Journal of Thermal Analysis, Vol. 38 (1992) 1243-1250

DTA MEASUREMENTS ON POLYMERS UNDER HIGH PRESSURE
Polyethylene and poly(diethylsiloxane)

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The construction of a high-pressure (up to 800 MPa), low-temperature (173–600 K) differential thermal analysis (DTA) apparatus is described. Some results on the phase transitions in polyethylene and poly(diethylsiloxane) under high pressure are presented.

Keywords: high-pressure, low-temperature DTA, polymers

Introduction

It is known that although polyethylene (PE) and poly(diethylsiloxane) (PDES) do not contain classical mesogenic groups in their macromolecules, under appropriate conditions they may form thermotropic mesophases. Moreover, PDES may form such a mesophase under atmospheric pressure (AP), while PE forme mesophase only under high pressures (HP). According to recent investigations [1–3] the formation of extended-chain crystals (ECC) in PE may be connected with the appearance of the high pressure mesophase (HPM) which is an intermediate between the orthorhombic phase and melt. In these studies it has been assumed that only the crystallization of the melt in HPM under further cooling leads to the formation of ECC (crystallization of the melt in the orthorhombic phase leads to the formation of folded-chain crystals). However, some results contradict this assumption. One of the purposes of this study was to obtain some additional data about such correlation.

The phase transitions in PDES under AP has been investigated well enough [4–7] but there are no data for the phase transitions under HP.

Differential thermal analysis (DTA) under HP is very well suited to provide data on the phase transitions in polymers under HP. A brief description of the DTA apparatus designed for the investigation of polymers in a broad range of pressures and temperatures is presented.

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Experimental

High-pressure DTA apparatus

The high-pressure apparatus described in detail elsewhere [8] has been used in the present studies and its scheme is shown in Fig. 1. The apparatus consists of three major components: a low-pressure cylinder with a piston unit, an intensifier shaft connected to the piston, and a high-pressure vessel. The high-pressure vessel can be heated by a 2 kW external heater up to 600 K or can be cooled down to 173 K by the special cryostat filled with liquid nitrogen, surrounding the high-pressure vessel.

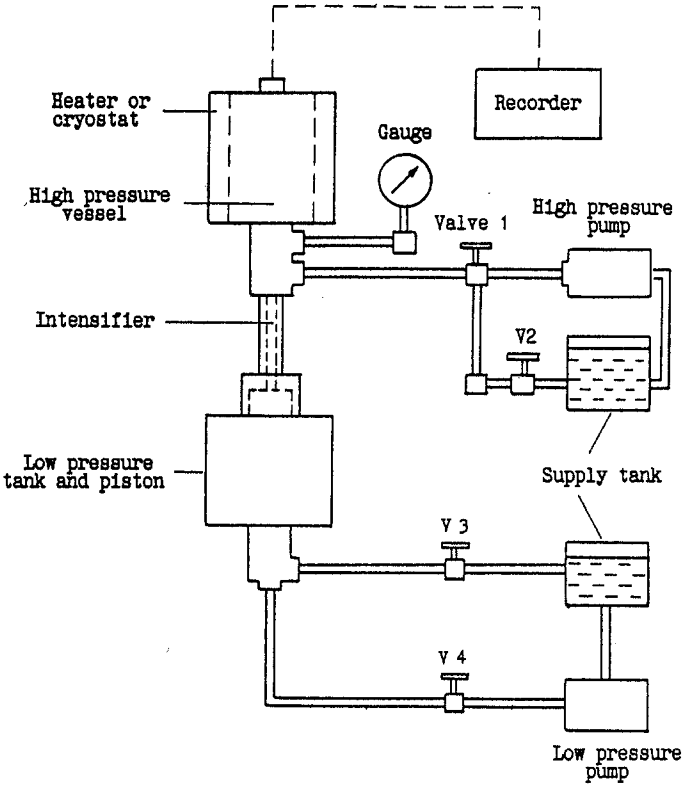

Fig. 1 The scheme of the high-pressure DTA apparatus

The central part of the high-pressure DTA apparatus is a measuring DTA cell (Fig. 2) consisting of two differentially connected thermobatteries. The two thermobatteries are neccessary because a temperature gradient exists in the high-pressure vessel. One of the batteries measures the heat flow between the sample (14) and the reference (6). The other thermobattery contains two references (9, 11) one of which (11) is placed instead of the sample. This thermobattery is used for a compensation of the temperature gradient in the high-pressure vessel. Each of the thermobatteries consists of forty differentially connected alumel-copel thermocouples (12) for measuring the heat flow. The temperature of the sample is measured by an alumel-chromel thermocouple (5). The thermocouple and thermobattery are electrically insulated from the sample holder (3) by a thin mica plate (13) (50 µm thickness). The sample holder provides a constant geometry of the sample. The sample is isolated from the silicone oil used as the pressure transmitting fluid by a sealed stainless steel membrane (80 µm thickness) (5). A copper plate (6) is used as a reference.

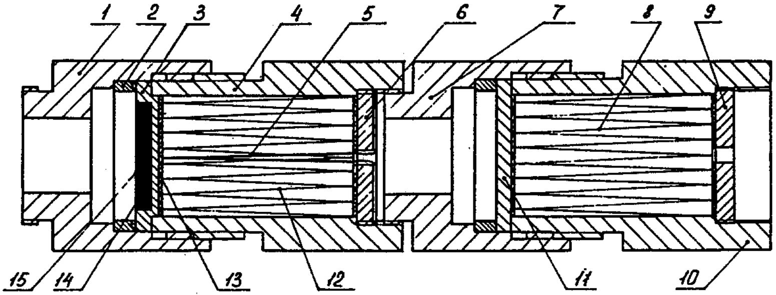

Fig. 2 The scheme of the DTA-cell: 1, 7 – the special nut, 2 – sealed ring, 3 – sample holder, 4, 10 – cell body, 5 – thermocouple, 6, 9, 11 – reference (copper plate), 8, 12 – thermobattery, 13 – mica plate, 14 – sample, 15 – membrane

The hydrostatic pressure was measured by a Bourdon gauge connected to the high-pressure vessel (Fig. 1) with a maximum of 1000 MPa and sensitivity of 10 MPa/division. The pressure was maintained constant during the experiment with an accuracy of 1%. The DTA cell was calibrated based on data [9] for the melting temperatures of In and Sn under high pressure. The calibration revealed that the temperature was measured with an accuracy better than 1 K. The heating and cooling rates were 1.5–3.0 deg/min. The weight of the sample was about 150 mg.

DTA of PE under HP

Phase diagrams of a linear PE with different molecular weights (MW) (from $3.5 \cdot 10^4$ to $2 \cdot 10^6$) obtained by DTA method under HP (up to 573 K) have been studied.

Figure 3 shows the DTA traces of PE ($MW = 3 \cdot 10^5$) under HP, the samples being crystallized previously under the same pressure. As it is seen in Fig. 3 the thermal curves of the samples crystallized under $P < P_{tp}$ (where P_{tp} is the pressure of the triple point) contain two endothermal melting peaks. These results suggest that PE may form ECC under $P < P_{tp}$. It is confirmed by the data on the selective dissolution of PE, which has been crystallized under $P < P_{tp}$.

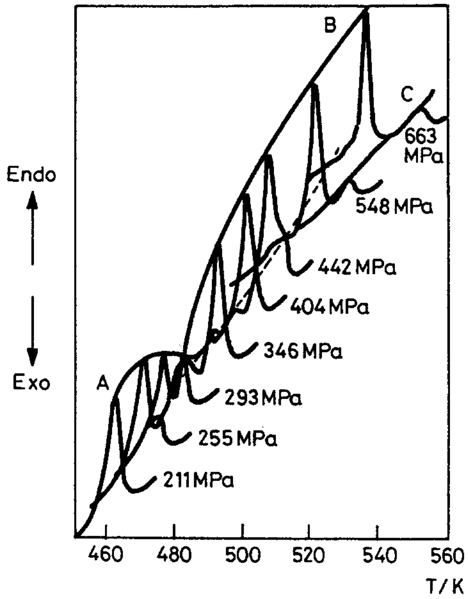

Fig. 3 DTA-curves of PE under various pressures crystallized previously under the same pressure. A – folded-chain crystals melting, B – melting or transition into HPM of ECC, C – transition of ECC from HPM to the melt

A comparison of curves (*a*) and (*b*) (Fig. 4) shows that large crystals are preferentially formed at a small undercooling, therefore, a decrease of the cooling rate of the melt under HP when $P < P_{tp}$ leads to an increase of the fraction of large crystals in the sample. The formation of ECC in PE under HP is connected with the appearance of the HPM [1–3]. The formation of ECC under $P < P_{tp}$ is explained by these authors by the fact that with an increase in the molecular weight P_{tp} moves to lower pressures. From their point of view the appearance of ECC below P_{tp} is caused by the existence of the higher molecular weight fractions in the sample, for which the triple point may be decreased down to 270 MPa.

The influence of the molecular weight on the position of P_{tp} has been studied. It was shown that with increasing molecular weight P_{tp} moves to lower pressures, this dependence being logarithmic. To decrease P_{tp} to 270 MPa the molecular weight must be of the order of 10^7. But in reality the formation of large crystals is possible even under 235 MPa and in this case almost half of the volume of the sample with $MW = 3\cdot 10^5$ (that was crystallized under this pressure) contains large crystals. Thus, one may conclude that the process of the formation of large crystals is not connected with the existence of HPM in PE under definite conditions.

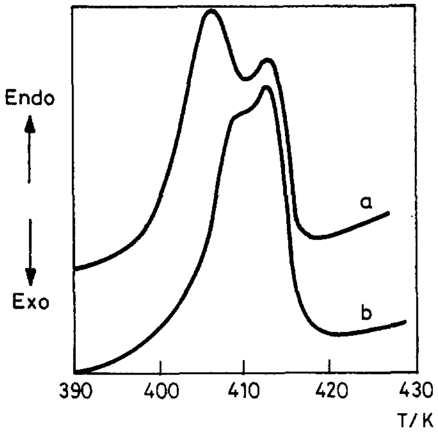

Fig. 4 DTA-curves of PE under AP, crystallized previously under 235 MPa with different rates of cooling: *a* – 2 deg/min, *b* – 0.1 deg/min

The appearance of HPM only accelerates this process. A distinct analogy may be found between the crystallization from HPM and crystallization of PDES from the mesomorphic state.

Phase transitions in PDES under HP

It is known [5] that linear PDES can exist in two high temperature polymorphs which melt at 280 and 290 K (denoted by α_2 and β_2 respectively). Each of the high-temperature forms arises from the corresponding low-temperature form on heating: the first (α_1) at 214 K and the second (β_1) at 206 K. The mesophase formed from the molten high-temperature crystalline phases melts in a rather broad temperature range of 290 to 327 K. It is known that the ratio of different crystal modifications in PDES is governed by the thermal prehistory and also depends on the degree of mesophase formation as well as on cooling conditions.

The melted samples of PDES ($MW = 5.1 \cdot 10^5$) were heated simultaneously with the application of pressure up to a definite pressure value. Then they were cooled under the same pressure at a cooling rate of 1.5–3.0 deg/min down to 173 K. After that the sample was heated under constant pressure.

Figure 5 shows the DTA curves under various pressures, the samples being crystallized previously under the same pressure. The corresponding pressure dependences of the transitions temperatures are plotted in Fig. 6. Figure 5 shows that crystallization under AP at a low cooling rate leads to the preferential formation of the β_1-modification, which transforms into the β_2-modification (peak B_1) on heating. It is clearly seen that crystallization under AP and HP differs greatly. The area of peak A_1 (corresponding to the transition $\alpha_1 \rightarrow \alpha_2$) increases and that of peak B_1 ($\beta_1 \rightarrow \beta_2$) decreases with the growth of the crystallization pressure up to 130 MPa, while the area of peak B_2 (β_2-form melting) remains almost the same. However, at higher pressures the low temperature peak (denoted by B_1, because we do not know the structure of PDES crystallized under such pressures) arises again and the area of the peak A_2 increases and that of peak B_2 decreases. At P above 160 MPa only peaks B_1 and A_2 may be observed.

It is known that the volume change resulting from the transition of the mesophase into the melt decrease as the pressure increases [10]. Two hyptotheses may be suggested for explaining this behaviour. First of all, one may assume that an increase in pressure influences the structure of the melt (densification) and it leads to a decrease in the volume change for the transition from the melt to the mesophase. On the other hand, it may be a result of an increase in the crystallization pressure, which make it difficult to form the mesophase and under a definite pressure it disappears.

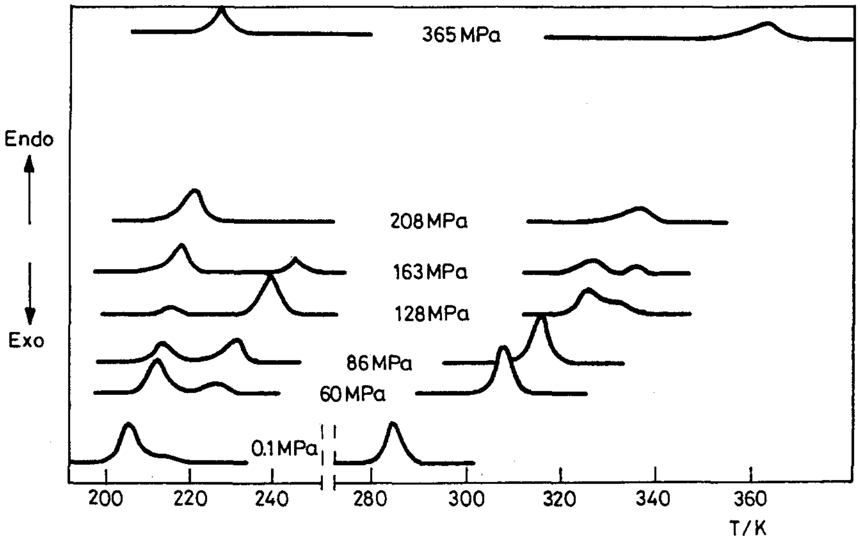

Fig. 5 DTA-curves of PDES under various pressures crystallized previously under the same pressure: B_1 ($\beta_1 \rightarrow \beta_2$); A_1 ($\alpha_1 \rightarrow \alpha_2$); B_2 ($\beta_2 \rightarrow$ mesophase or melt); A_2 ($\alpha_2 \rightarrow$ mesophase or melt); B_1 (unknown modification $\rightarrow \alpha_2$)

Let us examine the first hypothesis. Both the mesophase and α_2-modification have monoclinic form of the cell. Therefore, the activation energy for the transition from tthe mesophase into the monoclinic crystalline lattice will be lower than for the transition from the mesophase into the tetragonal crystalline lattice, because it does not require any reconstruction of the cell. Moreover, the transition into the tetragonal lattice must require slower rates of cooling because of kinetic difficulties. It coincides generally with the data obtained recently [5]. Finally, the applied pressure causes a decrease of molecular mobility. This leads to an increase of the activation energy for the transition into the β_2-modification. Hence, according to this suggestion only the transition from the mesophase into the α_2-modification may be observed under HP.

However, the second hypothesis can also explain the experimental data. If one assumes that the action of the applied pressure and influence of the cooling rate is analogous then one may expect that the content of the α_2-modification will increase and that of the β_2-modification will decrease with an increase in pressure. It is known that an increase of cooling rates increases the content of the α-modification [5]. Similarly, an increase of pressure should also be accompanied by an increase of the contant of α_1-modification.

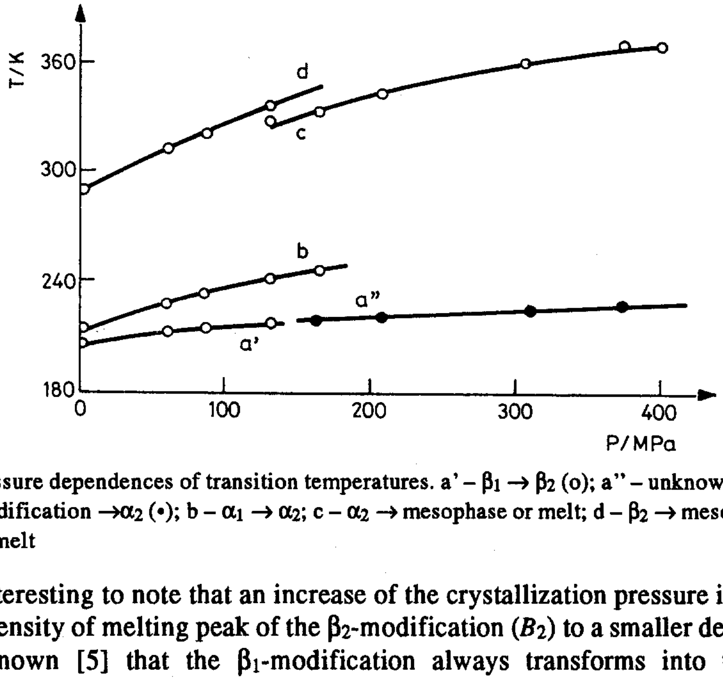

Fig. 6 Pressure dependences of transition temperatures. a' – $\beta_1 \rightarrow \beta_2$ (o); a" – unknown modification $\rightarrow \alpha_2$ (•); b – $\alpha_1 \rightarrow \alpha_2$; c – $\alpha_2 \rightarrow$ mesophase or melt; d – $\beta_2 \rightarrow$ mesophase or melt

It is interesting to note that an increase of the crystallization pressure influences the intensity of melting peak of the β_2-modification (B_2) to a smaller degree. It is well known [5] that the β_1-modification always transforms into the β_2-modification during heating under AP and the α_1-modification transforms into the α_2-modification. But in our case such correlation of the transitions is disturbed. It may be connected with a partial recrystallization of the α_2-modification into β_2-modification after its melting. According to this suggestion the mesophase practically disappears at $P > 100$ MPa and the sample crystallizes mainly in α-modification. An increase in the intensity of peak B_1 at $P > 130$ MPa may be connected with worse conditions of crystallization and with the appearance of small defect crystals, with a reduced temperature of the solid-solid transition. Under AP such behaviour corresponds to the quenching of the melt. Hence, independently of the accepted hypothesis we may conclude that the application of pressure make the crystallization process more difficult and leads to a less perfect crystalline structure of crystallized PDES.

Conclusions

The investigations have revealed that crystallization from mesomorphic states for PE and PDES leads to the formation of more perfect crystals. The consequence of phase transitions in PDES under AP and HP differs greatly. In contrast to PE, in which a mesophase appears under HP, a mesophase in PDES exists already under AP and probably disappears with an increase in pressure. While the application of pressure leads to a less perfect crystalline structure of PDES, the application of pressure provides better conditions for the formation of ECC in PE and the high pressure mesophase accelerates this process.

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Zusammenfassung — Mittels DSC wurde im Bereich 323 bis 1273 K die spezifische Wärme von $Bi_4Ge_3O_{12}$- und $Bi_4Ti_3O_{12}$-Einkristallen untersucht. Unter Zuhilfenahme des "normalen" Wärmekapazitätskurvenverlaufes für $Bi_4Ge_3O_{12}$ wurde derjenige Temperaturbereich bestimmt, in dem in $Bi_4Ti_3O_{12}$ die anomale Umwandlung von einer polarisierten in eine unpolarisierte Phase verläuft. Wärmeeffekt und Entropieänderung für diese Umwandlung wurden ermittelt.