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Influence of high pressure on the phase transitions in linear polysiloxanes as studied by high pressure DTA

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Abstract

The construction of a high-pressure (up to 800 MPa), wide temperature range (173–600 K) differential thermal analysis (DTA) apparatus is described. Some results on the phase transitions in poly(diethylsiloxane) and poly(dipropylsiloxane) under high pressure are presented. The influence of the mesophase on phase transitions in linear polysiloxanes under high pressure, as well as the influence of pressure on mesophase formation is considered.

INTRODUCTION

Linear poly(diethylsiloxane) (PDES) and poly(dipropylsiloxane) (PDPS) do not contain classical mesogenic groups in their macromolecules. However, under proper conditions they are able to form a thermotropic mesophase and this has attracted the attention of many researchers to these polymers. Lee et al. [1] were the first who published information about the phase transitions in PDES and PDPS. Later (in 1975) Beatty, Pochan, Karasz, and co-workers described the high-temperature phase of PDES in terms of "liquid crystalline" and "viscous crystalline" polymers [2–6].

Papkov and co-workers [7, 8] showed that linear PDES may exist in two high temperature polymorphic modifications α_2 and β_2, that melt (transform to the mesomorphic state) at 280 and 290 K, respectively. Each of these high-temperature modifications is formed from the corresponding low-temperature modification upon heating to 214 K (α_1) and to 206 K (β_1). After melting, the high-temperature modifications form the mesophase which melts over a wide temperature range from 290 to 327 K. These transitions are first order transitions.

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The ratio of α and β phases in PDES depends greatly on the conditions of crystallization and thermal prehistory [7, 9]. Thus, the observed fractions of α- or β-polymorph depend on the rate at which the sample is cooled from the mesophase. Increased cooling rates result in increasing amounts of the α-modification. Thermodynamic, structural, morphological and some other aspects of mesophase behaviour of linear and cyclolinear polyorganosiloxanes are considered in the review article [10].

Recently it was shown that the β-modification is thermodynamically more stable than the α-modification [7, 9, 11]. It is known that the previous formation of the mesophase provides conditions for a steadier crystallization process than fast crystallization from the supercooled amorphous state. From this point of view it is interesting to study the influence of pressure on the crystallization of PDES. According to recent investigations [12, 13] the mesophase in PDES disappears at pressures of 150 MPa and higher. The disappearance of the mesophase influences considerably the crystallization process and the corresponding phase transitions. We have now obtained some new data on this phenomenon. Therefore it is interesting to study PDPS under high pressure, because it is known [14] that PDPS has a wider temperature region of mesophase stability than PDES. The data on phase transitions in PDPS under pressure have not been described in the literature.

EXPERIMENTAL

PDES was obtained by ionic polymerization of hexaethylcyclotrisiloxane at appropriate temperatures with KOH as the polymerization initiator. PDES was then deactivated by washing with water. After that PDES was reprecipitated from benzene solution with methanol and carefully dried in vacuum at 353 K. A PDES sample with $MW = 5.1 \times 10^5$ g mol^{-1} was used.

PDPS was obtained by anionic polymerization of hexapropylcyclotrisiloxane in the presence of KOH under an argon flux at 115°C. The polymer obtained was fractionated at 25°C by fractional precipitation using the toluene–methanol solvent precipitation couple. Fractions were taken 24 h after reaching equilibrium conditions. The weight average molar masses of fractionated PDPS samples were measured in toluene at 25°C by means of a Fica light scattering photometer. A PDPS sample with $MW = 8.2 \times 10^4$ g mol^{-1} was used.

HIGH-PRESSURE DTA APPARATUS

The high-pressure apparatus which is described in detail elsewhere [15] is shown schematically in Fig. 1. The apparatus consists of three major components: a low-pressure cylinder with a piston unit, an intensifier shaft

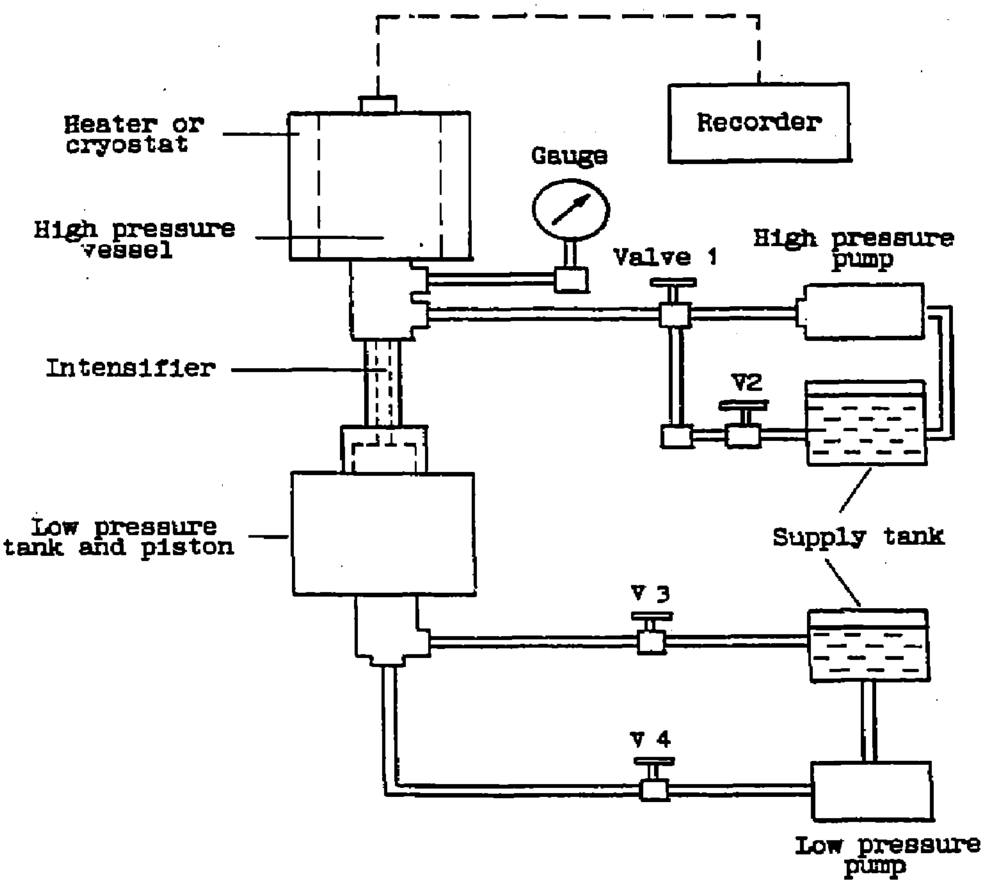

Fig. 1. Schematic diagram of the high-pressure DTA apparatus.

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 to 173 K by a special cryostat filled with liquid nitrogen, surrounding the high-pressure vessel.

The central part of the high-pressure DTA apparatus is the measuring DTA cell (Fig. 2) consisting of two differentially connected thermobatteries. The two thermobatteries are necessary because a temperature gradient exists in the high-pressure vessel. One of the batteries measures the heat flow between a sample (14) and a reference (6). The other thermobattery contains two (copper) references (9, 11) one of which (11) is placed in a position corresponding to that of the sample. This thermometer is used for 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 mm thickness).

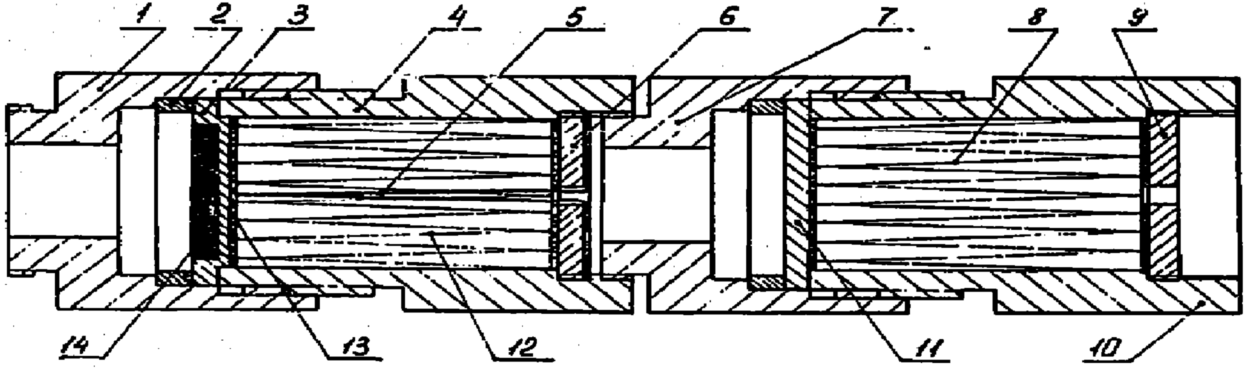

Fig. 2. Schematic diagram of the DTA cell: 1, special nuts; 2, sealed ring; 3, sample holder; 4, 10, cell body; 5, thermocouple; 6, 9, 11, reference (copper plates), 8, 12, thermobattery; 13, mica plate; 14, sample.

The sample holder provides a constant geometry of the sample. The sample is isolated from the silicon oil (PES–5) used as the pressure transmitting fluid by a sealed stainless steel membrane (80 μm thickness). A copper plate (6) is used as a reference.

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 per division. The pressure was maintained constant during the experiment with an accuracy of 1%. The DTA cell was calibrated using data [16] for the melting temperatures of In and Sn under high pressure. The calibration revealed that the temperature was measured with an accuracy of better than 1 K. The heating and cooling rates were 1.5–3.0°C min^{-1}. The mass of the sample was about 150 mg.

RESULTS AND DISCUSSION

DTA of PDES under high pressure

It has been shown [12] that the structure of PDES crystallized under pressure depends greatly on the crystallization pressure. This pressure influence is well seen in Fig. 3, where the corresponding curves, obtained upon heating at constant pressure, are represented by solid lines (the experimental scheme is shown in Fig. 4; the processes are analogous to 0–4–5–6, with 4–5–6 done at various pressures). Figure 3 shows that under atmospheric pressure the peaks B_1 and B_2 dominate, which may be explained by the low cooling rate of 1.5–3.0°C min^{-1} used in these experiments. With crystallization pressure increase, peak B_1 becomes smaller while peak A_1 becomes higher. Peak B_2 remains unchanged (except for a temperature shift) almost up to $P = 100$ MPa. We suppose that this is

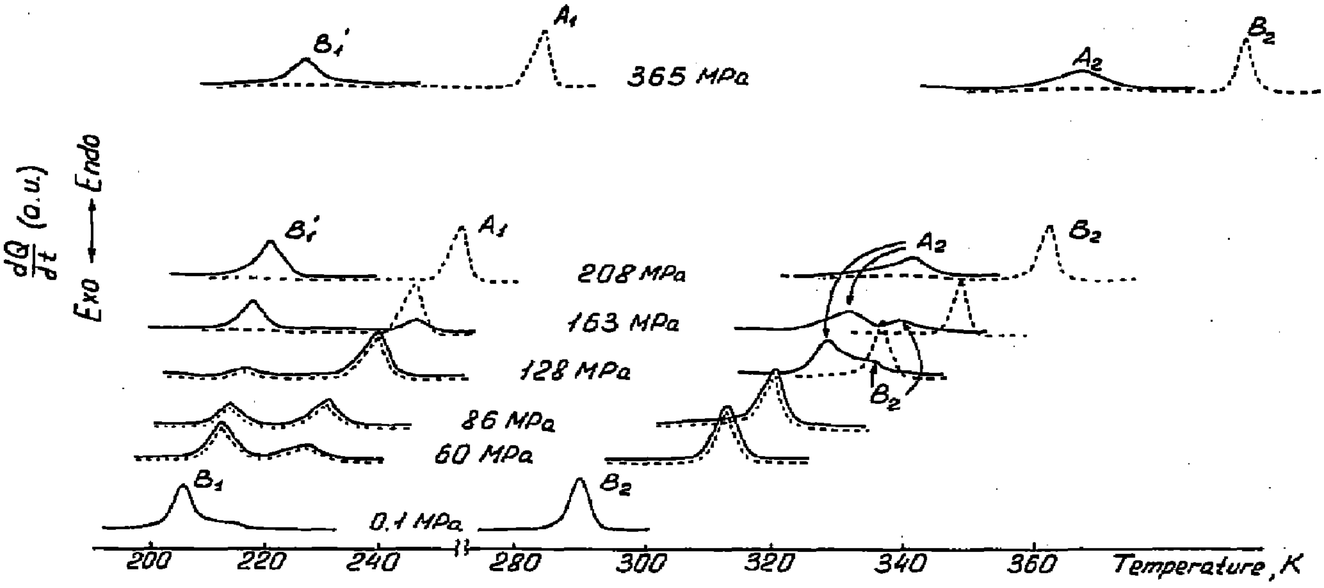

Fig. 3. DTA curves obtained upon heating different PDES samples at various pressures: samples crystallized previously at the same pressure by cooling; – – – samples crystallized previously at atmospheric pressure. The peaks indicated correspond to the following transitions: A_1, $\alpha_1 \rightarrow \alpha 2$; B_1, $\beta_1 \rightarrow \beta_2$; A_2, $\alpha_2 \rightarrow$ mesophase or melt; B_2, $\beta_2 \rightarrow$ mesophase or melt; B_1', transition of unknown modification.

connected to a possible partial change from α_2-modification into the β_2-modification (see heat effects in between 265 K and 285 K in Fig. 6). At higher pressures peak A_2 appears. As one can see in Fig. 3 peak A_1 reaches its maximum value at $P = 128$ MPa but at higher pressures begins to decrease again, while peak B_1' of unknown nature begins to grow. At $P = 200$ MPa only peaks B_1' and A_2 exist. These data are in good agreement with results [13] according to which the meosphase disappears at $P = 150$ mPa. In the absence of the mesophase the crystallization process may lead to the growth of small defect crystals (peaks B_1' and A_2).

All these data describe the behaviour of the samples crystallized under different pressures. Let us now consider the influence of pressure on the samples crystallized under atmospheric pressure. The corresponding experimental scheme is shown in Fig. 4 (process 0–1–2–3), according to which a sample was crystallized at atmospheric pressure in non-isothermal conditions (cooling rate 1.5–3.0°C min^{-1}), was then cooled to 173 K, the necessary pressure was applied and finally a heating curve was recorded at this pressure.

The DTA curves of samples heated at different pressures are indicated in Fig. 3 by dashed lines. As one can see, the thermal behaviour of the samples under pressures up to $P = 127$ MPa is identical to that of the samples

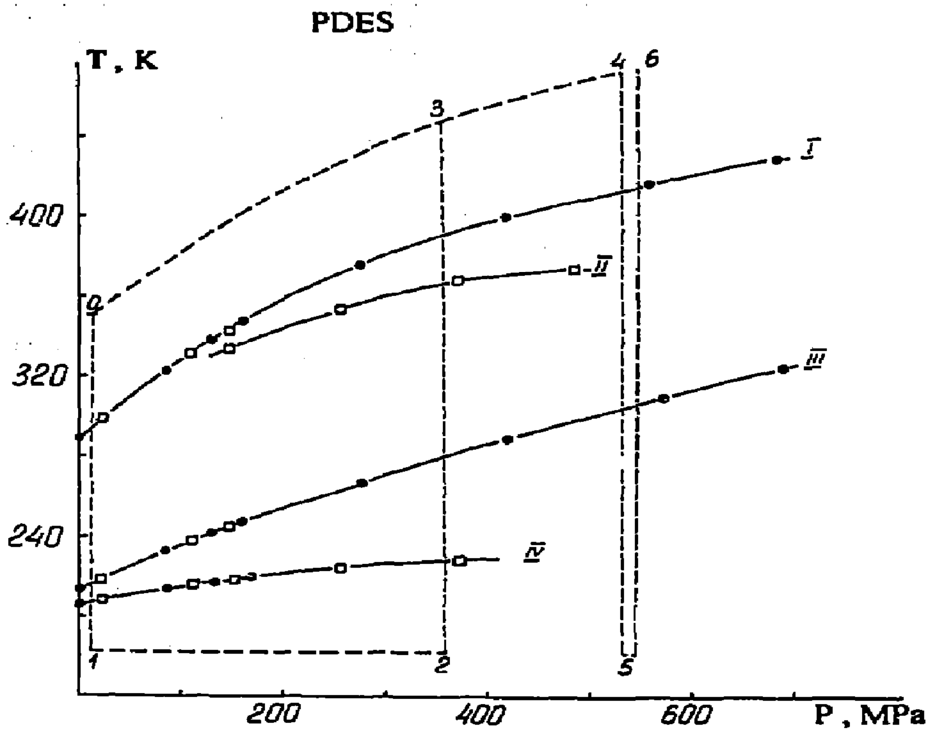

Fig. 4. Phase diagram of PDES. Pressure dependences of the transition temperatures are constructed on the basis of the data for the samples crystallized previously at atmospheric pressure (●) and for the samples crystallized previously at the same pressure (□). Solid lines correspond to the following transitions: I, $\beta_2 \rightarrow$ mesophase or melt; II, $\alpha_2 \rightarrow$ mesophase or melt; III, $\alpha_1 \rightarrow \alpha_2$; IV, $\beta_1 \rightarrow \beta_2$ and transition of defect crystals. The experimental scheme is shown by dotted lines.

crystallized under pressure, according to the first scheme. However, under high pressures some well pronounced differences appear. At $P > 127$ MPa peak A_2 does not occur, so we have only peaks A_1 and B_2. Such a picture may be observed up to 700 MPa.

A comparison of the results of these two sets of experiments allows us to draw some conclusions on the influence of the mesophase on the structure of crystallizing PDES and also on the pressure influence on mesophase formation. We may suggest the following explanation of the results described above. With increasing pressure the mesophase content decreases, which means, in turn, that the amount of α_1-crystals (or α_2-crystals at higher temperatures) increases. This corresponds to an increase of cooling rate at atmospheric pressure, which also leads to the primary formation of the α-modification. With increase of the crystallization pressure above 128 MPa (Fig. 3) peak B_1' starts to grow. We think that peak B_1' corresponds to the formation of the defect crystals, similar to that which occurs under quenching, rather than to an appearance of β_1-crystals, because in spite of the appearance of peak B_1', peak B_2 is absent. If the difference in the melting temperatures of not very perfect α-crystals and defect crystals is small, a splitting of peak A_2 into two may not be observed.

The appearance of peak B'_1 is closely related to the disappearance of the mesophase with pressure. This is supported by the experimental results obtained for the samples previously crystallized at atmospheric pressure. These samples have a higher content of the mesophase, and correspondingly a higher degree of crystallinity. For these samples peaks A_2 and B'_1 with pressure are not observed. Thus, we may assume that the mesophase disappears under pressure of about 160 MPa. Our results are in good agreement with data [13], according to which the mesophase disappears when $P = 150$ MPa. It is interesting that the redistribution of the intensity and area of B_1 to A_1 peaks with pressure takes place both for the samples crystallized under high pressure and for the samples crystallized at atmospheric pressure. The latter seems to mean that this process is not connected to the influence of pressure during cooling to low temperatures, but reflects the reaction of the material on the application of pressure during heating from temperatures below 200 K.

In order to identify the nature of peak A_1 under pressure the experiments schematically shown in Fig. 5 were carried out. During the first run PDES was cooled at atmospheric pressure to 183 K (process 0–3), pressure of 400 MPa was applied, and after that the sample was heated to 303 K (process 3–4–6) and then cooled to 233 K simultaneously with the decrease of pressure down to atmospheric pressure equidistant to the curve II (process 6–1), after which the sample was cooled to 183 K (process 1–3). After such treatment the heating trace at atmospheric pressure was recorded (process 3–0). The DTA curve of this sample upon heating is shown in Fig. 6 (curve 1). It is seen that at low temperatures peak A_1 (which at atmospheric pressure corresponds to the $\alpha_1 \rightarrow \alpha_2$ transition) dominates.

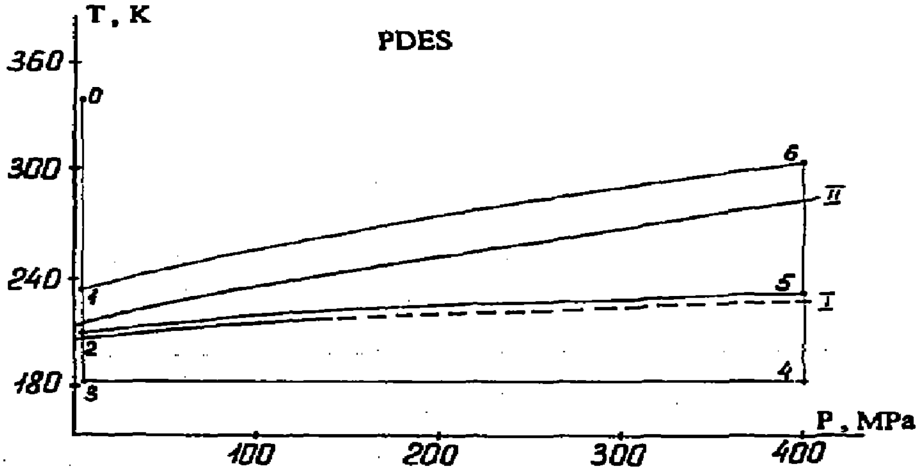

Fig 5. Experimental scheme for the detection of the $\beta_1 \rightarrow \alpha_1$ transition: I, $\beta_1 \rightarrow \beta_2$ and transition of unknown modification; II, $\alpha_1 \rightarrow \alpha_2$.

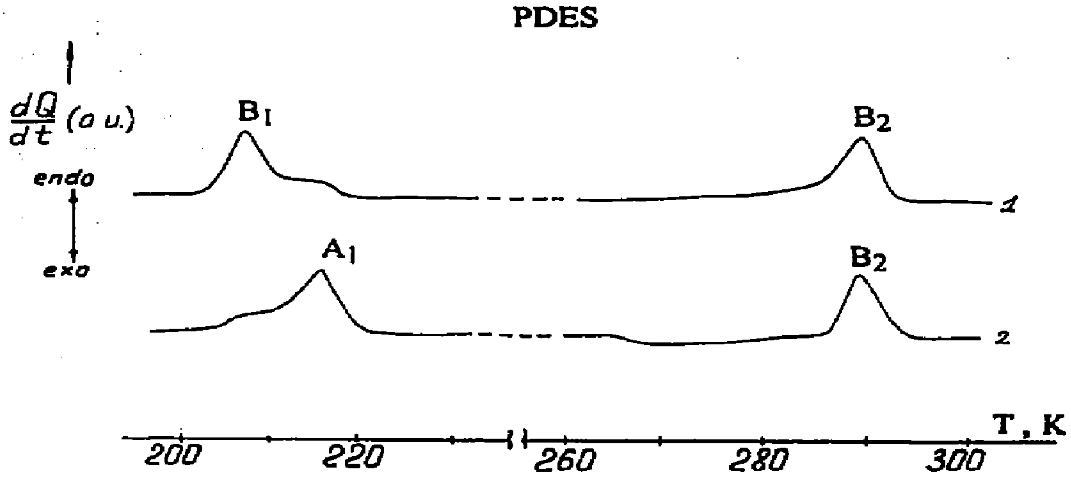

Fig. 6. DTA curves at atmospheric pressure of PDES samples with different pre-histories: 1. sample crystallized previously at atmospheric pressure: 2. sample treated by 400 MPa pressure at 183 K.

To determine whether the appearance of peak A_1 under pressure is a result of the applied pressure at 183 K or whether this peak occurs during heating under pressure, two more experiments were carried out. In the first, a pressure of 400 MPa was applied during 1 h (process 3–4) to PDES cooled to 183 K under atmospheric pressure (process 0–3). Later the pressure was slowly decreased to atmospheric (process 4–3) and the heating curve under atmospheric pressure was recorded (process 3–0). This curve does not differ from that obtained in the previous experiment (Fig. 6, curve 1). Thus, application of the 400 MPa pressure at $T = 183$ K results in the appearance of peak A_1, while peak B_1 disappears. One might expect that peak A_2 would follow the A_1 peak; however, only peak B_2 was observed in both the runs. As follows from Fig. 3, a similar picture is observed during heating under pressure of the samples crystallized under atmospheric pressure.

The next experiment was carried out in order to determine the temperatures under which pressure application leads to transformation of the β_1- to the α_1-modification. The sample was cooled under atmospheric pressure to $T = 210$ K (process 0–2), heated to 233 K (process 2–5), the pressure begin increased equidistant to curve I of Fig. 5. Then in 20 min the pressure and temperature were reduced in a similar manner to 210 K under atmospheric pressure (process 5–2). After that the sample was cooled to $T = 183$ K (process 2–3) and the heating curve was recorded under atmospheric pressure (process 3–0). This curve did not show any changes in comparison with the heating curve of the sample crystallized under atmospheric pressure (Fig. 6, curve 2).

Thus, on the basis of the obtained data, one may conclude that if pressure is applied at temperatures below the $\beta_1 \rightarrow \beta_2$ transition it leads to the transformation of the β_1- into α_1-modification. Under heating the α_1-modification transforms into the α_2-modification when $T = T(A_1)$. At higher temperatures the α_2-modification transforms into the β_2-modification. Finally, the β_2-modification melts when $T = T(B_2)$. Pressure dependences of the transition temperatures based on data for the samples previously crystallized at atmospheric pressure and for the samples previously crystallized at the same pressure are shown in Fig. 4.

We note that the picture observed for the phase transitions in PDES crystallized under pressure is similar to that observed in ref. 7 for PDEs with various degrees of transformation to the mesophase state at atmospheric pressure. Briefly the latter experiments comprised cooling of PDES from the melt down to various temperatures T_i (Fig. 7) corresponding to the formation of different mesophase contents (φ). These samples were quenched to 100 K. DSC heating traces for the samples with different

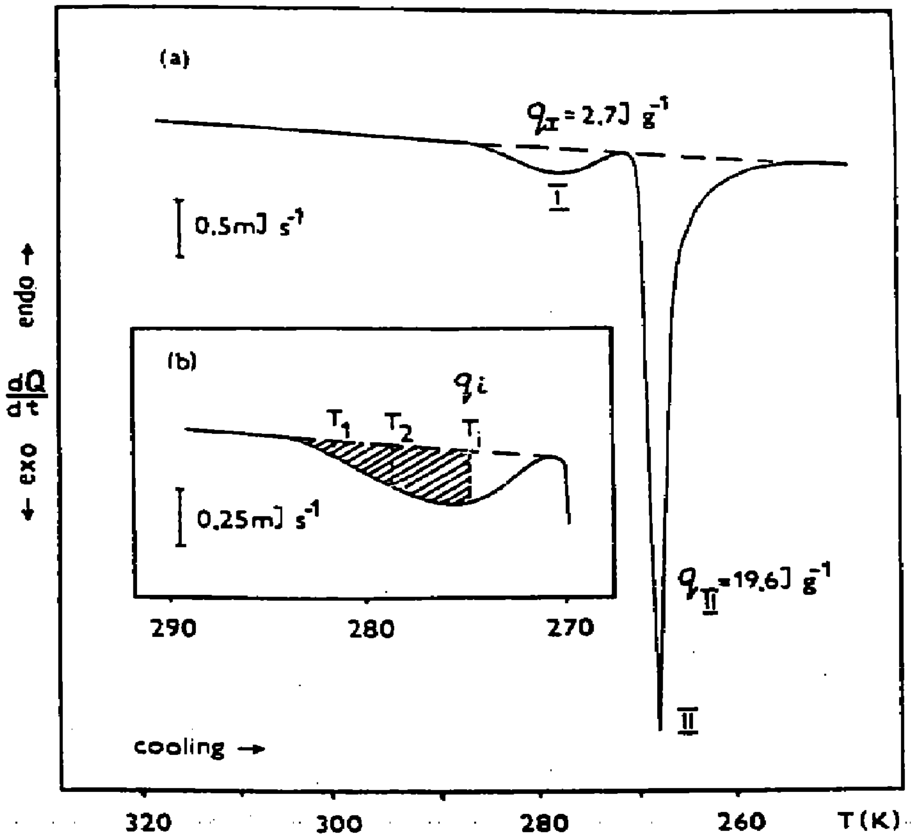

Fig. 7. (a) DSC traces for PDEs cooled at the rate of 2.5°C min^{-1} showing the successive stages of mesophase formation (peak I) and crystallization (peak II). (b) An enlarged view of the meosphase formation peak to illustrate the method of determining the degree of conversion to mesophase $\varphi = q_i/q(\mathrm{I})$ achieved at a temperature T_i, from which the sample had been crystallized by rapid cooling [7].

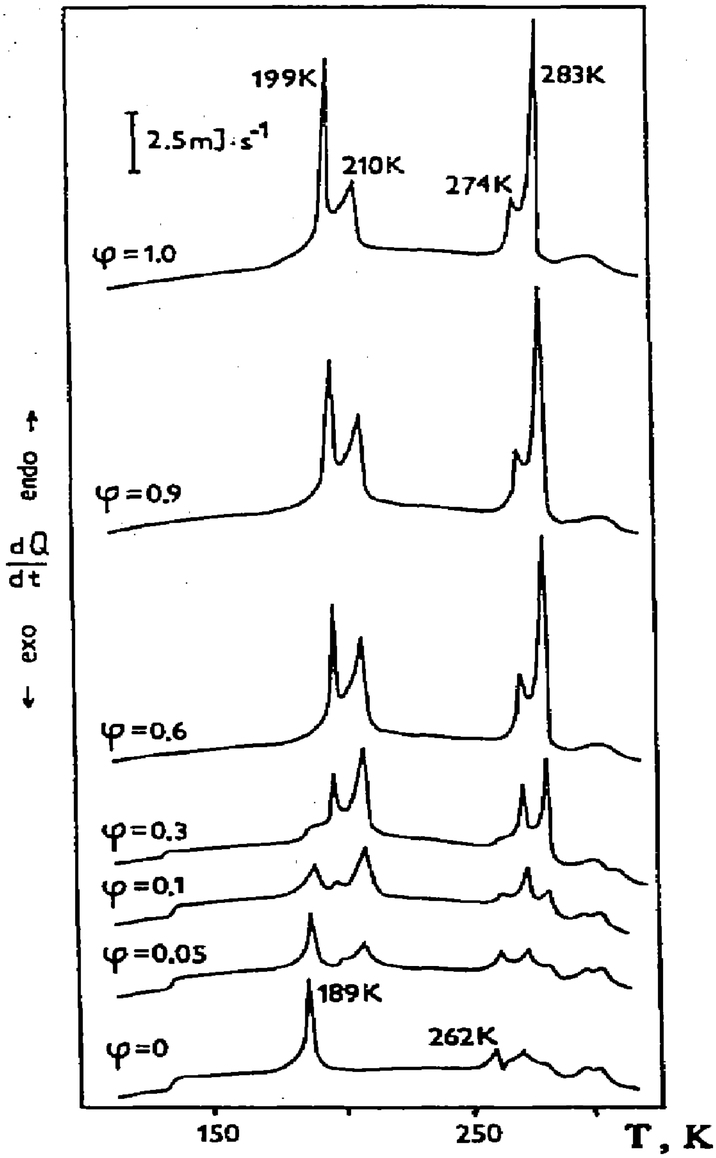

Fig. 8. The complete DSC traces of PDES samples crystallized at different degrees of conversion to mesophase φ by cooling at the rate of 320°C min^{-1}. Heating rate, 10°C min^{-1} [7].

degrees of mesophase formation are shown in Fig. 8. It is seen that with the decrease of φ from 1 to 0.6 transformation of peak B_1 to peak A_1 occurs; however an analogous transformation of peak B_2 to peak A_2 is not observed. At $\varphi < 0.6$ an increase of the intensity of peak A_2 was observed. When $\varphi < 0.3$ an additional low-temperature peak at $T^* = 189$ K connected with the formation of small defect crystals, occurred.

Our results obtained for the samples crystallized under pressure are analogous to these results. In our case the crystallization pressure has the meaning of T_i. According to Fig. 3 $\varphi = 0.05$ corresponds to $P = 163$ MPa, while $\varphi = 0.6$ must correspond to $P = 68$ mPa, which means that with increase of crystallization pressure the mesophase content decreases, which leads to the appearance of the α-modification. Without any mesophase only the small defect crystals with small heat effects occur, which makes it difficult to estimate heat effects when $P > 400$ MPa.

DTA of PDPS under high pressure

Recently phase transitions in PDPS at atmospheric pressure have been studied [14, 17]. According to ref. 14, the T_g of PDPS is 164 K, the crystal I → crystal II phase transition takes place at 218 K, melting of PDPS occurs at 331 K, and the transition from the mesomorphic state to the isotropic melt occurs at about 479 K. We have previously studied the influence of the mesophase on other phase transitions in PDPS [17]. On the basis of these experimental data it was suggested that two low-temperature crystal modifications may exist in PDPS, each of which may transform to the corresponding high-temperature modification. A more detailed consideration allows us to assume that the presence of two low-temperature (and corresponding high-temperature) peaks may be connected with the fact that one part of the material is crystallized via mesophase formation, while the other part is crystallized directly from the melt. It is obvious that crystallites formed from the melt are less perfect and possess lower transition temperatures.

It is almost impossible to obtain amorphous PDPS by quenching of the melt, because the mesophase exists in a rather wide temperature range. In this connection it seems very interesting to study the crystallization of PDPS under pressure. At present such data are absent from the literature.

Figure 9 shows the heating curves at atmsopheric pressure of the initial PDPS (curve 1) and PDPS previously crystallized under pressure (curve 2). The initial PDPS was crystallized at atmospheric pressure from isotropic melt (500 K) with low cooling rate (1.5–3.0°C min^{-1}). The thermal history of the second sample was the following: pressure of 686 MPa was applied to the initial sample at room temperature, it was heated to 575 K and was held during 20 min at this pressure. Then the sample was cooled at constant pressure to 230 K with a rate of 1.5–3.0°C min^{-1}. It is seen that for the second sample the second melting peak at 326.7 K occurs, while the peak with $T = 340.7$ K does not disappear but becomes smaller. This allows us to conclude that the mesophase in PDPS does not disappear with the pressure application up to $P = 700$ MPa.

The fact that the transition temperatures for samples 1 and 2 almost coincide allows to consider them as the temperatures of the phase transitions. The pressure dependences of the solid–solid transition (curve a) and melting (curve b) in PDPS are shown in Fig. 10.

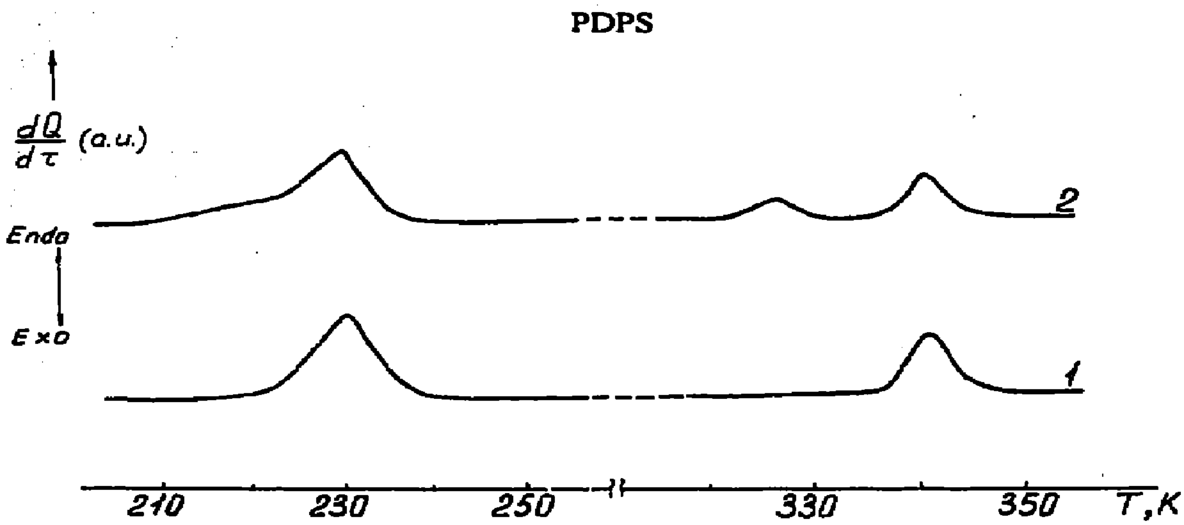

Fig. 9. DTA curves of PDPS samples (heated at atmospheric pressure) crystallized previously at atmospheric pressure (1) and the same sample pressure treated (2) by the following procedure: 686 MPa pressure was applied at room temperature, then the sample was heated to 575 K and 20 min later it was cooled down to 230 K at the same pressure, the pressure subsequently being decreased to atmospheric.

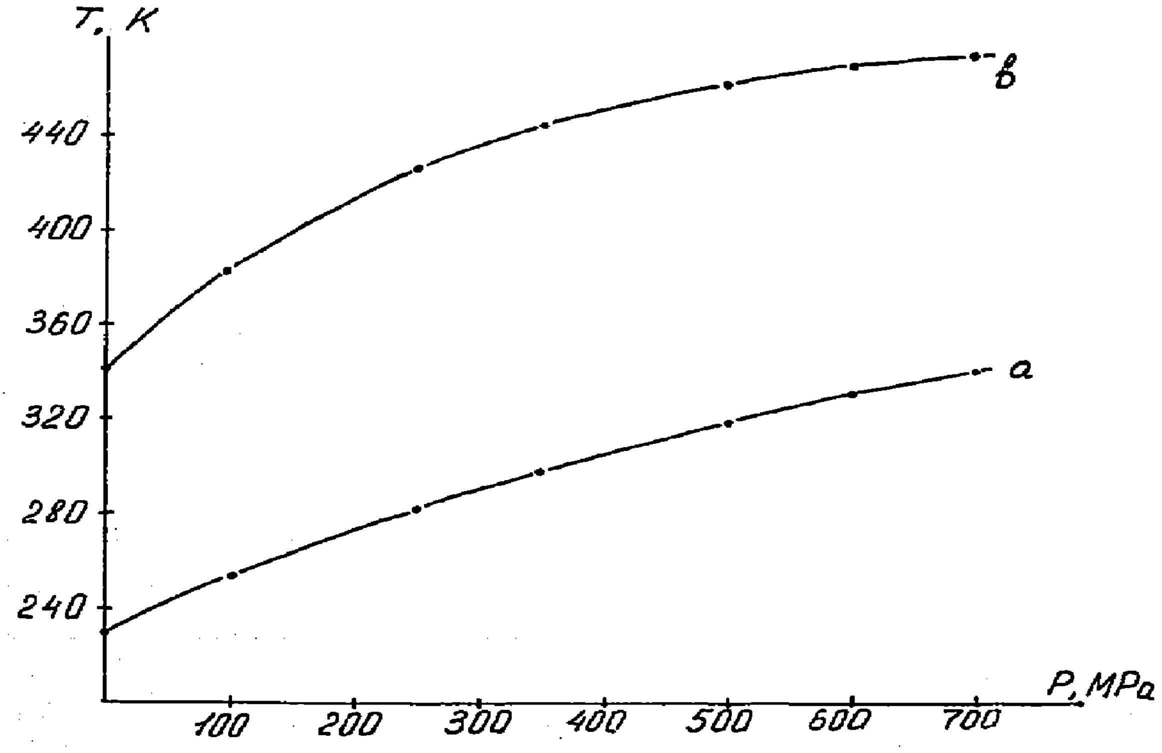

Fig. 10. Pressure dependences of transition temperatures of PDPS: curve a, crystal I → crystal II; curve b, crystal II → mesophase or melt.

Thus, the application of pressure at temperatures below the temperature of the lower polymorphic transition in PDES leads to transformation of the β_1-modification into the α_1-modification. Under heating the α_1-modification transforms into the α_2-modification with the subsequent transformation of the α_2-modification into the β_2-modification.

The difference in the temperature interval of the mesophase stability in PDES and PDPS results in a considerable change in their crystallization behaviour. The rather small temperature interval of the mesophase in PDES decreases with pressure and at some pressure the mesophase disappears, which slows down the crystallization rate of PDES. As a result it is possible to obtain PDES in a practically amorphous state. However the interval of the mesophase stability in PDPS under pressure is probably increased, and therefore it cannot be transformed to the completely amorphous state.

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