

High Pressure Dilatometry of *n*-Perfluoroicosane

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(Received January 31, 1992)

ABSTRACT: The high pressure dilatometry of *n*-perfluoroicosane (C₂₀F₄₂) was carried out in the isothermal compressing process at 296 K and isobaric heating processes at various pressures up to 500 MPa. The dilatometry in the isothermal compressing process at 296 K showed the possibility that there are two second-order transition points at about 200 and 250 MPa, which could not be detected by high pressure differential thermal analysis carried out in the previous work. From the data of the dilatometry in the isobaric heating processes, the thermodynamic parameters, enthalpy change ΔH and entropy one ΔS at two crystal-crystal transitions under high pressure, denoted by Tr3 and Tr4, were calculated based on Clausius-Clapeyron's equation. The entropy change per one mole of repeating units, ΔS_e , in the pressure region between 400 and 500 MPa is 1.5—1.8 and 0.7—0.9 JK⁻¹ mol⁻¹ at Tr3 and Tr4, respectively, which indicate that moderate rotation of molecular chains starts at Tr3 and then becomes more active at Tr4 in the heating process under high pressure.

KEY WORDS *n*-Perfluoroicosane / C₂₀F₄₂ / Polytetrafluoroethylene /
n-Alkane / Rotator Phase / Phase Transition / Dynamic Disorder / High
Pressure / Dilatometry /

In the previous work,¹ the authors studied the phase transitions of *n*-perfluoroalkanes, *i.e.*, polytetrafluoroethylene (PTFE) oligomers by high pressure differential thermal analysis (DTA) and first determined their phase diagrams. It was shown that *n*-perfluoroicosane (C₂₀F₄₂) and *n*-perfluorotetracosane (C₂₄F₅₀) have interesting phase diagrams quite different from that of PTFE.

The phase diagram of C₂₀F₄₂ is shown in Figure 1. Below about 300 MPa, a sequence of crystal-crystal transitions denoted by Tr1 and Tr2 occurs in the isobaric heating process. In the pressure region between about 300 and 400 MPa, there are two cases of crystal-crystal transitions, one case in which a pair of Tr3 and

Tr4 occurs (→Tr3→Tr4→) and the other case in which only Tr5 occurs (→Tr5→). Above about 400 MPa, only →Tr3→Tr4→ occurs. The phase diagram of C₂₄F₅₀ is also similar to that of C₂₀F₄₂ except the differences of transition points.

Although the phase diagrams of these *n*-perfluoroalkanes were determined by high pressure DTA, the thermodynamic parameters at transitions under high pressure, such as volume change Δv , enthalpy one ΔH , and entropy one ΔS could not be obtained only from the data. These thermodynamic parameters give information as to the type of dynamic disorder² activated at the transitions in the heating process. In this work, C₂₀F₄₂

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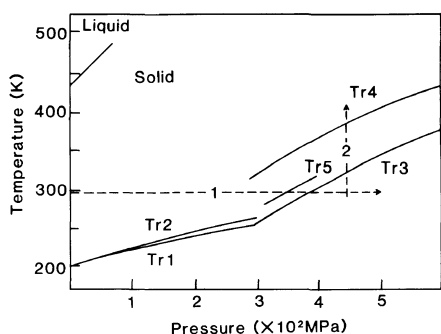


Figure 1. Phase diagram of $C_{20}F_{42}$, determined by high pressure DTA.¹ The dotted lines 1 and 2 show paths along which dilatometry was carried out.

whose detailed mechanism of phase transition had been clarified at atmospheric pressure,³ was studied by high pressure dilatometry. Its thermodynamic parameters at Tr3 and Tr4 were determined. From these results, the dynamic disorders activated at these transitions are discussed.

EXPERIMENTAL

$C_{20}F_{42}$ used in this work was the same high pure sample as that used for high pressure DTA.¹ Its high pressure dilatometry was carried out using high pressure dilatometry apparatus described in detail elsewhere.⁴ Figure 2 shows the schematic diagram of its main parts. The total volume change of the sample and liquid medium encapsulated together in the bellows cell, with temperature and pressure, was converted to the displacement of the steel wire and detected by the differential transformer. The hydrostatic pressure in the high pressure vessels was measured with a calibrated manganin manometer with an accuracy of ± 1 MPa, and the temperature of the sample was monitored with an Alumel–Chromel thermocouple placed near the cell.

The sample of $C_{20}F_{42}$ was melt-crystallized from the original one at atmospheric pressure and annealed at a temperature close to its melting point (437 K) in a vacuum in order to

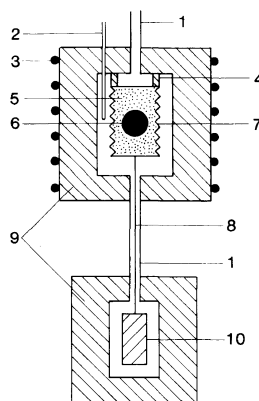


Figure 2. Schematic picture of a high pressure dilatometry apparatus. 1, high pressure pipe; 2, sheathed Alumel–Chromel thermocouple; 3, sheathed heater; 4, supporting part; 5, liquid medium (silicone oil); 6, sample; 7, bellows cell; 8, steel wire; 9, high pressure vessel; 10, differential transformer.

remove the air in crystal voids. By this annealing treatment, paths linking the voids to outer space around the crystals were made. The sample was set in the cell and the excess space including the crystal voids was filled with silicone oil (Toshiba TSF451-10, 10cSt) used as the liquid medium. The space around the cell and differential transformer in the high pressure vessels was also filled with the same silicone oil (pressure transmitting fluid).

The total volume change of the sample and silicone oil in the cell was examined in the isothermal compressing process at 296 K (path 1 in Figure 1) and in the isobaric heating ones at various pressures (for example, path 2 in the same figure). The measurement below room temperature could not be carried out because the used high pressure vessel cannot endure high pressure in the low temperature range. The volume change of the sample in each process was obtained later by deducting that of the silicone oil in the bellows cell from the total one. The volume change of the silicone oil in the process had been previously obtained from the measurement as to the silicone oil alone in the same process.

The specific volume of $C_{20}F_{42}$ at 296 K and

atmospheric pressure was calculated using lattice parameters obtained by X-ray measurement on the assumption that the purity of the sample was 100%.

RESULTS AND DISCUSSION

Figure 3 shows the pressure change of the specific volume of $C_{20}F_{42}$, measured in the isothermal compressing process at 296 K (path 1 in Figure 1). It was measured at 20 MPa intervals because its continuous change with pressure could not be done in the used apparatus. The specific volume and compressibility at 296 K and atmospheric pressure are $0.4752 \text{ cm}^3 \text{ g}^{-1}$ and $2.125 \times 10^{-10} \text{ Pa}^{-1}$, respectively.

The line expressing the pressure change of specific volume bends at about 200 and

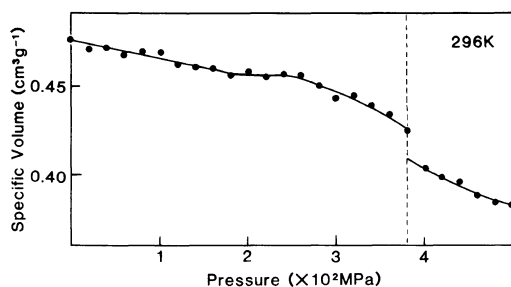


Figure 3. Pressure change of the specific volume of $C_{20}F_{42}$ at 296 K. It was measured at 20 MPa intervals in the isothermal compressing process along path 1 in Figure 1.

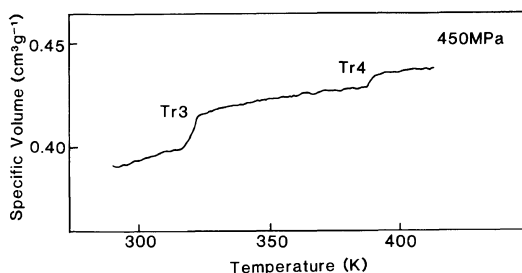


Figure 4. Temperature change of the specific volume of $C_{20}F_{42}$ at 450 MPa. It was measured continuously at a very slow rate in the isobaric heating process along path 2 in Figure 1.

250 MPa. Compressibility becomes very small value at about 200 MPa and increases again at about 250 MPa with pressure. This indicates the possibility that second order transitions which could not be detected by high pressure DTA¹ occur at these pressures. The authors carried out high pressure X-ray measurement on the same sample, and the paper that reports the results is in preparation.⁵ In this measurement, two second-order transition points were also recognized in the same pressure region. At 380 MPa that corresponds to Tr3, the specific volume decreases discontinuously. On the other hand, no change occurs at 344 MPa that corresponds to Tr5, suggesting that in this isothermal compressing process, Tr3 occurs but Tr5 does not.

Figure 4 shows the temperature change of the specific volume of $C_{20}F_{42}$, measured in the isobaric heating process at 450 MPa (path 2 in Figure 1). This measurement was carried out continuously at a very slow rate. The specific volume increases with temperature and changes discontinuously at two temperatures which correspond to Tr3 and Tr4. The volume change at Tr3 is much larger than that at Tr4. The coefficient of cubical expansion decreases with temperature as $9.22 \times 10^{-4} \text{ K}^{-1}$ below Tr3, $4.83 \times 10^{-4} \text{ K}^{-1}$ between Tr3 and Tr4, and $3.50 \times 10^{-4} \text{ K}^{-1}$ above Tr4.

Similar dilatometric measurements in the isobaric heating processes were conducted at various pressures. In Table I, the thermodynamic parameters of $C_{20}F_{42}$ at Tr3 and Tr4 for various pressures are given. The end temperatures of the volume changes due to these transitions correspond to the peak temperatures of the DTA curve in the same process, used as the transition points in previous work.¹ Therefore, the transition points, T in Table I, were obtained from the end temperatures. The value of dT/dP was obtained from the gradient of the transition lines of Tr3 and Tr4 in Figure 1. The enthalpy change ΔH and entropy one ΔS , which are values per one mole of molecules, were

Table I. Thermodynamic parameters of C₂₀F₄₂ at Tr3 and Tr4

Tr3

<i>P</i>	<i>T</i>	<i>dT/dP</i>	Δv	ΔH	ΔS	ΔS_c
MPa	K	$\times 10^{-7} \text{ K Pa}^{-1}$	$\times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$	kJ mol^{-1}	$\text{JK}^{-1} \text{ mol}^{-1}$	$\text{JK}^{-1} \text{ mol}^{-1}$
425	314	4.11	1.190	9.42	30.1	1.51
450	324	3.98	1.183	9.98	30.8	1.54
500	343	3.71	1.270	12.18	35.5	1.78

Tr4

<i>P</i>	<i>T</i>	<i>dT/dP</i>	Δv	ΔH	ΔS	ΔS_c
MPa	K	$\times 10^{-7} \text{ K Pa}^{-1}$	$\times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$	kJ mol^{-1}	$\text{JK}^{-1} \text{ mol}^{-1}$	$\text{JK}^{-1} \text{ mol}^{-1}$
290	317	5.40	0.317	1.93	6.1	0.31
300	323	5.29	0.350	2.21	6.9	0.35
320	333	5.09	0.476	3.23	9.7	0.49
350	348	4.79	0.492	3.71	10.7	0.54
400	371	4.29	0.580	5.20	14.0	0.70
450	391	3.78	0.577	6.19	15.8	0.79
500	408	3.28	0.571	7.38	18.1	0.91

calculated from *T*, *dT/dP*, and Δv based on Clausius–Clapeyron's equation,

$$dT/dP = T\Delta v/\Delta H = \Delta v/\Delta S$$

ΔS_c is the entropy change per one mole of repeating units (CF₂), calculated from $\Delta S_c = \Delta S/20$ based on the assumption that two end groups contribute to ΔS to the same degree as other repeating units. At each pressure above about 400 MPa, the changes of all thermodynamic parameters at Tr3 are larger than those at Tr4. The change of ΔH at Tr4 increases with pressure.

From the values of entropy change in Table I, information on types of dynamic disorders activated at Tr3 and Tr4 can be obtained by analogy with *n*-alkanes in which similar types of disorders are expected. It is well known that *n*-alkanes transit to rotator phase prior to melting, where the rotation of molecular chains around the chain axes occurs. In addition, two other types of dynamic disorders, 180°-rotational jump and flip-flop screw jump were reported for *n*-tritriacontane (C₃₃H₆₈) by

Strobl *et al.*⁶ The same types of dynamic disorders were confirmed to occur in other odd-numbered *n*-alkanes.⁷

For transition to the rotator phase, the transition point and enthalpy change of each *n*-alkane were summarized by Broadhurst.⁸ From these values, the authors calculated the entropy change for the transition based on $\Delta S = \Delta H/T$ and $\Delta S_c = \Delta S/n$, where *n* is the number of carbon atoms. According to the results, ΔH and ΔS increase with *n*, but ΔS_c does not depend on *n* for odd and even-numbered *n*-alkanes. ΔS_c is 2.2–3.3 JK⁻¹ mol⁻¹ and 3.7–4.1 JK⁻¹ mol⁻¹ for odd and even-numbered *n*-alkanes, respectively. The value for odd-numbered ones was also confirmed by detailed thermal analysis as to *n*-alkanes, carried out recently by Takamizawa *et al.*⁷ They reported that the values of ΔS at transitions accompanying the other types of dynamic disorders are very small compared with that at the transition to the rotator phase and independent on the number of carbon atoms.

Entropy changes of similar types of dynamic disorders are expected to be comparable as Wunderlich showed for three types of disorders, *i.e.*, positional, orientational, and conformational ones.⁹ Therefore, the types of disorders of $C_{20}F_{42}$ at Tr3 and Tr4 can be supposed by a comparison of entropy changes with those of *n*-alkanes. ΔS_c at Tr3 in $C_{20}F_{42}$, $1.5\text{--}1.8\text{ JK}^{-1}\text{ mol}^{-1}$ between 400 and 500 MPa, is somewhat smaller than that at the transition to the rotator phase in *n*-alkanes. ΔS_c at Tr4 in this pressure region, $0.7\text{--}0.9\text{ JK}^{-1}\text{ mol}^{-1}$, is about half that at Tr3, and the sum of ΔS_c values at Tr3 and Tr4, $2.2\text{--}2.7\text{ JK}^{-1}\text{ mol}^{-1}$, is comparable with that at the transition to the rotator phase in odd-numbered *n*-alkanes. From these facts, it is supposed that the rotation of molecular chains is activated to some degree at Tr3, and the rotation becomes more active at Tr4. In fact, the results of high pressure X-ray measurement

support this supposition as to the rotational dynamic disorders activated at Tr3 and Tr4 in the heating process under high pressure.⁵

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