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Melting Curve of *o*-Terphenyl

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Melting of high purity *o*-terphenyl was investigated in the range 0–500 MPa by differential thermal analysis. The sample was purified by repeated recrystallization from methanol, followed by vacuum sublimation. This material was approximately 99.995% pure, and the results suggest that sample purity was maintained to within the experimental uncertainty. The sample was loaded into a high pressure cell with a teflon/nylon composite pressure transmitting diaphragm. A differential thermocouple and a calibrated temperature measuring thermocouple were in direct contact with the sample. The data are best fitted by a quadratic melting equation: $t_m = 56.0 + 0.357\,P - 0.000129\,P^2$, where t_m is in °C and P is in MPa. The intercept and initial slope agree well with existing ambient pressure melting data.

KEY WORDS: high pressure; melting; *o*-terphenyl; thermal analysis.

1. INTRODUCTION

The properties of *o*-terphenyl (1, 1′ : 2′, 1″-terphenyl or 1,2-diphenylbenzene) have been extensively studied because of its glass forming tendencies and its potential as a nuclear reactor coolant. However, only a few researchers have made measurements on *o*-terphenyl at high pressures. Bridgman [1], Opdycke et al. [2], and Schmidt et al. [3] measured the molar volume of *o*-terphenyl as a function of pressure. Other researchers [4, 5] studied chemical reactions induced by high pressure and shear stress in various aromatic hydrocarbons including *o*-terphenyl.

Measurements on *o*-terphenyl in the superpressed state would comple-

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Table I. *o*-Terphenyl Melting Data at Ambient Pressure

Purification method	t_m (°C)	t_m(pure)[a] (°C)	ΔH_m (kJ · mol^{-1})	ΔV_m (cm^3 · mol^{-1})	Ref.
Recrystallization and sublimation	56.202	56.204	17.191		[6]
Recrystallization and distillation	56.15	56.25			[7]
Chromatography and recrystallization	56.2				[8]
Recrystallization	56.1				[9]
Chromatography and sublimation	55.5			18.9	[10]
Recrystallization and vacuum melting			16.95	18.9	[11]
Mean	56.0		17.07	18.9	

[a] Extrapolated.

ment the supercooling data; however, interpretation of such measurements requires knowledge of the melting curve of *o*-terphenyl. Therefore, we measured this curve using differential thermal analysis. Table I lists the determinations of melting temperature, enthalpy, and volume made by various researchers at ambient pressure on high purity *o*-terphenyl. Sample purity is of particular importance since it strongly influences the melting temperature [12], and even the best commercially available materials have 1–10% impurities.

2. EXPERIMENTAL PROCEDURE

o-Terphenyl of nominal 90–95% initial purity was recrystallized three times from spectroscopically pure methanol, then sublimed twice to remove any traces of the solvent. Using this same technique, Chang and Bestul [6] obtained samples of 99.995% purity. Differential scanning calorimetry showed that samples of their material (supplied by S. S. Chang) and ours had the same melting temperature and melting peak shape, implying that the two samples were of similar purity.

Figure 1 shows the sample cell configuration. The sample (A) was confined inside a nylon annulus (B) between a sheet of brass (C) and a flexible diaphragm (D), which consisted of a 0.125 mm polytetrafluoroethylene sheet and two 0.025 mm nylon sheets. The composite diaphragm design proved most satisfactory for pressure transmission because the highly deformable polytetrafluoroethylene provided a cushion from shear stresses at the sample interface, while the impermeable nylon maintained

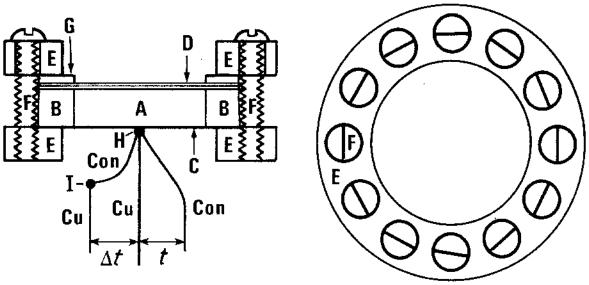

Fig. 1. Sample cell design: (A) Sample; (B) nylon ring; (C) brass sheet; (D) flexible composite diaphragm; (E) brass clamping rings; (F) brass clamping screws; (G) nylon cushion ring; (H) copper-constantan thermocouple junction; (I) differential thermocouple reference junction.

sample purity. The entire assembly was clamped between two brass rings (E) that were held together by twelve brass screws (F) with a thin nylon ring (G) cushioning the diaphragm from the sharp ring edges.

We loaded *o*-terphenyl crystals into the sample cell, which had been assembled without the diaphragm. The sample was melted and allowed to solidify into a disc; then the diaphragm was installed. Although all traces of air could not be eliminated during loading, it was limited to a minute fraction. The assembled cell consisted of 6.404 g of brass and 0.509 g of plastic and contained 0.422 g of *o*-terphenyl.

We placed the cell in an externally heated pressure vessel that was pressurized with di(2-ethylhexyl)sebacate. Pressure was measured with a calibrated Bourdon tube gauge equipped with a potentiometric pickup that permitted continuous recording. Pressure was readable to ± 1 MPa with an uncertainty of ±0.1%. Sample temperature was measured using a copper-constantan thermocouple with one junction (H) soldered to the brass sheet (C) in direct contact with the sample (see Fig. 1) and a cold junction in an ice bath. The differential thermal signal was measured between the junction at the sample cell (H) and a reference junction (I) nearby in the pressurizing fluid.

We measured each point on the melting curve by heating with a constant power input at nearly constant pressure (increasing slightly owing to thermal expansion of the pressure fluid). Heating rates were 4–8 $°\mathrm{C} \cdot \mathrm{hr}^{-1}$ in the melting region. Higher heating rates were too fast for the melting kinetics, but lower rates, down to 0.07 $°\mathrm{C} \cdot \mathrm{hr}^{-1}$, produced no change in the recorded melting temperature. Sample temperature, vessel pressure, and the differential thermal signal (amplified by a factor of 1000) were continuously recorded. Figure 2 shows the shape of a typical melting peak; the melting point is defined as the extrapolated onset (measurable to ±0.5 °C) in accord with the International Confederation for Thermal

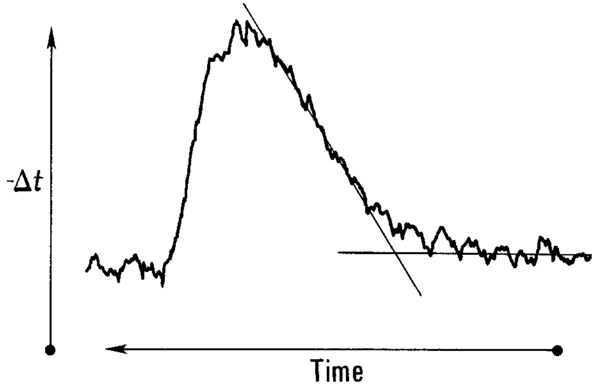

Fig. 2. Typical chart recording of an *o*-terphenyl melting peak showing the extrapolated onset.

Analysis [13]. Also the peak areas, which are proportional to the enthalpies of melting, were measured with a compensating polar planimeter.

We took measurements from ambient pressure to 500 MPa at increasing intervals of ~100 MPa, then from 450 to 50 MPa at decreasing intervals of ~100 MPa, and finally at ambient pressure again. Throughout the study the same sample was used and, after each melting, it crystallized at or near the pressure of the next measurement. Unfortunately, the tendency of *o*-terphenyl to supercool made crystallization measurements impractical.

Following the two highest temperature runs, the response of the temperature sensing thermocouple changed slightly. Apparently the soldered junction melted, allowing contamination of the thermocouple by the pressure fluid. To achieve a complete temperature calibration curve, both this thermocouple and a new one made from the same starting material were calibrated against a platinum resistance thermometer. Application of these separate calibrations yielded good agreement (within the calibration uncertainty of ± 1%) between the data taken before and after the thermocouple contamination.

3. RESULTS AND DISCUSSION

Table II and Fig. 3 show the results. The Simon melting equation and polynomials of first, second, and third degree were fit to the data. The following quadratic polynomial gave the best fit:

$$t_m = 56.0 + 0.357\,P - 0.000129\,P^2$$

where t_m is in °C and P is in MPa. The standard devation of the data from this curve was 0.54 °C, and the largest deviation of any point was 0.73 °C,

Table II. Differential Thermal Analysis Results

P (±1 MPa ± 0.1%)	t_m[a] (±0.5 °C ± 1%)	Peak area (°C · hr)	Peak width[b] (°C)	Heating rate (°C · hr^{-1})
0	56.0	0.097	1.5	7.8
111	93.9	0.102	1.8	5.1
205	123.8	0.102	1.6	4.8
308	153.2	0.110	1.8	4.2
413	181.6	0.106	1.7	4.6
503	203.7	0.112	2.0	6.8
465	193.3	0.090	2.0	5.0
351	165.0	0.115	1.4	5.2
242	135.4	0.099	1.6	6.1
134	101.6	0.100	1.8	5.9
47	72.9	0.098	2.0	6.9
0	55.4	0.111	1.7	7.1

[a] Extrapolated onset.

[b] Full width at half-maximum.

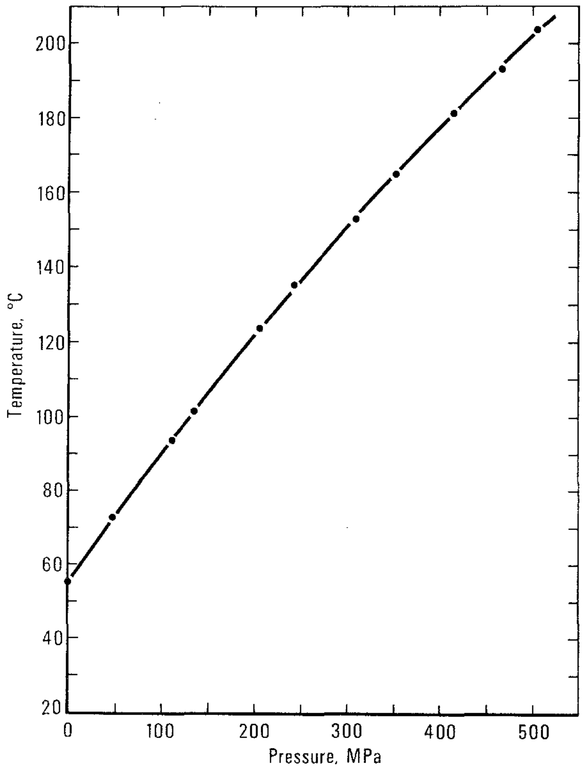

Fig. 3. Melting curve of *o*-terphenyl.

both well within the experimental uncertainty. The intercept of this curve agrees exactly with the mean of the ambient pressure data from other sources (see Table I). Using the melting enthalpy and volume data from Table I, the Clapeyron equation yields a value of 0.364 $°C \cdot MPa^{-1}$ for the initial slope of the melting curve, which is in close agreement with the value of 0.357 $°C \cdot MPa^{-1}$ determined above.

Any contamination introduced during loading or during the experiments would effect these results. Data on biphenyl [12] and the as received *o*-terphenyl suggest that the melting temperature at ambient pressure decreases ~0.5 $°C \cdot (\text{mol\% impurity})^{-1}$. Thus, at ambient pressure, our experimental uncertainty was equivalent to ~2 mol% impurity. Our initial ambient pressure value exactly matches the mean from Table I, suggesting that any contamination during loading was less than this uncertainty. Our final value is 0.6 °C lower. Although this deviation could represent ~1 mol% impurity, it is within the experimental uncertainty (±2 mol%) and does not constitute proof of contamination.

The enthalpy of melting [14] and the fractional melting versus temperature [6] also change with impurity content and would respectively influence the peak area and peak width. The data for these parameters (see Table II) show no systematic variation, suggesting that any sample contamination was small and would not strongly effect the results.

4. CONCLUSIONS

The melting curve of high purity *o*-terphenyl in the range 0–500 MPa obeys the relation:

$$t_m = 56.0 + 0.357\,P - 0.000129\,P^2$$

where t_m is in °C and P is in MPa. This equation agrees with existing ambient pressure melting data and provides a basis for determining the degree of supercooling or superpressing of *o*-terphenyl at high pressures.

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