good agreement with data of one other group who also used nitrogen as the pressurizing medium.

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