

Effect of Pressure on Melting Temperature and Other Associated Thermodynamic Functions of Polyethylene

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Synopsis

The melting temperature of polyethylene was determined at pressures up to 30 kbar. Using these results and the calculated values of the volume change on melting in the Clausius-Clapeyron equation, the enthalpy and entropy of fusion as a function of pressure were also determined.

INTRODUCTION

The melting behavior of polyethylene under pressure has been investigated by a number of authors.¹⁻⁸ Most of these studies, however, were confined to pressures below 6 kbar. Only Osugi and Hara³ carried out their measurements up to 30 kbar. These authors detected the phase transition below 5 kbar by the volume discontinuity method. This involved the isothermal compression of polyethylene melt and the determination of the pressure at which the volume discontinuity occurred. The temperature of the isotherm was taken as the melting point corresponding to that pressure. The solidified samples, however, showed a variation in crystallinity by about 8%. Since in the case of polymers the melting temperature is dependent to a certain extent on the degree of crystallinity, the procedure of Osugi and Hara cannot be regarded as really satisfactory. For pressures above 5 kbar, a different technique, using a cubic press and differential thermal analysis, has been employed to determine the melting temperature. The results obtained by this method are less reliable due to the nonhydrostatic character of the pressure involving very large pressure gradients.

In this paper, the results of our study of the melting behavior of polyethylene at pressures up to 30 kbar are reported. The samples used in all the measurements were characterized by the same degree of crystallinity. Furthermore, the experimental arrangement and the technique for locating the melting temperature were also the same over the entire pressure range. We also determined the enthalpy and the entropy of fusion up to 9 kbar by the help of the Clausius-Clapeyron equation.

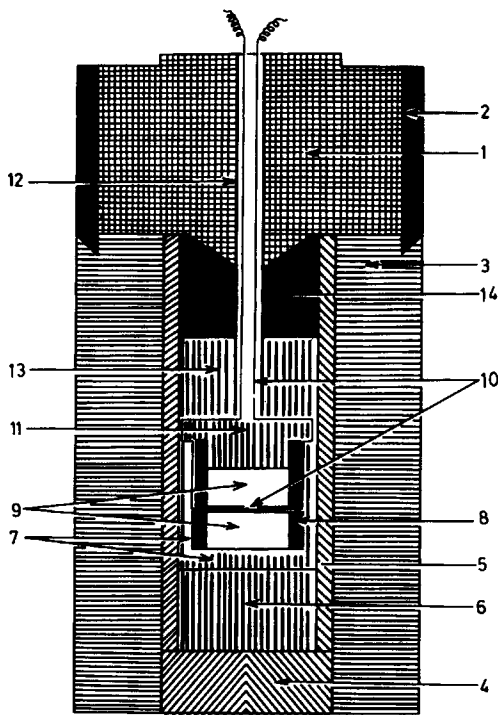


Fig. 1. Constructional details of the cell used in the melting experiment: (1) stainless steel seal; (2) pyrophyllite ring; (3) talc cylinder; (4) graphite disc; (5) graphite heater; (6) talc disc; (7) talc cup; (8) pyrophyllite rings; (9) polyethylene sample; (10) thermocouple; (11) talc cap; (12) ceramic tubing; (13) talc seal; (14) pyrophyllite conical seal.

EXPERIMENTAL

The polymer used for this investigation was linear polyethylene (GF 5750) supplied by Hoechst Dyes and Chemicals Ltd., India. The commercial material, in granular form, was first melted and then allowed to crystallize at 120°C for 2 hr, after which it was cooled to the room temperature at a rate of $2^{\circ}\text{C}/\text{min}$. The density of the sample so formed was found to be 0.951 g/cc at 25°C . According to the procedure adopted in our earlier work,⁹ this density corresponds to 72% crystallinity.

The melting experiment was carried out in a piston cylinder assembly. The required pressures were generated with the help of a 1000-ton hydraulic press. The sample was located in a specially designed talc-pyrophyllite cell. The constructional details are shown in Figure 1. The cell, along with the sample, was placed in the cylinder where it was compressed to the desired pressure by the advancing piston. The value of the pressure was calculated from the oil pressure in the press by area multiplication. No effort was made to calibrate the system by using standard pressure points. However, the error involved in pressure determination, due to the frictional loss and the deformation of the piston as a result of heating, is estimated to be not greater than 2%. The heating of the sample was carried out isobarically with the help of the cylindrical graphite heater shown in Figure 1. Different heating rates were tried; a rate of $6^{\circ}\text{C}/\text{min}$ was found to be the most suitable for locating the transition. Similar heating

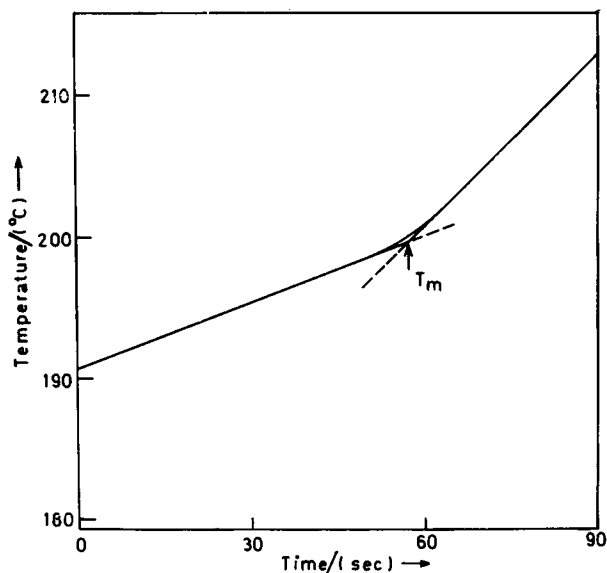


Fig. 2. Sample temperature vs time in a typical isobaric run at 3 kbar (choice of reference for time is arbitrary).

rates have also been employed by other workers.⁶ A Chromel-Alumel thermocouple was used to read the temperature of the polyethylene sample. The output of the thermocouple was fed to an X-Y recorder which plotted the thermo-emf, and hence the temperature as a function of time.

A typical plot at 3 kbar pressure is shown in Figure 2. Here, the curve shows only that part of the melting curve where the melting is near completion. In polymers, unlike other substances, melting is not a sharp phenomenon but is extended over a range of temperatures. The crystallinity slowly starts disappearing till it vanishes completely. The temperature at which the crystallinity disappeared completely was taken as the melting temperature (T_m). The uncertainty involved in the determination of T_m was never larger than $\pm 1.5^\circ\text{C}$.

RESULTS AND DISCUSSION

The smoothed values of the melting temperature for polyethylene as a function of temperature obtained from our raw experimental data are shown in Table I. The melting temperature at atmospheric pressure is in agreement within a degree with the value quoted by the suppliers of the material used in the present experiment. It is rather low as compared to the reported values for a high-density polyethylene. Such a low value could be due to some branching present in the sample.

The plot in Figure 3 shows ΔT_m , the change in melting temperature, as a function of pressure. Here, the results of Osugi and Hara,³ Davidson and Wunderlich,⁶ and Bassett and Turner⁸ are also shown. Since the melting temperature at atmospheric pressure is slightly different in various cases considered, the role of pressure in changing T_m is brought out better by taking ΔT_m instead of T_m as the dependent variable. It may be noted that the smoothed values of Osugi and Hara on the low-pressure side lie below the curve while, above 20 kbar

TABLE I
Smoothed Values of Melting Temperature as a Function of Pressure

P , kbar	T_m , °C
0	126
1	154
2	180
3	200
4	217
5	234
8	277
10	296
15	333
20	357
25	378
30	396

the trend is opposite. The results of Davidson and Wunderlich, available only below 6 kbar for folded chain crystals, show an even more marked disagreement. Their data for extended-chain crystals (not shown in the figure) surprisingly are in conformity with this curve. On the other hand, results of Basset and Turner, for folded-chain crystals, show good agreement with the present work.

The enthalpy of fusion, ΔH , as a function of pressure can be obtained from the results of the melting experiment using the Clausius-Clapeyron equation

$$\frac{dP}{dT_m} = \frac{(\Delta H/T_m)}{\Delta V} \quad (1)$$

provided ΔV , the volume change on melting, is known. Osugi and Hara mea-

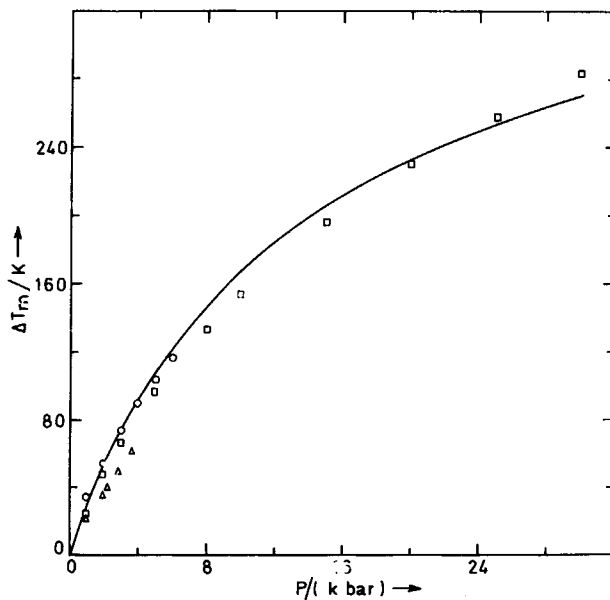


Fig. 3. Variation of melting temperature as a function of pressure: full curve, present results; (□) Osugi and Hara; (Δ) Davidson and Wunderlich; (○) Bassett and Turner.

TABLE II
Coefficients of Eq. (2) with kbar as Unit of Pressure and °C as Unit of Temperature

Coefficient	Value
a_0	125.98
a_1	32.168
a_2	-3.2071
a_3	0.27651
a_4	-0.010549

TABLE III
Values of dP/dT_m ^a

P , kbar	dP/dT_m		
	1	2	3
0	31.1	40	—
1	37.7	45	46.1
1.5	—	—	48.3
2	44.8	50	50.8
3	51.9	55	56.5
4	58.5	61	63.7
5	64.3	65	73.0
6	69.3		85.5
7	74.4		
8	81.0		
9	92.0		

^a 1: Present results; 2: results of Osugi and Hara; 3: results of Bassett and Turner; rest as for Table II.

sured the volume change on melting for their semicrystalline sample for pressures up to 4 kbar. Knowing the degree of crystallinity of the sample, it is possible to determine from their results the true volume change on melting of a completely crystalline sample. In this work, we followed a different procedure for determining ΔV for pressures up to 9 kbar. It is based on the knowledge of the equation of states of the crystalline and the amorphous phases. The uncertainty involved in the estimation of ΔV by this method varies between 0.5% and 1% for the lowest and the highest pressure limits. The necessary details are given in the Appendix.

For the determination of dP/dT_m , the smoothed experimental values of T_m for pressures up to 10 kbar were fitted into a fourth-degree polynomial:

$$T_m = a_0 + a_1P + a_2P^2 + a_3P^3 + a_4P^4 \quad (2)$$

The values of the coefficients are given in Table II. The error in the determination of dP/dT_m , taking account of the errors in T_m and P , is estimated to be about 3% for pressures up to 7 kbar, and it becomes 6% at higher pressures. The results for dP/dT_m are given in Table III. The results of our calculation of ΔH from eq. (1) are plotted in Figure 4 along with the results of other workers. The values of Osugi and Hara in this figure have been duly corrected to apply to a completely crystalline sample.

It is observed that the results from various sources show quantitatively marked differences. For a clear understanding of the reasons, reference may be made

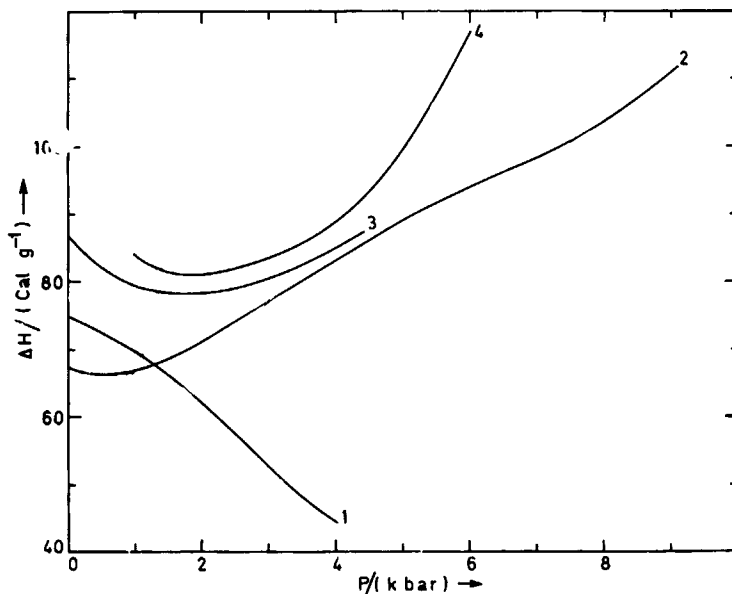


Fig. 4. Variation of ΔH (cal/g) with pressure: (1) Osugi and Hara; (2) present work; (3) Osugi and Hara, with our ΔV values; (4) Basset and Turner.

to Tables III and IV where dP/dT_m and ΔV values used in these references are compared. It may be observed that the ΔV values of Osugi and Hara are lower* than ours, and percentagewise, this difference widens with P . For $P \approx 0$, where the crystalline and amorphous specific volumes are known experimentally with greatest accuracy, we should have $\Delta V = 0.224$ cc/g.⁶ The results of Osugi and Hara³ show here a serious disagreement. On the other hand, our equation-of-state procedure gives a ΔV value in close agreement with this result. The departures in dP/dT_m values in the various cases could be partly ascribed to the differences in the samples employed. It can be shown that the qualitative trend

TABLE IV
Volume Change on Melting, ΔV , for Fully Crystalline Polyethylene^a

P, kbar	ΔV , cc/g	
	1	2
0	0.227	0.195
1	0.174	0.154
2	0.147	0.116
3	0.132	0.086
4	0.121	0.063
5	0.115	
6	0.109	
7	0.103	
8	0.097	
9	0.090	

^a As in Table III.

* The volume discontinuity method used by these authors tends to underestimate the volume change because of lack of sharpness in the melting or freezing process for polymers.

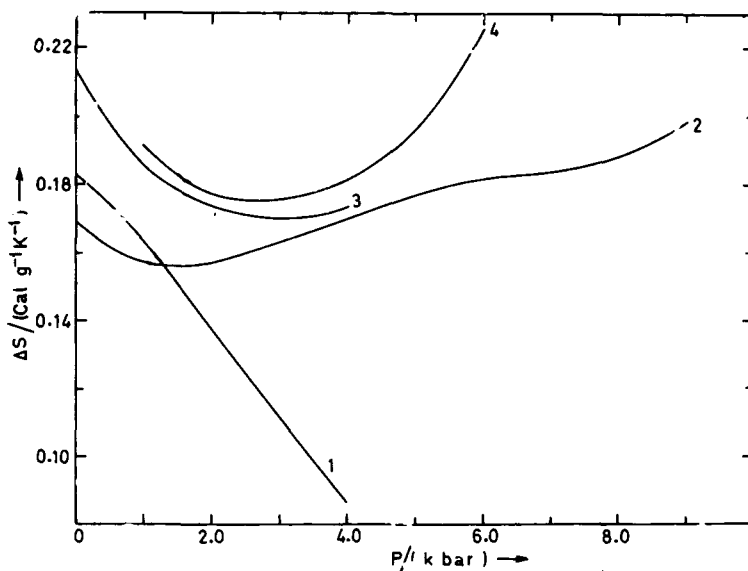


Fig. 5. Variation of ΔS ($\text{cal g}^{-1} \text{ } ^\circ\text{K}^{-1}$) with pressure. The remainder as in Fig. 4.

of variation of ΔH with P depends markedly on the ΔV values. For example, it may be noted from Figure 4 that the ΔH results of Osugi and Hara, based on our ΔV values, show a variation with pressure which agrees qualitatively with our results. Further, it may be mentioned that in the limit $P \simeq 0$, our ΔH result is very close to the currently accepted value,¹⁰ which is 70 cal/g.

Finally, in Figure 5, the entropy of melting, ΔS , as a function of pressure is shown. The differences between the results from various sources are seen to be qualitatively similar to the ΔH case. It is seen from our results that the entropy of fusion after a slow initial decrease with pressure increases comparatively more steeply beyond 2 kbar. This implies that pressure is less effective in producing order in the liquid phase beyond this pressure.

CONCLUSIONS

In the determination of thermodynamic functions of fusion, the weakest link in the purely experimental determination seems to be the measurement of volume change on melting. We have in this study bypassed this difficulty by making use of theoretical or semitheoretical equations of state. An experimental confirmation of the ΔV results is, however, desirable. This would be possible by carrying out unit cell measurements¹⁴ at elevated pressure as close to T_m as possible and PVT measurements of the melt on the other side of the transition.

The authors would like to thank Dr. S. Ramaseshan for allowing the use of high-pressure equipment at the N.A.L. for this investigation.

Appendix

Here, we shall describe the procedure adopted for determining the volume change upon melting as a function of pressure from the knowledge of the melting temperature and the equation of states of the melt and the crystal.

The procedure for the calculation of the melt volume from the Tait equation at a given temperature and pressure has been discussed by us in an earlier publication.¹¹ The range of applicability of eq. (4b) of this reference implies that for polyethylene, the temperature should not exceed 300°C. Since the melting pressure for polyethylene corresponding to this temperature is nearly 10 kbar, the amorphous specific volume, and hence ΔV , calculations were carried out below this pressure.

For the polymer crystal phase, we have recently developed an equation of state¹² which is based on the quantum mechanical version of the cell model. Such a theory in the harmonic approximation has already been used by us for explaining the low-temperature thermal expansivities of the polymer glasses.¹³ In our recent PVT studies of polymer crystal phase, since the interest was in the relatively higher-temperature region, the theory involved two important differences. First, an account of anharmonicity was taken by including the first anharmonic term in the expansion of the cell potential. Secondly, for the sake of simplicity, the vibrational frequency spectrum for the volume-dependent degrees of freedom was replaced by a single frequency. This approximation is known to be good except at very low temperatures.

The resulting equation of state has the form

$$\bar{P}\bar{V} = 2(A\bar{V}^{-4} - B\bar{V}^{-2}) + 3\gamma\bar{\theta}F_1\left(\frac{\bar{\theta}}{\bar{T}}\right) + \frac{9}{8}\gamma\beta\bar{V}^2\bar{\theta}^2F_2\left(\frac{\bar{\theta}}{\bar{T}}\right) - \frac{9}{4}\alpha\beta\bar{V}^2\bar{\theta}^2F_3\left(\frac{\bar{\theta}}{\bar{T}}\right) \quad (\text{A.1})$$

here \bar{P} , \bar{V} , and \bar{T} are the reduced pressure, reduced volume, and reduced temperature, respectively, while

$$F_1\left(\frac{\bar{\theta}}{\bar{T}}\right) = \frac{1}{2} + \frac{1}{e^{\bar{\theta}/\bar{T}} - 1} \quad (\text{A.2})$$

$$F_2\left(\frac{\bar{\theta}}{\bar{T}}\right) = \frac{1}{2} + \frac{3e^{\bar{\theta}/\bar{T}} + 1}{(e^{\bar{\theta}/\bar{T}} - 1)^2} - \frac{\bar{\theta}}{\bar{T}} \frac{e^{\bar{\theta}/\bar{T}}(e^{\bar{\theta}/\bar{T}} + 3)}{(e^{\bar{\theta}/\bar{T}} - 1)^3} \quad (\text{A.3})$$

$$F_3\left(\frac{\bar{\theta}}{\bar{T}}\right) = \frac{1}{2} + \frac{2e^{\bar{\theta}/\bar{T}}}{(e^{\bar{\theta}/\bar{T}} - 1)^2} \quad (\text{A.4})$$

$$\alpha = 1 + \frac{2A_1\bar{V}^{-2}}{(A_1\bar{V}^{-2} - 2B_1)} - \frac{A_2\bar{V}^{-2}}{(A_2\bar{V}^{-2} - 2B_2)} \quad (\text{A.5})$$

$$\beta = \frac{A_2\bar{V}^{-2} - 2B_2}{(A_1\bar{V}^{-2} - 2B_1)^2} \quad (\text{A.6})$$

$$\gamma = \gamma_0 \left[1 - \beta\bar{\theta}_0\bar{V}^2 \left\{ F_1\left(\frac{\bar{\theta}_0}{\bar{T}}\right) - \frac{(\bar{\theta}_0/\bar{T})e^{\bar{\theta}_0/\bar{T}}}{(e^{\bar{\theta}_0/\bar{T}} - 1)^2} \right\} \right] - \alpha\beta\bar{\theta}_0\bar{V}^2 F_1\left(\frac{\bar{\theta}_0}{\bar{T}}\right) \quad (\text{A.7})$$

$$\gamma_0 = \left[\frac{4}{3} + \frac{A_1\bar{V}^{-2}}{(A_1\bar{V}^{-2} - 2B_1)} \right] \quad (\text{A.8})$$

and

$$\bar{\theta} = \bar{\theta}_0 \left[1 + \beta\bar{\theta}_0\bar{V}^2 F_1\left(\frac{\bar{\theta}_0}{\bar{T}}\right) \right]^{1/2} \times \left[1 + \frac{3}{8}\beta\bar{V}^2\bar{\theta}_0 \left[1 + \beta\bar{\theta}_0\bar{V}^2 F_1\left(\frac{\bar{\theta}_0}{\bar{T}}\right) \right]^{1/2} \right] \quad (\text{A.9})$$

where $\bar{\theta}_0 = h\nu_0/kT^*$ is the reduced characteristic temperature corresponding to the harmonic oscillation frequency ν_0 , and T^* is the temperature-reducing parameter. Further, A and B are numerical constants with values $A = 1.011$, $B = 1.2045$, $A_1 = 22.1060$, $B_1 = 5.2797$, $A_2 = 200.6530$, and $B_2 = 14.3340$.

It was found that, for polyethylene, if we take $\bar{\theta}_0 = 0.054$, $T^*/K = 6918$, and the volume-reducing parameter V^* (cc/g) = 0.9954, the experimental VT results of Davis, Eby, and Colson¹⁴ for the crystal phase are explained accurately above 130°K. Further, the PVT results of Hellwege et al.¹⁵ and Olabisi and Simha¹⁶ for semicrystalline polyethylene below 60°C could be explained nicely by making the reasonable assumption that the degree of crystallinity is not affected by pressure.

The results of calculation of volume change upon melting as a function of pressure are given in Table IV.

References

1. S. Matsuoka, *J. Polym. Sci.*, **57**, 569 (1962).
2. E. Baer and J. L. Kardos, *J. Polym. Sci.*, **A-3**, 2827 (1965).

3. J. Osugi and K. Hara, *Rev. Phys. Chem. Jpn.*, **36**, 28 (1966).
4. F. E. Karasz and L. D. Jones; *J. Phys. Chem.*, **71**, 2234 (1967).
5. D. V. Rees and D. C. Basset, *J. Polymer Sci.*, **B7**, 273 (1969).
6. T. Davidson and B. Wunderlich, *J. Polym. Sci. A-2*, **7**, 377 (1969).
7. P. D. Calvert and D. R. Uhlmann, *J. Polym. Sci. A-2*, **10**, 1811 (1972).
8. D. C. Bassett and B. Turner, *Phil. Mag.*, **29**, 925 (1974).
9. R. K. Jain, R. N. Gupta, and V. S. Nanda, *J. Macromol. Sci. Phys.*, **B11**, 411 (1975).
10. B. Wunderlich, *Macromolecular Physics*, Academic Press, New York, 1973, Chap. 4, p. 388.
11. V. S. Nanda and R. Simha, *J. Chem. Phys.*, **41**, 3870 (1964).
12. Y. R. Midha and V. S. Nanda, to be published; Y. R. Midha, Equation of State and Related Properties of Polymeric and Monomeric Materials, Ph.D. Thesis, University of Delhi, 1975.
13. R. Simha, J. M. Roe, and V. S. Nanda, *J. Appl. Phys.*, **43**, 4312 (1972).
14. G. T. Davis, R. K. Eby, and T. R. Colson, *J. Appl. Phys.*, **41**, 4316 (1970).
15. K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z.*, **183**, 110 (1962).
16. O. Olabisi and R. Simha, *Macromolecules*, **8**, 206 (1975).

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