High pressure X-ray studies of polymers. II. Variation of pressure with temperature in the diamond-anvil cell

High pressure X-ray diffraction and optical studies of polymers using the gasketed diamond-anvil cell have been reported by a number of investigators [1–5]. The use of such a device is particularly interesting since crystal phase transitions and crystallization of polymers at high pressures and temperatures can be observed directly [5] or by X-ray diffraction [4]. There are, however, several difficult experimental problems that must be overcome if a successful experiment is to be carried out. The first is to ensure that hydrostatic pressure is achieved in the device so as to avoid gross anisotropic distortion of the polymer sample. This can be accomplished if the sample in the gasket is surrounded by a pressure-transmitting fluid. The second is that an accurate method of pressure measurement must be developed for at least the range of pressures used in the study [6]. Furthermore, there are other problems associated with the use of the device if high temperatures are introduced in addition to high pressures.

In this paper, the problems associated with the use of the diamond-anvil cell with combinations of high pressure and temperature are discussed. It appears in the literature that the pressure in the cell is assumed to be constant during temperature change and during crystallization. It is convenient to make this assumption and then compare thermal treatments in the diamond cell with high pressure differential thermal analyses (DTA) or dilatometric data. Both Bassett *et al.* [4] and Jackson *et al.* [5] made comparisons with crystallization experiments carried out under constant pressure in DTA, although the former did discuss the problem that the pressure was not constant during crystallization. If the pressure in the diamond cell changes during the course of crystallization, then, of course, so does the degree of supercooling, and it is well known that this latter parameter is a critical factor in crystallization. Furthermore, an accurate measurement of pressure in the diamond cell at elevated temperatures is another associated problem. Optical methods based on ruby flourescence cannot be used for precision measurements at temperatures above 200° C [7]. The method utilizing the equation of state for NaCl developed by Dekker is not sufficiently accurate over the pressure range of interest for polymer studies [8]. A method used by other workers is to measure the melting point of the pressurized polymer and compare this value to values obtained in a dilatometric device. This method certainly provides a measurement of pressure at the temperature where melting of the polymer is observed. If pressure constancy with temperature is assumed, then this method can serve a useful purpose. However, as already discussed, this assumption remains to be tested.

An alternative method of measurement of pressure at elevated temperatures has been developed by the authors, deriving the equation of state for hexamethylene tetramine (HMT) [9]. A functional form for the equation of state was derived by consideration of the potential energies between non-bonded atoms in neighbouring molecules, with due consideration for thermal vibrations. The parameters of this functional form were determined by comparing the functional dependence with experimental data. With this more accurate technique available to determine pressure at various temperatures, it is possible to test the assumption of constancy of pressure in the diamond-anvil cell with varying temperatures.

Evidence that the pressure in the diamond-anvil cell can vary by as much as 100% over a 150° C temperature interval is presented here. It will be demonstrated that the pressure in the device is a non-linear function of temperature and that the pressure also depends on the relative volume of the components in the device, the sample material, the pressure standard, and the pressure-transmitting fluid.

The experimental techniques employed in this study have been described elsewhere [3, 6]. A brass gasket $\frac{3}{8}$ in. diameter and $\frac{1}{32}$ in. thick with an axial cavity $\frac{1}{32}$ in. diameter was used. The gasket was inserted inside a resistance heater, and an iron–constantan thermocouple, together with a current-adjusting silicon rectifier controller, was used to measure temperature within ±0.1° C accuracy.

Earlier workers [2, 4] appeared not to have used a pressure-transmitting fluid, although our experiments indicate that, under these conditions, pressure gradients caused severe distortion of the sample. All our experiments were carried out using silicon oil as a pressure-transmitting fluid. It is believed, however, that the conclusions arrived at in this study apply equally to the case when no pressure medium is used. A small sample consisting of linear polyethylene (Marlex 6009) mixed thoroughly with powdered HMT was moulded and deposited in the cavity and silicon oil added. Changes in the *d*-spacing of the (1 1 0) reflection of HMT were measured and, by using the equation of state for HMT [9], the pressure in the cavity determined. The sample was pressurized to some initial value and then the temperature raised in steps. After every temperature increment, the pressure was determined.

Two separate experiments were carried out with two different samples and two different initial pressures. The initial pressure exerted on sample A was 4.1 kbar and the initial pressure on sample B was 2.8 kbar. The measured pressure on each sample at various temperatures is shown in Table I. As the temperature increased, the pressure increased in a non-linear fashion as shown in Fig. 1. Lowering the temperature caused non-linear decrease in pressure. When crystallization is associated with the decrease in temperature, a more than usual drop in pressure (1 to 2 kbar) was observed. This is probably due to the denser morphology and increase in crystallinity of the material as it crystallized under high pressure. This drop in the pressure may also be attributed to irrecoverable deformation in the gasket material which had been formed at higher pressures.

A simple analysis to a first approximation of this situation throws some light on the pertinent features of this phenomenon.

(a) *Case when no pressure medium is used.* This is important, since some reports have been published on data obtained with use of a pressure medium. If the volume of a solid at zero pressure and the absolute zero of temperature is V_0, then according to Slater [10], the volume at some pressure P and temperature T can be

$$V = V_0[1 + a_0(T) - a_1(T)P + a_2(T)P^2 \ldots]$$

where a_0, a_1, a_2 etc are functions of temperature.

TABLE I

	Temperature (° C)	Pressure	
		($\times 10^3$ kg cm^{-2})	(kbar)
Sample A	24	4.01	4.09
	100	4.58	4.67
	150	5.42	5.53
	180	5.87	5.99
	190	6.13	6.25
	200	6.28	6.40
	210	6.57	6.70
	220	6.72	6.85
	240	7.76	7.91
	260	8.68	8.85
	280	10.04	10.24
	290	10.42	10.63
Sample B	24	2.72	2.77
	150	4.26	4.34
	180	4.47	4.56
	200	5.37	5.48
	215	6.03	6.15
	230	6.70	6.83
	240	7.39	7.54

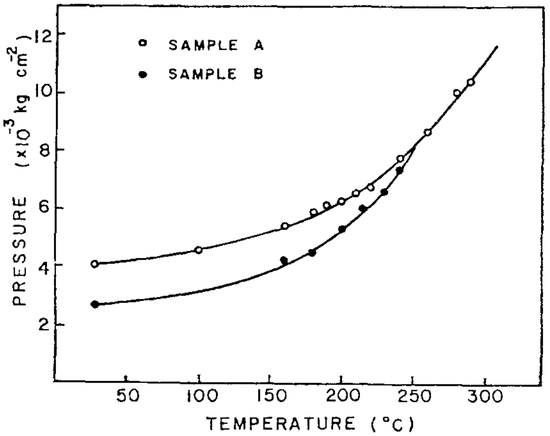

Figure 1 Variation of pressure with temperature in high pressure diamond-anvil cell.

In the case when no pressure medium is used and the solid is pressurized to some initial pressure P_i at room temperature T_r, some initial volume V_i can be expressed as

$$V_i = V_0[1 + a_0(T_i) - a_1(T_i)P_i + a_2(T_i)P_i^2 + \ldots]$$

The temperature of the sample is then raised to a value $T_i + \Delta T$, and we assume this causes the pressure to change by an amount ΔP. If the thermal expansion of the solid α and the compressibility of the solid χ is approximately constant over ΔP and ΔT, neglecting second-order and higher terms, we have the volume

$$V = V_i + \alpha\Delta T - \chi\Delta P$$

We will assume that the volume of the pressurized sample remains constant during the temperature increase. Actually, there may be some small change, but frictional forces exerted by the diamond facets, and the relatively low thermal expansion of the gasket material will ensure that V_i is approximately equal to V, in which case we have

$$\alpha\Delta T = \chi\Delta P$$

or

$$\Delta P = \frac{\alpha}{\chi}\Delta T.$$

This would imply a linear increase of pressure with temperature. Moreover, if changes in the α and the χ with temperature and pressure are taken into consideration in the above analysis, the pressure increase will be non-linear and even more exaggerated at higher temperatures. Another factor not accounted for in the analysis is the change in specific melting and recrystallization.

(b) *Case when a pressure medium is used.* This is the case actually investigated in some detail. If V_p, V_h, and V_m are the volumes of the polymer sample, the pressure standard HMT, and the pressure medium respectively, a similar analysis will lead to

$$(\alpha_\text{p} V_\text{p} + \alpha_\text{h} V_\text{h} + \alpha_\text{m} V_\text{m})\Delta T = (\chi_\text{p} V_\text{p} + \chi_\text{h} V_\text{h} + \chi_\text{m} V_\text{m})\Delta P$$

or

$$\Delta P = \left(\frac{\alpha_\text{p} V_\text{p} + \alpha_\text{h} V_\text{h} + \alpha_\text{m} V_\text{m}}{\chi_\text{p} V_\text{p} + \chi_\text{h} V_\text{h} + \chi_\text{m} V_\text{m}}\right)\Delta T$$

where α_p, α_h, α_m are the respective thermal expansion coefficients and χ_p, χ_h, χ_m the respective compressibilities of the sample, HMT, and the medium.

A simplification of the above equation can be achieved by neglecting V_h since it is small compared with V_p and V_m, and by assuming $V_\text{p} = V_\text{m}$, that is, very close to the actual situation, then

$$\Delta P = \left(\frac{\alpha_\text{p} + \alpha_\text{m}}{\chi_\text{p} + \chi_\text{m}}\right)\Delta T$$

This does predict the dependence of pressure on temperature in the diamond-anvil cell: linear dependence if α_p, α_m, χ_p, and χ_m are assumed to be constants and non-linear dependence if α_p, α_m, χ_p, and χ_m are functions of pressure and temperature.

Acknowledgment

The authors are grateful to the Office of Naval Research for financial support of this work under Contract N00014-75-C-0540.

References

1. H. D. FLACK, *J. Polymer Sci. A-2* **10** (1972) 1799.
2. D. KLEMPER and F. E. KARASZ, *ACS Polymer Preprints* **13** (2) (1972) 976.
3. T. P. SHAM, B. A. NEWMAN and K. D. PAE, *J. Mater. Sci.* **12** (1977) 771.
4. D. C. BASSETT, S. BLOCK and A. J. PIERMARINI, *J. Appl. Phys.* **45** (1974) 4146.
5. J. F. JACKSON, T. S. HSU and J. W. BRASCH, *Polymer Letters* **10** (1972) 207.
6. B. A. NEWMAN, T. P. SHAM and K. D. PAE, *J. Mater. Sci.* **12** (1977) 1064.
7. A. J. PIERMARINI and S. BLOCK, *Rev. Sci. Instrum.* **46** (1975) 973.
8. D. L. DEKKER, *J. Appl. Phys.* **36** (1965) 157.
9. T. P. SHAM, B. A. NEWMAN and K. D. PAE, (to be published).
10. J. C. SLATER, "Introduction to Chemical Physics", (McGraw-Hill, New York, 1939).

Received 17 November 1976
and accepted 17 February 1977

B. A. NEWMAN,
K. D. PAE,
T. P. SHAM
High Pressure Research Laboratory and
Department of Mechanics and Materials Science,
Rutgers University,
New Brunswick,
New Jersey, USA