

Pressure-Volume-Temperature Behavior of High Density Polyethylene

GEORGE N. FOSTER III,* NATHAN WALDMAN, and
RICHARD G. GRISKEY, *Chemical Engineering Department, Virginia
Polytechnic Institute, Blacksburg, Virginia*

Synopsis

Equilibrium pressure-volume-temperature behavior in both the solid and molten regions was determined for a high density ($\rho = 0.958$ g./cm.³) polyethylene. Data were measured with a recently developed compressibility device capable of obtaining precise and accurate data. Residual curve treatment showed that the data were true equilibrium data. Compressibilities calculated from the data of this work compared favorably to existing data which were limited to 205°C. The present work extended the compressibility behavior to 250°C. It was also found that differences in compressibility of low and high density polyethylenes were not eliminated in the molten region, indicating that the effect of differences in morphology was not eliminated. The Spencer-Gilmore equation was fitted to the data of the present work. The internal pressure (π) term of the equation showed a definite relation to polymer morphology.

Lack of fundamental physical data is a major deterrent to the progress of polymer science. A particularly serious instance is the need for compressibility behavior of high polymers.

A number of investigators, among them Bridgeman,¹ Parks and Richards,² Spencer and Gilmore,^{3,4} Weir,⁵⁻⁷ Matsuoka,⁸⁻¹⁰ Hellwege et al.,¹¹ and Heydemann and Guicking¹² have measured such data. These studies have, however, been limited both in the range of temperature and/or pressure investigated and the types of polymers studied.

A particular example is the case of polyethylene. A number of investigators^{2,4,7-11} have studied polyethylenes having low densities at ambient pressure and temperature (i.e., $\rho_0 = 0.920$ g./cm.³ or less). However, only two studies^{10,11} were found that considered the higher density material ($\rho_0 = 0.973$ and 0.981 g./cm.³). Both these studies were limited with respect to temperature.

The present study was undertaken to satisfy the need for higher temperature data and also to determine the behavior of a polyethylene having a density intermediate ($\rho_0 = 0.958$ g./cm.³) to those previously studied.

The apparatus used in the study is shown schematically in Figure 1. The compressibility chamber is depicted in Figure 2. Polymer samples were placed in the chamber which was evacuated after it had been immersed

* Present address: Union Carbide Plastics Company, Bound Brook, New Jersey.

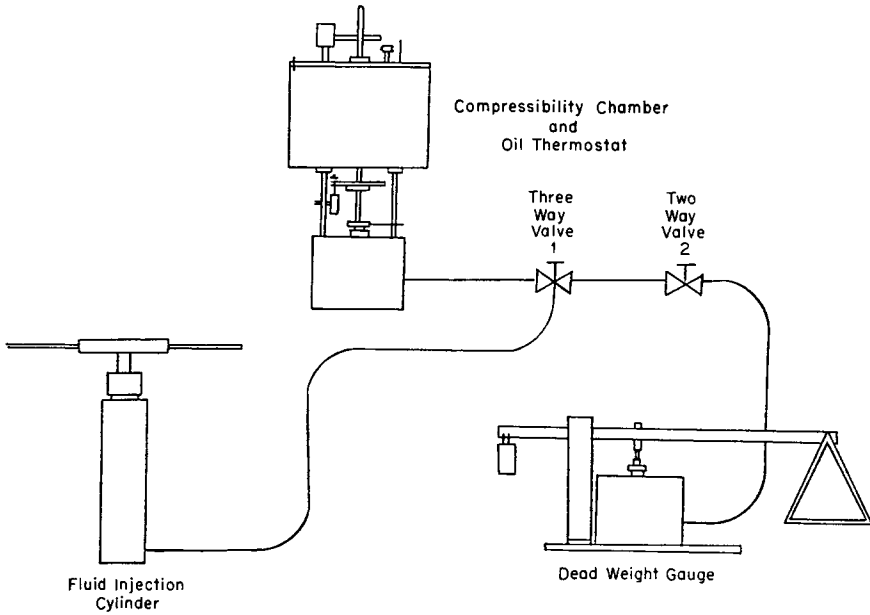


Fig. 1. Schematic of compressibility equipment.

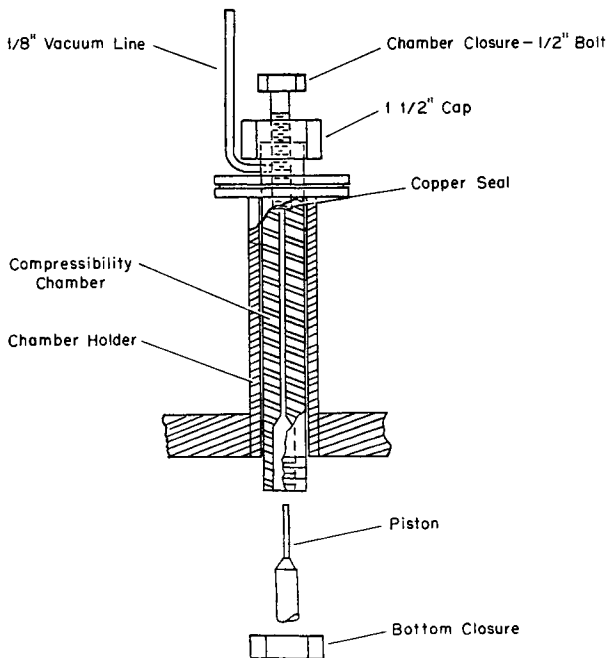


Fig. 2. Compressibility chamber and holder.

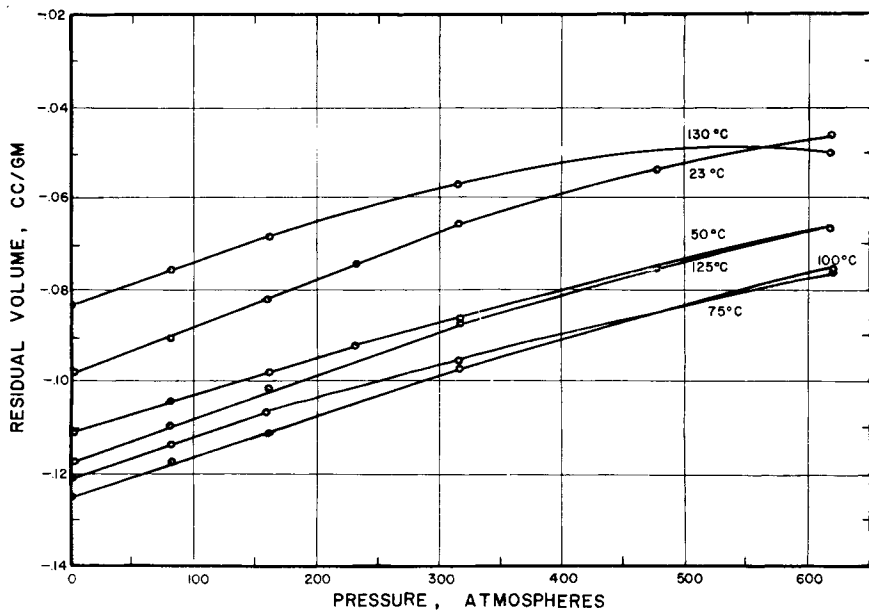


Fig. 3. Volume residuals for solid polyethylene.

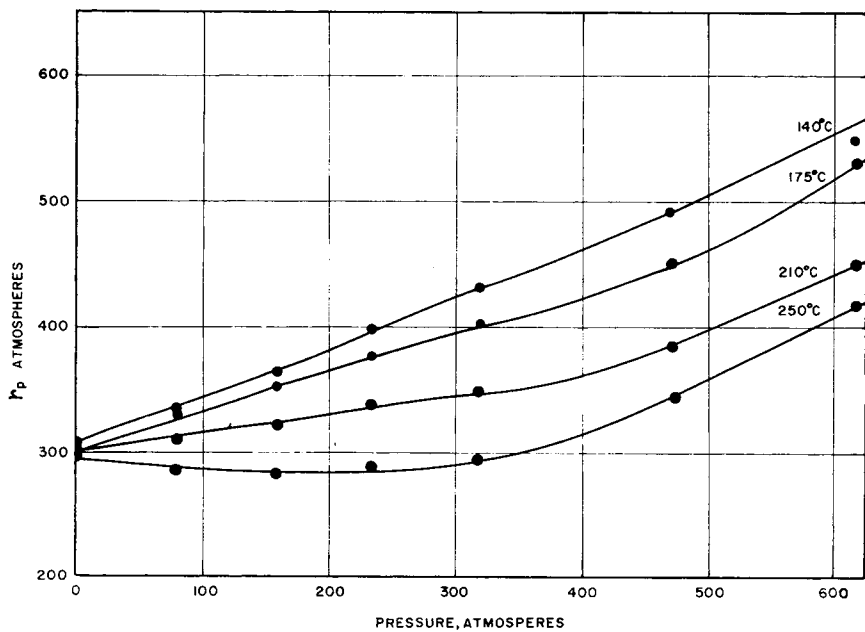


Fig. 4. Pressure residuals for molten polyethylene.

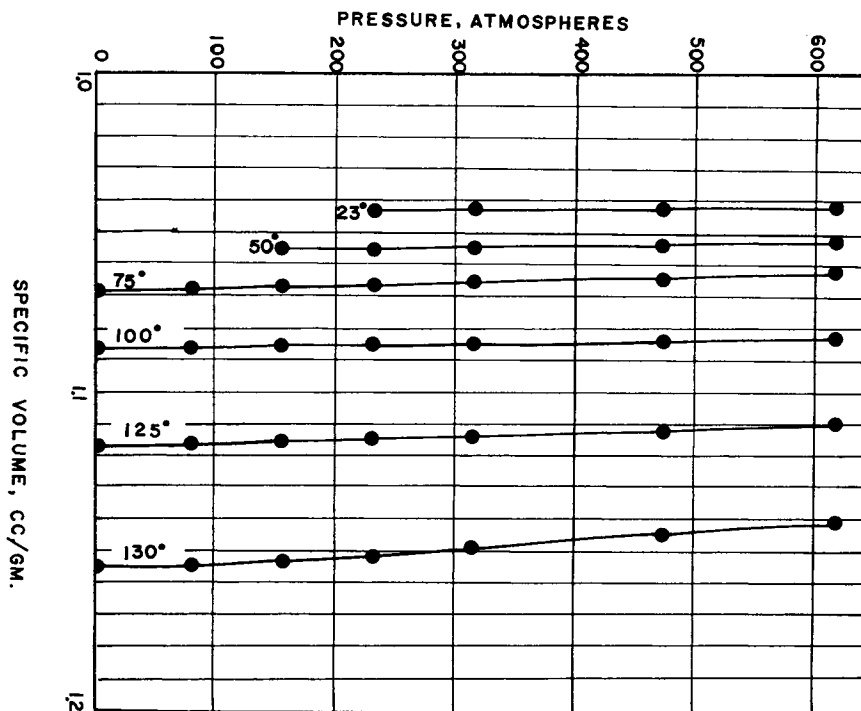


Fig. 5. Pressure-volume-temperature data for solid polyethylene.

in the oil bath thermostat. The device was then thoroughly seasoned. A careful annealing procedure was followed for solid-phase measurements. Readings were then taken by holding temperature constant, changing volume, and then balancing the pressure for a long enough period of time to assure the proper equilibrium pressure-volume-temperature combination. A detailed description of apparatus and procedure is given elsewhere.¹³

Temperatures were controlled to $\pm 0.10^\circ\text{C}$. Volume accuracy was 0.25% or better while the accuracy of pressure measurements were 1% or less than 1%.

Data were measured for both the solid and molten regions from pressures of 1 to 618 atm. and temperatures from 23 to 250°C . These raw data were smoothed by using volume and pressure residual curves. The technique of smoothing with residuals involves first calculating either a volume or pressure from an equation of state (at a selected temperature and pressure or a selected volume and pressure). In this work the Spencer and Gilmore^{3,4} equation of state,

$$(P + \pi)(V - W) = (R/M)T \quad (1)$$

was used, where P is pressure, V is volume, T is absolute temperature, R is the gas constant, M is the molecular weight of an interaction unit, and

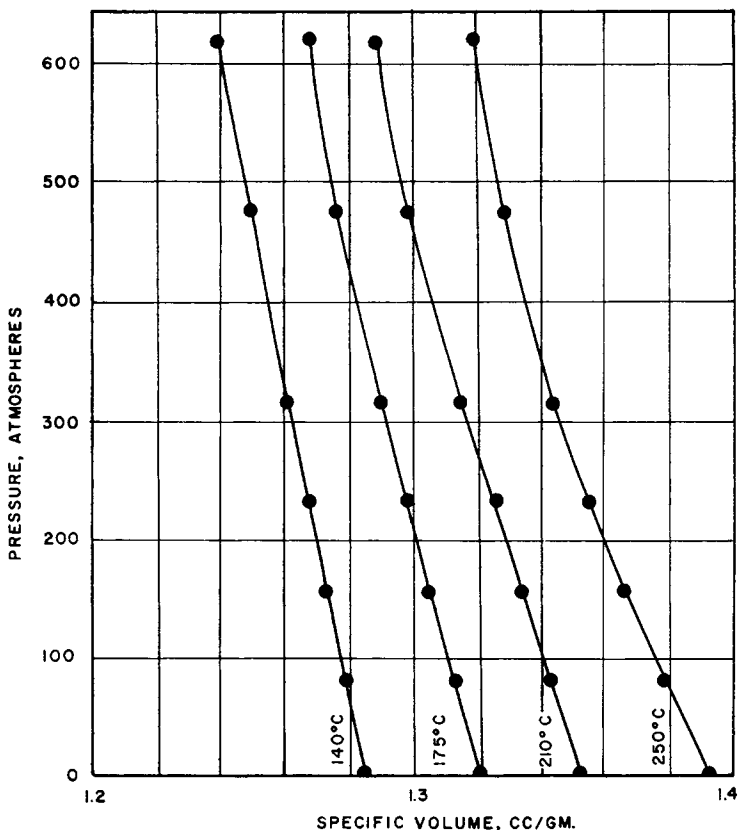


Fig. 6. Pressure-volume-temperature data for molten polyethylene.

π and W are constants of the Spencer-Gilmore equation. Next the pressure or volume residual r is calculated:

$$r_p = P_{\text{calc}} - P_{\text{exptl}} \quad (2)$$

$$r_v = V_{\text{calc}} - V_{\text{exptl}} \quad (3)$$

These residual values can then be plotted as isothermal curves versus either volume or pressure. Figures 3 and 4 represent such plots. Next smoothed data points can be obtained by using the residual together with calculated values:

$$P_{\text{exptl}} = P_{\text{calc}} - r_p \quad (4)$$

$$V_{\text{exptl}} = V_{\text{calc}} - r_v \quad (5)$$

The smoothed data are presented in Tables I and II and Figures 5 and 6.

Residual curves also provide a means of checking the consistency of experimental data as well as the attainment of equilibrium during the experiments.^{14,15} Smooth curves show that data are consistent and that

TABLE I
Pressure-Volume-Temperature Data for High Density Polyethylene
($\rho_0 = 0.958 \text{ g./cm.}^3$)

Temperature, °C.	Volume, cm. ³ /g.						
	1 atm.	79.3 atm.	158.5 atm.	232 atm	316 atm.	474 atm.	618 atm.
23	—	—	—	1.0424	1.0423	1.0422	1.0419
50	—	—	1.0542	1.0542	1.0540	1.0537	1.0528
75	1.0680	1.0676	1.0669	1.0660	1.0650	1.0640	1.0621
100	1.0861	1.0857	1.0853	1.0852	1.0843	1.0840	1.0827
125	1.1162	1.1157	1.1152	1.1140	1.1137	1.1119	1.1101
130	1.1549	1.1530	1.1513	1.1490	1.1446	1.1446	1.1405

TABLE II
Pressure-Volume-Temperature Data for Molten High Density Polyethylene

Temperature, °C.	Volume, cm. ³ /g.						
	1 atm.	79.3 atm.	158.5 atm.	232 atm.	316 atm.	474 atm.	618 atm.
140	1.2852	1.2793	1.2725	1.2675	1.2607	1.2493	1.2393
175	1.3211	1.3132	1.3047	1.2979	1.2899	1.2759	1.2679
210	1.3526	1.3430	1.3336	1.3254	1.3147	1.2983	1.2887
250	1.3925	1.3784	1.3653	1.3549	1.3431	1.3282	1.3187

equilibrium is attained. The relative smoothness of the plots in Figures 3 and 4 indicate that this indeed seems to be the case for the present work.

No direct comparison was made between the pressure-volume-temperature data of the present work and that of the previous investigations. The reason for this was that the morphology of the polyethylene of the present study differed from that of the polyethylenes studied previously. These morphological differences were reflected in the ρ_0 values for the various polymers.

Instead, the data were compared on the basis of compressibilities $(1/V)(\Delta V/\Delta P)_T$ for molten polymer behavior. It was considered that the compressibility behavior would give a truer reflection of similarities or dissimilarities than a comparison of specific volumes at a given temperature and pressure. In addition, such a comparison in the melt region would be more meaningful since morphological differences should be minimized.

The comparison is shown in Figure 7. As can be seen, there is excellent agreement between the data of the present work and that determined for high density polyethylene by Hellwege et al.¹¹ In addition, the data for low density polyethylene of Hellwege et al.¹¹ and those of Parks and Richards² shows fair agreement. However, all of the data of Matsuoka¹⁰ deviates considerably.

A number of conclusions can be drawn from Figure 7. First, the excellent agreement of the data of this work with those of Hellwege et al.

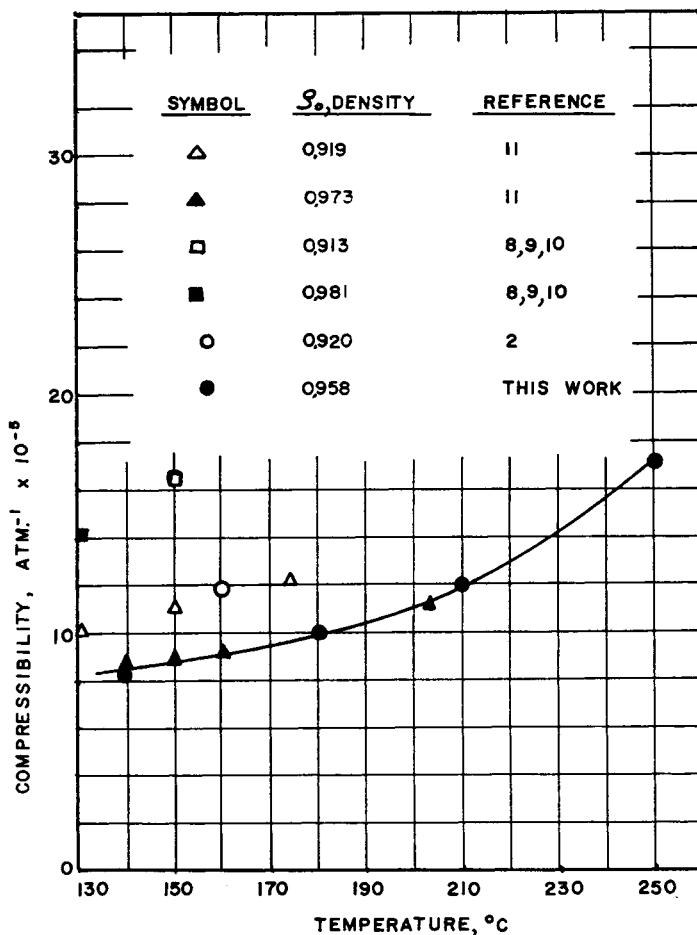


Fig. 7. Comparison compressibility data for molten polyethylene: (Δ) $\rho_0 = 0.919$ g./cm.³;¹¹ (\blacktriangle) $\rho_0 = 0.973$ g./cm.³;¹¹ (\square) $\rho_0 = 0.913$ g./cm.³;⁸⁻¹⁰ (\blacksquare) $\rho_0 = 0.981$ g./cm.³;⁸⁻¹⁰ (\circ) $\rho_0 = 0.920$ g./cm.³;² (\bullet) $\rho_0 = 0.958$ g./cm.³.

establishes the compressibility behavior of high density molten polyethylene up to 250°C.

Next, differences in the compressibility behavior of high and low density polyethylene are still apparent even in the molten state. Thus, apparently the effect of morphological differences between high- and low-density polyethylenes is not completely eliminated in the molten region. Finally, it appears that the data of Matsuoka disagree drastically with those of other investigators.

A possible reason for this last occurrence might be the degree of temperature control attained in the various studies. For example, Matsuoka reports a $\pm 1.0^\circ\text{C}$. control as compared to $\pm 0.1^\circ\text{C}$. for the present work. This in itself could account for the disagreement.

The Spencer and Gilmore equation of state was fitted to the data of the present work in both the molten and solid regions. Values of constants obtained were $M = 28.1$, $\pi = 6769$ atm., and $W = 0.917$ cm.³/g. for the solid polymer. M and π values were the same for the molten polymer and W was 1.11 cm.³/g. Spencer and Gilmore⁴ report values of 28.1, 3240 atm. and 0.875 cm.³/g. for M , π , and W , respectively for low density polyethylene. Differences in the π (internal pressure) values between the present work and that of Spencer and Gilmore can be attributed to two reasons. First, the value reported by the latter investigators was derived from nonequilibrium data while that of the present work was obtained from equilibrium data. The second reason is that polymer morphology influences the π value. This can be seen from Spencer and Gilmore's⁴ work which reported a higher π value for low density polyethylene than for polystyrene, the former polymer being more crystalline in nature than the highly amorphous polystyrene. On this basis it is not surprising that a still higher π value was obtained from the even more crystalline high density polyethylene.

Grateful acknowledgment is made to the National Science Foundation for support of this research by means of grant GP-2099, and to E. I. du Pont de Nemours and Co., Inc. for the polyethylene samples.

References

1. Bridgeman, P. W., *Proc. Am. Acad. Arts Sci.*, **76**, 71 (1948).
2. Parks, W., and R. B. Richards, *Trans. Faraday Soc.*, **45**, 206 (1949).
3. Spencer, R. S., and G. D. Gilmore, *J. Appl. Phys.*, **20**, 502 (1949).
4. Spencer, R. S., and G. D. Gilmore, *J. Appl. Phys.*, **21**, 523 (1950).
5. Weir, C. E., *J. Res. Natl. Bur. Std.*, **45**, 468 (1949).
6. Weir, C. E., *J. Res. Natl. Bur. Std.*, **50**, 153 (1953).
7. Weir, C. E., *J. Res. Natl. Bur. Std.*, **53**, 245 (1954).
8. Matsuoka, S., *J. Polymer Sci.*, **42**, 511 (1960).
9. Matsuoka, S., *J. Polymer Sci.*, **57**, 567 (1962).
10. Matsuoka, S., and Maxwell, B., *J. Polymer Sci.*, **32**, 131 (1958).
11. Hellwege, K. H., W. Knappe, and P. Lehmann, *Kolloid-Z.*, **183**, 110 (1962).
12. Heydemann, P., and H. D. Guicking, *Kolloid-Z.*, **193**, 16 (1963).
13. Foster, G. N., and R. G. Griskey, *J. Sci. Instr.*, **41**, 759 (1964).
14. Li, K., and L. N. Canjar, *Chem. Eng. Progr. Symp. Ser.*, **49**, No. 7, 147 (1953).
15. Canjar, L. N., paper presented at the meeting of the Division of Petroleum Chemistry, American Chemical Society, New York, September 9, 1957.

Résumé

Le comportement à l'équilibre pression-volume-température dans les régions à l'état solide et à l'état fondu des polyéthylènes a été déterminé pour le polyéthylène de densité élevée ($\rho = 0,958$ g/cc). Les résultats ont été mesurés en employant une méthode de compressibilité récemment décrite et capable de fournir des résultats récis et reproductibles. Le traitement ultérieur de la courbe montre que les résultats sont des véritables résultats d'équilibre. Des compressibilités calculées au départ des résultats de ce travail se comparent favorablement aux données existantes, qui étaient limitées à 205°C. Ce présent travail étend le domaine de compressibilité jusque 250°C. On a trouvé que les différences de compressibilité des polyéthylènes de basses et hautes densités ne sont pas éliminées dans la région à l'état fondu, ce qui indique que les effets des différences de mor-

phologie ne sont pas éliminées. L'équation de Spencer-Gilmore s'adapte aux résultats du présent travail. La pression interne, π , de l'équation montre une relation définie avec la morphologie du polymère.

Zusammenfassung

Die Abhängigkeit des Gleichgewichtsvolumens von Druck und Temperatur in den festen und geschmolzenen Bereichen eines Polyäthylens hoher Dichte ($\rho = 0,958 \text{ g/cc}$) wurde bestimmt. Die Messergebnisse wurden mit einer neu entwickelten Kompressibilitätsvorrichtung erhalten, welche zuverlässige und genaue Daten liefert. Die Residualkurvenbehandlung zeigt, dass die Daten wahre Gleichgewichtsdaten sind. Die aus den Daten der vorliegenden Arbeit berechneten Kompressibilitätswerte stimmen gut mit vorhandenen, bei 205°C erhaltenen Daten überein. In der vorliegenden Arbeit wird das Kompressibilitätsverhalten bis zu 250°C untersucht. Weiters wurde gefunden, dass die Kompressibilitätsunterschiede zweier Polyäthylene niedriger und hoher Dichte im geschmolzenen Bereich nicht eliminiert werden, was beweist, dass der Einfluss der morphologischen Unterschiede weiter besteht. Die Gleichung von Spencer-Gilmore wurde zur Wiedergabe der erhaltenen Daten verwendet. Der Term für der inneren Druck, π , der Gleichung zeigte eine definierte Beziehung zur Polymermorphologie.

Received September 7, 1965

Prod. No. 1283