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Technical Report No. 6

HIGH PRESSURE X-RAY STUDIES OF POLYMERS. I. PRESSURE CALIBRATION FOR THE DIAMOND ANVIL-CELL IN THE RANGE 0-15 KBARS

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Pressure-volume data for hexamethylene tetramine up to 7 kbars was obtained using a dilatometer, combined with some data obtained by Bridgeman, and the total fitted to a quadratic function :

$$\frac{\Delta V}{V_o} = k_{1p} - k_{2p^2}$$

deltaV / Vsubo = K sub 1p - K sub 2 p square

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for pressures up to 15 kbars. A good fit was obtained, the constants obtained were $k_1 = 9.77 \times 10^{-12}$ cm^2/dyne and

** $k_2 = 2.16 \times 10^{-22}$ cm^4/dyne^2.

Using this equation the interplanar spacings of the crystalline H.M.T. can be calculated as a function of pressure, and this provides a convenient and accurate method of pressure calibration for high pressure X-ray cameras based on the diamond cell technique. This method is particularly suitable for high pressure studies of polymers since for these materials the greatest interest is directed toward lower pressures. A comparison with other techniques reveals that this new method is significantly more accurate for pressures in the range 0-5 kbars.

* Ic sub 1 = 9.77 x 10 to the -12th power sq cm/dyne

** K2 = 2.16 x 10 to the -22nd power cm to the 4th power/ sq dynes

HIGH PRESSURE X-RAY STUDIES OF POLYMERS. I. PRESSURE CALIBRATION FOR THE DIAMOND-ANVIL CELL IN THE RANGE 0-15 KBARS*

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Introduction

The diamond-anvil pressure cell, first reported in 1959 (1), has been used to study materials at high pressures with a variety of methods, including optical observation (2), X-ray diffraction (2-8), absorption spectroscopy (9), and Raman scattering (10). The most serious drawback in using the diamond-anvil pressure cell is the measurement of the high pressure attained in the device. The usual method is to incorporate a NaCl standard with the sample and to make measurements of the lattice parameter using X-ray diffraction. The pressures can be determined through an equation of state (11). Recently a more convenient method has been reported by Piermarini and Block using ruby fluorescence (12). Both these methods are accurate at the ultrahigh pressures that can be achieved using the diamond-anvil pressure cell.

However, a variety of interesting phenomena is known to occur at comparatively low pressures for the case of polymeric materials. Crystallization of polyethylene at pressures of 3-5 kbars can give rise to unique morphologies, and it has been suggested that crystallization into a new crystal phase, not observed at room pressure (13-15), may be related to this. A reversible phase transition for

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the case of polytetrafluoroethylene has been reported at 7 kbars (16). There are many other examples and, in fact, studies of polymers have been limited to pressures less than 15 kbars.

It would obviously be convenient to use the diamond cell to study these transitions, but neither the NaCl method nor the ruby fluorescence method providessufficient accuracy at low pressures. When X-ray diffraction techniques are being used, the NaCl method is convenient but the changes in d-spacings at low pressures are too small to measure accurately. Molecular crystals, with weaker secondary bonds, have higher compressibilities than ionic crystals, and therefore would be more suitable pressure standards at low pressures. Two materials were considered, adamantane and hexamethylene tetramine (HMT). Adamantane would not be suitable, however, since a phase transition occurs at higher pressures (17). No phase transition has been reported for the case of HMT, and the material is readily available in purified form. The compressibility of HMT has been reported as 1.23×10^{-11} cm^2/dyne, approximately three times greater than the compressibility of NaCl. For these reasons, it was decided to compare the accuracy of the pressure determination using NaCl with the accuracy using HMT.

Experimental

If a particular material is to be used as a pressure standard, it is necessary that the d-spacings be known for various pressures. For the case of NaCl, the change in d-spacing at various pressures has been calculated by Dekker (11) from the equation of state. For the case of HMT, the equation of state has not been derived, but the pressure-volume relationship at 295°K for HMT has been investigated by Bridgeman (19). Bridgeman measured the specific volume of HMT at different pressures up to 40 kbars. Unfortunately, his data in the low-pressure region of interest to us (0-15 kbars) are rather few and, in fact, only three measurements could be used in this range: at 5, 10, and 15 kbars.

For this reason, Bridgeman's experiment was repeated by us using a dilatometer. Several measurements were made in the pressure range of greatest interest to us (0-7 kbars). These data are shown in Table 1. In Figure 1, the data are shown in graphical form combined with the three data points of Bridgeman.

According to Slater (20), at low pressures the pressure-volume relationship can be assumed to have the form:

$$\frac{V_o - V}{V_o} = k_1 p - k_2 p^2 \tag{1}$$

where V_o is the initial volume. k_1 and k_2 are constants related to the thermal expansion coefficient of the material used, the compressibility, and the Grüneisen constant. A least-squares program was used to obtain the best fit for the data, and the following values were obtained: $k_1 = 9.77 \times 10^{-12}$ cm^2/dyne; $k_2 = 2.16 \times 10^{-22}$ cm^4/dyne^2. The best fit to the data is shown by the solid line in Figure 1.

Discussion

Since HMT has a cubic lattice, the d-spacings of any set of planes (hkl) can be easily obtained from equation (1) when k_1 and k_2 are known. As an example, the d-spacings of the (110) reflection (the most intense reflection) were calculated, and are shown tabulated in Table 2. With the aid of equation (1), HMT can be used as a pressure standard for the diamond cell.

HMT is a molecular crystal with a high melting point, and therefore can be used as a filler for most polymers. The advantage of this method is that the pressure on the HMT crystals embedded in the polymer matrix truly reflects the pressure on the polymer sample. Moreover, the HMT crystal-to-film distance is identical with the polymer-to-film distance.

The constants of the best fit, k_1 and k_2, are given by

$$k_1 = \frac{a_1}{1 + a_o}; \qquad k_2 = \frac{a_2}{1 + a_o}$$

where a_1 is approximately equal to the volume compressibility at zero pressure, a_o is related to the thermal expansion coefficient α by $a_o = \int_o^T \alpha dT$, and a_2 is a measure of the change of compressibility with pressure. If we neglect a_o, small compared with unity in the above equations, we have

$$k_1 = a_1; \qquad k_2 = a_2$$

Using our data, we obtain a value for the compressibility of HMT of 9.516×10^{-12} cm^2/dyne.

The value for a_2 provides a measure of the anharmonicity of thermal vibrations for HMT. Slater gives an approximation for the Grüneisen constant at zero pressure:

$$\gamma_o = -\frac{2}{3} + \frac{a_2}{a_1^2\left(\frac{1 + a_o a_2}{a_1^2}\right)} \doteq -\frac{2}{3} + \frac{a_2}{a_1^2}$$

Using the *values for* k_1 *and* k_2 *obtained*, a value for γ_o of 1.597 was obtained. This is the first determination of γ_o for HMT reported.

Comparison with Other Techniques

At low pressures, the change in d-spacing is very small and so the principal source of error in the pressure determination is the measurement of the HMT d-spacing from the X-ray film. Using film techniques, lattice parameters can be measured with an accuracy of 0.02-0.1% (21) on a routine basis, but the highest accuracy is normally obtained from only lines with the largest reflection angles ($2\theta > 150°$). In the case of the diamond cell, only lines with small Bragg angles can be studied ($2\theta < 30°$). For this reason, high accuracy would not be expected.

In addition, it is well known that different observers may choose different points as the position of the line (22). Differences between the center of blackening, the center of intensity, and the peak intensity are appreciable. Moreover, specimen displacement and divergence of the primary beam will lead to systematic errors. Also, film shrinkage due to processing and aging and absorption effects caused by the diamond anvil can be significant.

Since only the change in d-spacing is required in order to determine the pressure, a number of methods which eliminate the systematic errors can be used. Flack (16) has suggested recording the diffraction pattern from a sample under pressure and the pattern from a sample at room pressure on the same film. However, if it is required to record patterns at several different pressures, this is not a convenient method. It is more convenient to record each pattern separately, but to use the Debye-Scherrer ring diameters of the sample at room pressure to establish the film-to-specimen distance. In essence, this method achieves the same result as Flack's technique providing care is taken to minimize film-shrinkage differences.

The proportional change in d-spacing $\Delta d/d_o$, which is used to determine the pressure, has some error $\delta d/d_o$. The error in pressure determination δp resulting from this will depend on the compressibility. If the compressibility of the pressure standard is C, then

$$\delta p = \frac{1}{C}\frac{\delta d}{d_o}$$

Now $\delta d/d_o$ will be a function of angle. We can use the well-known relation

$$\frac{\delta d}{d_o} = \cot\theta \cdot \delta\theta$$

where $\delta\theta$ arises from the error in ring-diameter measurement. If the ring diameter is D and the specimen-to-film distance is z, then

$$\tan 2\theta = \frac{D}{2z}$$

and

$$\delta\theta = \frac{1}{4} \sin 4\theta \left(\frac{\delta D}{D} + \frac{\delta z}{z} \right)$$

If z is determined using the known d-spacing for the pressure standard at room pressure,

$$\frac{\Delta z}{z} = \frac{\delta D'}{D'}$$

where D' is the measured ring diameter at room pressure. Since the error of measurement for D and D' is the same, $\Delta z/z = \delta D'/D' = \delta D/D$. Collecting these terms, we find

$$\delta p = \frac{1}{2} \frac{1}{C} \cot \theta \sin 4\theta \frac{\delta D}{D}$$

and this equation can be used to compare NaCl and HMT in their effectiveness as pressure standards at low pressures.

As an example, we consider two assumed working pressures, 3 kbars and 5 kbars. In order to make a good comparison, it is convenient to assume measurements are made at the same Bragg angle 2θ. If we use the (220) reflection for NaCl ($2\theta = 20.6°$) and the (222) reflection for HMT ($2\theta = 20.2°$), this condition is approximately true. We can assume a specimen-to-film distance of 8 cm and a proportional error in the measurement of the diameter of 0.1%. The resulting errors are shown in Table 3.

From these calculations, it is clear that NaCl should not be used as a pressure standard at pressures less than 5 kbars. The errors involved in the case of HMT are large, but certainly acceptable in this range. It should also be noted that the specimen-to-film distance assumed (8 cm) is quite large. Smaller distances are often used, since this reduces the exposure time; for example, Flack used a film-to-specimen distance of 3 cm. If this practice is carried out, it is likely that the errors could be even higher than indicated by Table 3.

A careful error analysis for the ruby fluorescence method was not carried out. Piermarini and Block (12) suggest that the pressure dependence of the R_1 ruby fluorescence line at 6942 Å is linear (0.365 Å/kbar) at 25°C. The shift in wave number is -0.77 ± 0.03 cm^{-1}/kbar. However, different measurements at the same pressure can give a spread in wave number of ± 2 cm^{-1}, and a report by Forman et al. (23) gives a standard deviation of 1.5 kbars. For comparison with the X-ray results, it is clear that the errors at 3 and 5 kbars would be 50 and 30%, respectively; this is slightly more inaccurate than the NaCl method. We suggest that the ruby fluorescence method should also not be used for pressures less than 5 kbars.

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Table 1

Pressure (dyne/cm^2)	Volume (%)
9.806×10^5	0.00
1.718×10^9	1.54
2.120×10^9	2.05
2.885×10^9	2.64
3.864×10^9	3.46
4.835×10^9	4.25
5.770×10^9	4.93
6.862×10^9	5.67

(1 kbar = 980.7 kg/cm^2 = 10^9 dynes/cm^2)

Table 2

Pressure (kg/cm^2)	d_{110} (Å)
1	4.9800
1,000	4.9644
2,000	4.9494
3,000	4.9350
4,000	4.9212
5,000	4.9080
6,000	4.8955
7,000	4.8837
8,000	4.8725
9,000	4.8620
10,000	4.8522
11,000	4.8430
12,000	4.8346
13,000	4.8268
14,000	4.8198
15,000	4.8135

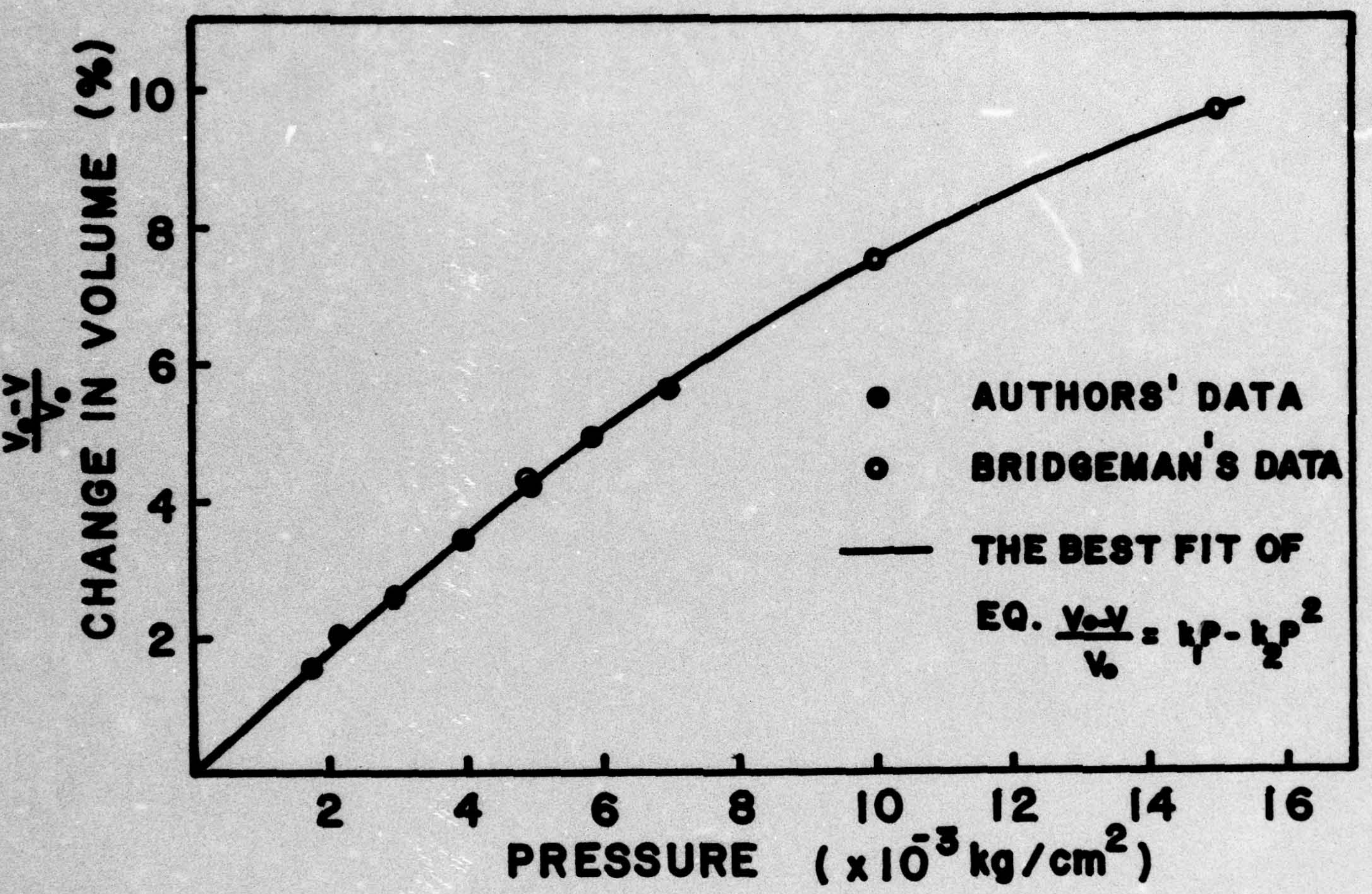
(1 kbar = 980.7 kg/cm^2 = 10^9 dynes/cm^2)

Table 3

Pressure Standard	% Error at 3 Kbars	% Error at 5 Kbars
NaCl	44	27
HMT	20	12

Legend for Figure 1

Fig. 1. Volume-pressure relationship of hexamethylene tetramine at room temperature.


$\frac{V_0 - V}{V_0}$ CHANGE IN VOLUME (%)
10
8
6
4
2
2
4
6
8
10
12
14
16
PRESSURE ($\times 10^{-3}$ kg/cm^2)
● AUTHORS' DATA
○ BRIDGEMAN'S DATA
THE BEST FIT OF
EQ. $\frac{V_0 - V}{V_0} = k_1 P - k_2 P^2$