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PVT-studies on polymeric and oligomeric compounds

I. Linear diblock perfluoroalkyl alkanes

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SUMMARY

The pressure dependence of transitions in perfluorododecyloctane - *F12H8* - and in perfluorododecylhexadecane - *F12H16* - has been measured from 10 to 200 MPa, from room temperature up to 220° C. The two transitions within this range - the transition of the alkane block from crystalline to mesomorphic, T_{ss} , and the transition to melt, T_m - exhibit different pressure coefficients. As a pecularity, for *F12H16* T_{ss} and T_m superimpose at 10 MPa, in accordance to atmospheric pressure DSC data. Pressure dependences of transitions are given as well as their melting enthalpies.

It has been shown, that PVT-measurements open up the possibility to gain new insight into the nature of certain phase transitions. A transition formerly to be thought of as a melting transition, turned out to be actually composed of two contributions, one due to disordering and the other due to melting.

1. INTRODUCTION

Oligomeric and polymeric diblock molecules exhibit strong scientific and technological interest as surface active components which may emulsify thermodynamically incompatible components. The tendency of the blocks of such diblock systems for phase separation is increasing with their length as well as with their mutual incompatibility. Diblock molecules of fluorocarbon and hydrocarbon blocks show up phase separation even with blocks of minor length, because of their pronounced repulsion. They exhibit interesting thermal properties. Within the temperature range of -130°C to 100°C, they undergo pronounced phase transitions - a melting transition and possibly one or two solid-solid transitions[1,2].

However, quite no knowledge exists up to now concerning pressure dependence of phase transitions of such blocks. This makes PVT studies on such compounds attractive, before the background of their applicational relevance, e. g. for processing or reactive blending of polymers.

The present paper relates to the Ph. D. thesis of J. Höpken[1) , in which a systematic investigation of linear perfluoroalkyl alkanes is given. Using differential scanning calorimetry (DSC) Höpken - and partly Russel et al.[2) before him - investigated the phase transitions that diblock molecules of the type $F\text{-}(CF_2)_n\text{-}(CH_2)_m\text{-}H$ undergo.

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For n=12 it was observed that their number and temperature depend on m: For 4 ≤ m≤ 14 one can observe one solid-solid transition in the temperature range between 40°C and 90°C[1,2], and for 4 ≤ m ≤ 12 there is an additional one in the range between -126°C and -57°C[1]. The melting points range between 71°C and 93°C[1,2].

For m ≥ 16 the solid-solid transitions vanish, and only the melting transition remains. There is a marked difference, however, to the melting transitions of the shorter molecules: The heat of fusion is increased by an appreciable amount.

The structure of the occuring phases has been investigated as well[1,2]. While the origin of the lower solid-solid transition remains unknown, the other one is a transition from a crystalline to a mesomorphic state which is mainly due to a disordering of the hydrocarbon chains; they are already in a liquid-like state, whereas the fluorocarbon chains remain ordered. On the other hand, the transition from the mesomorphic to the molten state predominantly is caused by the fluorocarbon chains. The mesomorphic state has been identified as a smectic liquid crystalline state.

In this paper we supplement some of the results stated above by PVT-measurements (for m = 8 and m = 16). Since PVT-measurements only can be performed above room temperature, we confine ourselves to the higher solid-solid and to the melting transition.

2. EXPERIMENTAL

Measurements of the pressure dependence of specific volume were performed with a Gnomix-PVT-apparatus (Boulder, Col. USA) which basically consists of a sample cell containing about 1g of sample, and mercury as a confining fluid. Flexible bellows close off one end of the cell, and the movement of the bellows on changing temperature or pressure is used to calculate the volume change of the sample. The Gnomix apparatus permits to perform PVT-measurements in the temperature range between room temperature and 400°C, and pressures ranging from 10 MPa to 200 MPa. Details are described in the literature[3].

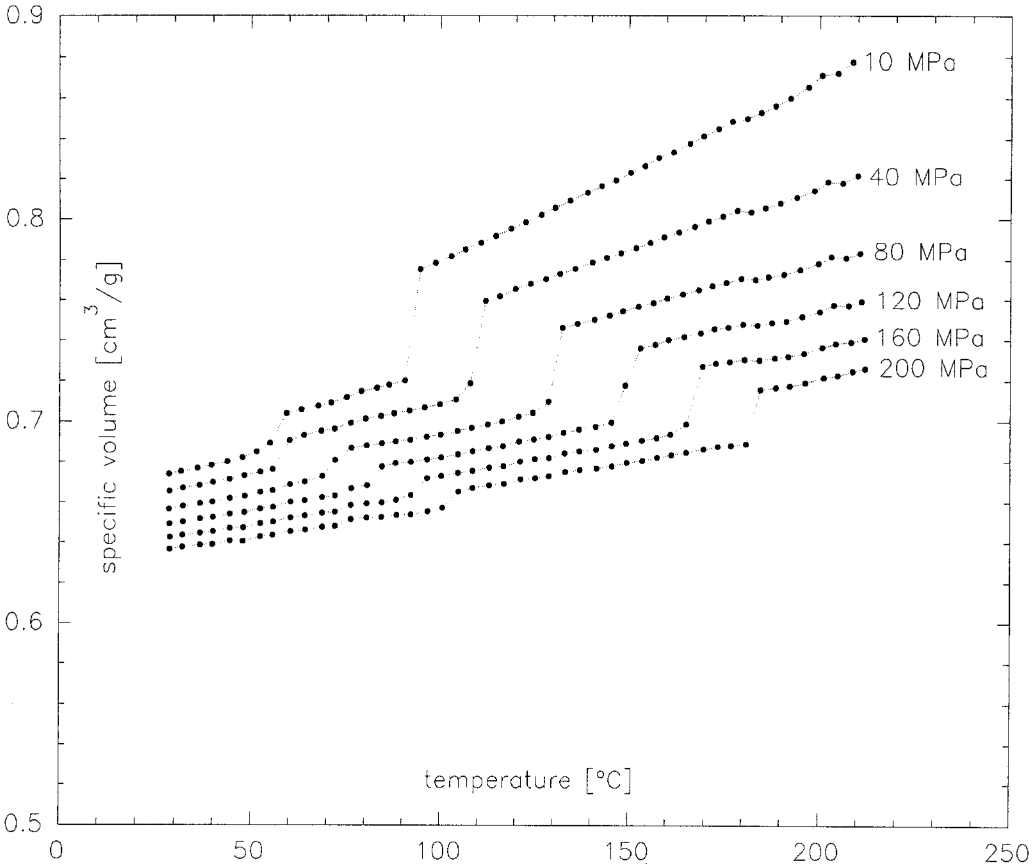
The PVT-measurements were performed in the so-called isothermal mode, i.e. the sample was held at a certain temperature, and the pressure was raised from 10 MPa up to 200 MPa in steps of 10 MPa. The volume changes corresponding to those pressures were recorded. Subsequently this procedure was repeated at other temperatures.

The samples were synthesized by J. Höpken, University of Twente/NL. Before loading into the sample cell they were compressed at RT in vacuo at 20 MPa pressure.

3. RESULTS AND DISCUSSION

3.1 MEASUREMENTS OF PERFLUORODODECYLOCTANE

Fig. 1 shows a plot of the specific volume of $F\text{-}(CF_2)_{12}\text{-}(CH_2)_8\text{-}H$ (*F12H8*) versus temperature at various pressures. One can clearly see two distinct transitions, the first one being the solid-solid transition, the second - much stronger - one the melting transition. On raising the pressure, these transitions move towards higher temperatures, however at different rates; they drift further apart.



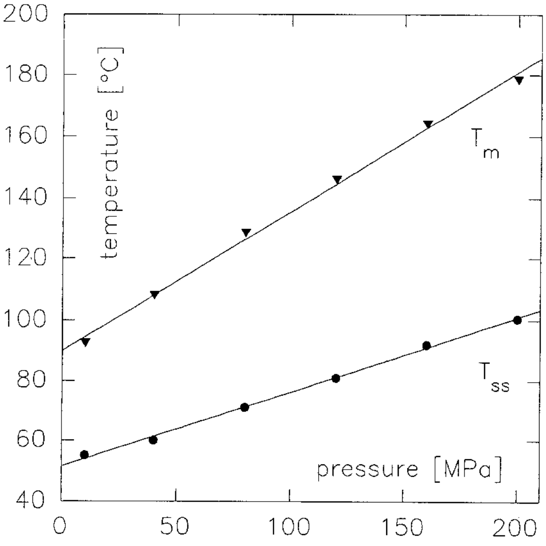


Figure 1: Specific volumes of perfluorododecyloctane vs. temperature at indicated pressures

Figure 2: Pressure dependence of the transition temperatures, T_{ss} and T_m, of perfluorododecyloctane

Fig. 2 shows the dependences of the transition temperatures on pressure (phase diagram). They can be well described by straight lines. Therefore, - in order to estimate the transition temperatures at zero pressure - we made a linear regression through the data (solid lines in Fig. 2). Extrapolation yields for the solid-solid transition T_{ss} = 51°C, compared to 56°C of reference 1 and 51°C of reference 2. For the melting transition we obtained T_m = 90°C compared to 88°C and 82°C of reference 1 and 2 respectively.

The rate of change of the transition temperatures differs almost by a factor of two for the two transitions, and is given by:

$$(1) \qquad \frac{dT_{ss}}{dp} = 2.47 * 10^{-7} \frac{°C}{Pa} \qquad \frac{dT_m}{dp} = 4.55 * 10^{-7} \frac{°C}{Pa}$$

3.2 MEASUREMENTS OF PERFLUORODODECYLHEXADECANE

The temperature dependence of the specific volume of $F\text{-}(CF_2)_{12}\text{-}(CH_2)_{16}\text{-}H$ (*F12H16*) is shown in Fig. 3. For higher pressures the curves look similar to those of Fig. 1, but the two transitions are closer together. They show the same principle behavior upon increasing the pressure, i. e. the transitions move to higher temperatures and drift further apart. Conversely, on lowering the pressure, they approach each other until they coincide. This explains the sudden increase in the heat of fusion in going from $m < 16$ to $m \geq 16$. One is not dealing with one transition as was thought before, but in fact there are two transitions. The phase diagram belonging to Fig. 3 is shown in Fig. 4.

Again the dependences are well described by straight lines. Extrapolation to zero pressure yields T_{ss}= 94°C and T_m= 97°C. Considering the errors in determining the transition temperatures, one might take these temperatures as equal, or at least one can say they are too close to be resolved by DSC-measurements, so they just yield one transition (94° C).

The rate of change of the transition temperatures with pressure is similar as in the case of m = 8, namely:

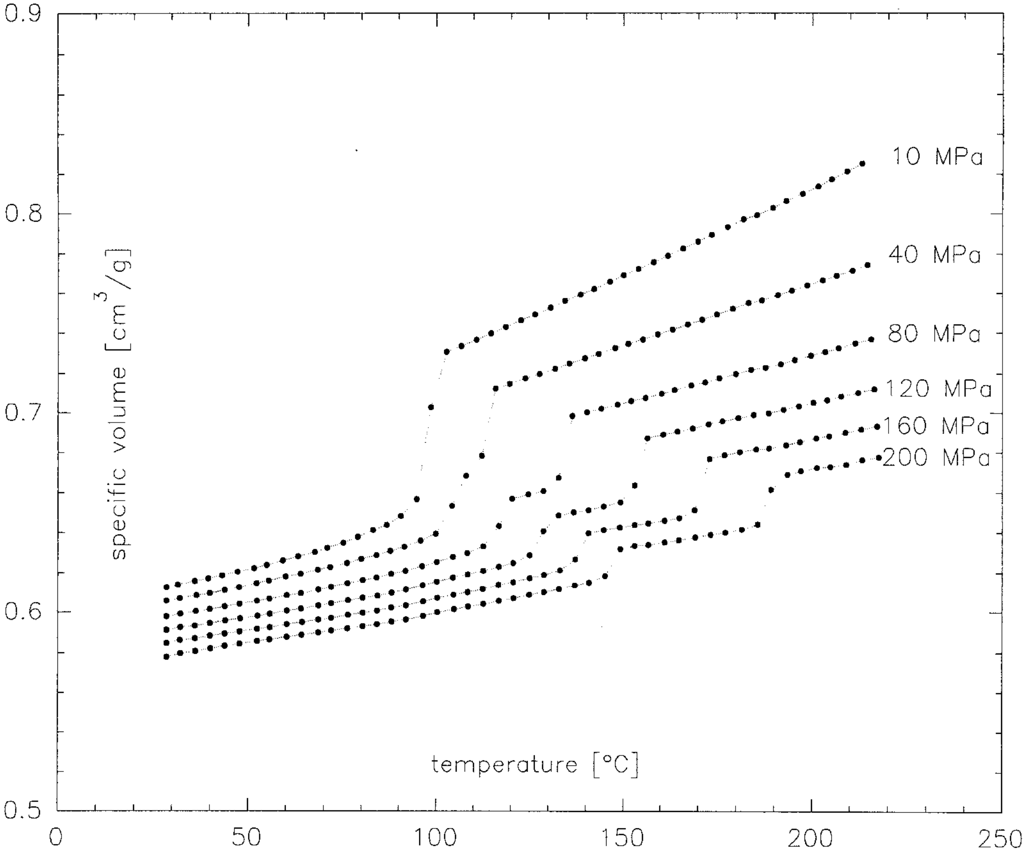
$$(2) \qquad \frac{dT_{ss}}{dp} = 2.55 * 10^{-7} \frac{°C}{Pa} \qquad \frac{dT_m}{dp} = 4.28 * 10^{-7} \frac{°C}{Pa}$$

3.3 ESTIMATION OF THE TRANSITION ENTHALPIES

For first-order transitions it is in principle possible from the knowledge of the phase diagram and the volume change at the transition, to determine the enthalpy of the corresponding transition via the Clausius-Clapeyron equation:

$$(3) \qquad \frac{dp}{dT} = \frac{\Delta H}{T \Delta v}$$

dp/dT is the slope of the curve in the p-T phase diagram (i. e. the reciprocal of (1) and (2) respectively), ΔH and T [°K] are respective transition enthalpy and temperature, and Δv the volume change.



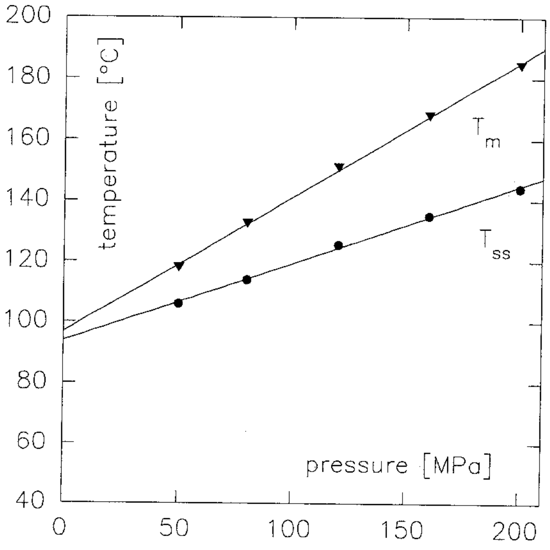


Figure 3: Specific volumes of perfluorododecylhexadecane vs. temperature at indicated pressures

Figure 4: Pressure dependence of the transition temperatures, T_{ss} and T_m, of perfluorododecylhexadecane

However it turned out, that the enthalpies obtained from (3) deviate appreciably from those obtained by DSC. At this time no unequivocal interpretation of this systematical deviation was possible.

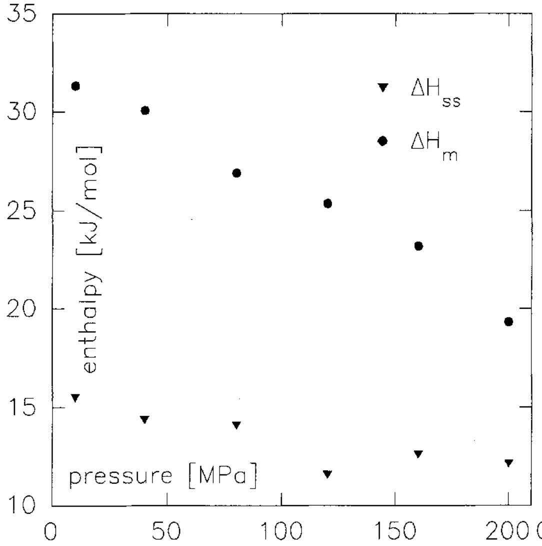


Figure 5: Transition enthalpies for *F12H8* as a function of pressure

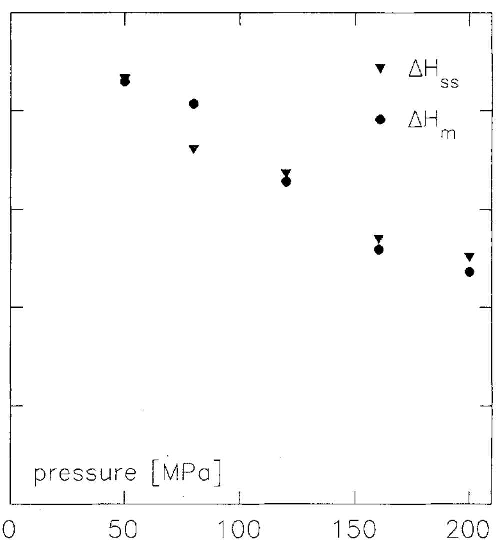


Figure 6: Transition enthalpies for *F12H16* as a function of pressure

The enthalpies as a function of pressure calculated for $F\text{-}(CF_2)_{12}\text{-}(CH_2)_8\text{-}H$ are shown in Fig. 5. They decrease with increasing pressure because the mobile phases become more ordered and more dense, consequently. Again, the dependences can fairly well be described by straight lines, and extrapolation to zero pressure yields ΔH_{ss} = 15.2 kJ/mol and ΔH_m = 32.2 kJ/mol. This strongly deviates from DSC-results: Reference 1 reports ΔH_{ss} = 6.4 kJ/mol, ΔH_m = 23.7 kJ/mol, and reference 2 yields ΔH_{ss} = 5.6 kJ/mol and ΔH_m = 21.9 kJ/mol.

The analogue for $F\text{-}(CF_2)_{12}\text{-}(CH_2)_{16}\text{-}H$ is shown in Fig. 6. Here we obtain ΔH_{ss} = 35.2 kJ/mol and ΔH_m = 33.6 kJ/mol, i. e. for the overall transition 68.8 kJ/mol. This again strongly deviates from DSC data, which give 41.8 kJ/mol(1) and 43.1 kJ/mol(2), respectively. One can state, however, that both transitions contribute about equal parts to the overall transition.

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