

Fig. 3. X-ray diffraction for the pressure-crystallized and injection-molded samples after annealing. Densities are 0.984 and 0.976 g./cm.³, respectively.

While the high density resulting from the high pressure of crystallization thus seems largely due to the high degree of crystallinity, this general increase in crystallinity does not seem to be the only characteristic of the high pressure process. After the data shown in Figure 1 were taken, the same two samples were annealed for 17 hr. at 120°C., for 5 hr. at 129°C., and for 16 hr. at 110°C., successively. Upon cooling the specimens down to 25°C., the densities of the molded sample and the high pressure-crystallized sample were both found to have increased to 0.977 and 0.984 g./cm.³, respectively. The x-ray diffractions of these samples after annealing are shown in Figure 3. Although the 110 peak of the pressure-crystallized sample still remains higher than that of the originally molded sample, the 200 peak of the latter has increased above that of the denser material. Also by comparing the x-ray results on the pressure-crystallized specimen before and after annealing, it was found that the 110 peak had decreased after annealing, even though the density has increased. The fact that the ratio of the 110 peak to the 200 peak for the pressure-crystallized sample is greater than that for the ordinary sample (both annealed and unannealed) confirms that there are some morphological differences between the two. There should then be a difference in some physical properties, even if these two are of an identical density. This view is supported by the experiments of Brazier and Maxwell⁹ on some fracture properties of Marlex polyethylene crystallized at various pressures and temperatures. Long-time brittle fracture tests were made on these specimens, since this has long been suspected to be sensitive to the crystalline texture of polyethylene.¹⁰ The results show that samples with identical densities exhibit markedly different fracture characteristics depending on the pressure of crystallization.

Summary

By inducing crystallization in linear polyethylene by hydrostatic pressure, an unusually high density can be attained. Such a high density seems largely due to high crystallinity. The high density material thus prepared can generally be annealed to even a higher density. The crystalline texture of such a material is different from that of an ordinary molded sample.

The author wishes to thank Dr. W. P. Slichter for making all the x-ray measurements reported in this paper, as well as for various useful discussions.

References

1. Mandelkern, L., *Rubber Revs.*, **32**, 1392 (1959).
 2. Matsuoka, S., *J. Polymer Sci.*, **42**, 511 (1960).
 3. Mandelkern, L., in *Growth and Perfection of Crystals*, R. H. Doremus, Ed., Wiley, New York, 1958, p. 467.
 4. Flory, P. J., and A. D. McIntyre, *J. Polymer Sci.*, **18**, 592 (1955).
 5. Price, F. P., *J. Chem. Phys.*, **31**, 1679 (1959).
 6. Lauritzen, J. I., Jr., and J. D. Hoffman, *J. Research Natl. Bur. Standards*, **64A**, 73 (1960).
 7. Matsuoka, S., and B. Maxwell, *J. Polymer Sci.*, **32**, 131 (1958).
 8. Slichter, W. P., presented at Am. Phys. Soc. D.H.P.P. Meeting at Detroit, Michigan, March, 1960.
 9. Brazier, T. S., and B. Maxwell, *Plastics Laboratory Tech. Report 54B*, Princeton University, 1959.
 10. Hopkins, I. L., W. O. Baker, and J. B. Howard, *J. Appl. Phys.*, **21**, 206 (1950).
- Bell Telephone Laboratories, Inc. S. MATSUOKA
Murray Hill, New Jersey

Received May 5, 1960

On Melting Characteristics of Linear Polyethylene

Dilatometric data on semicrystalline polymers, both above and below their melting temperatures are numerous, and linear polyethylene has perhaps been investigated most often.¹⁻³ These data usually differ in some details. Difficulties arise because (1) below the melting point the existence of equilibrium is uncertain, since the density of the polymer depends on the conditions of crystallization and also because (2) the volume-temperature curve is sensitive to the rate of heating.

In this study, dilatometric measurements were made on Marlex 6000 type 50 linear polyethylene. A commercial dilatometer (Scientific Glass No. 1025) was modified for the purpose, and a procedure similar to that by Bekkedahl⁴ was followed. An automatic temperature control system designed by J. L. Lundberg of these laboratories was used. It controlled the bath temperature within 0.01°C., for an indefinite period of time.

Dilatometric measurements were first taken on a compression-molded sample (density 0.963 at 23°C.) at two different rates of heating. On the first run, a heating rate of 1°C./42 hr. (in increments of 0.2°C.) was employed near the melting point. After this run was complete, the bath and the sample were allowed to cool to 20°C., and the second experiment was made on the same sample (somewhat denser as the result of slow cooling) at the rapid heating rate of 10°C./hr.

It is clear from the results shown in Figure 1 that a rapid rate of heating induces partial melting at lower temperatures. Furthermore, it was also noticed during the experiment that some volume increase would immediately follow an initial temperature increase, but when the temperature was kept constant at this new level the volume would de-

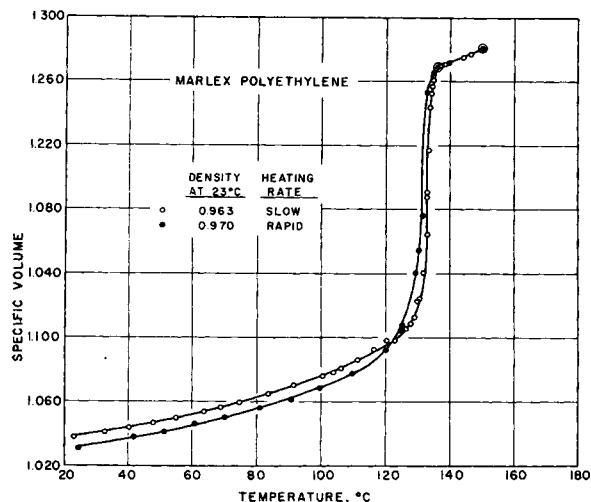


Fig. 1. Specific volume-temperature curves for Marlex polyethylene with two different rates of heating: (O) 1°C./42 hr.; (●) 10°C./hr.

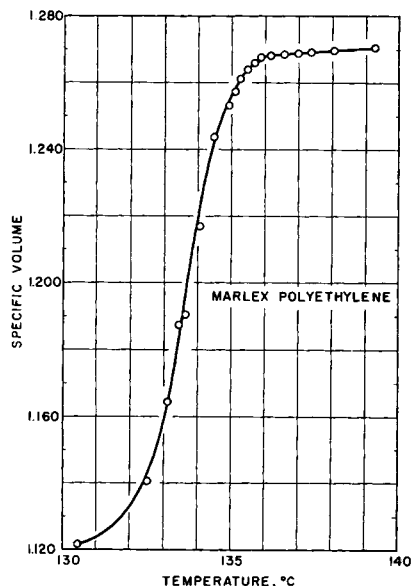


Fig. 2. Details of the specific volume-temperature curve near the melting point for the slow rate of heating shown in Fig. 1.

crease with time. The decrease continued for more than 4 hr. at each temperature level once the partial melting range had been reached. This volume sensitivity to the rate of heating in the partial melting region seems to support Flory's theory^{5,6} of imperfect crystalline segments melting to form more perfect crystals.

The portion of the volume-temperature curve for the slow rate of heating from 130 to 140°C. is expanded in Figure 2 to show more detail near the melting point. Instead of having a sharp, well-defined melting point,^{1,6} it can be seen that Marlex exhibits a sigmoidal transition curve of the type previously observed in copolymers.⁶ Upon a close examination, this curve was found to diverge from the supercooled curve at about 137°C. In Figure 3

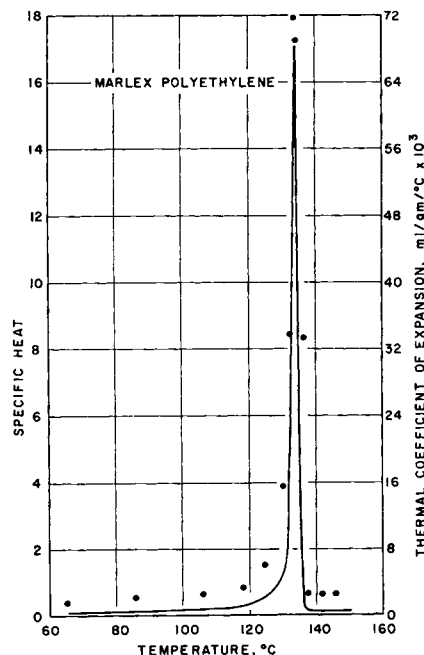


Fig. 3. Specific heat (●) (from Wunderlich and Dole⁷) and thermal expansion coefficient (—) (from Fig. 2) vs. temperature for Marlex.

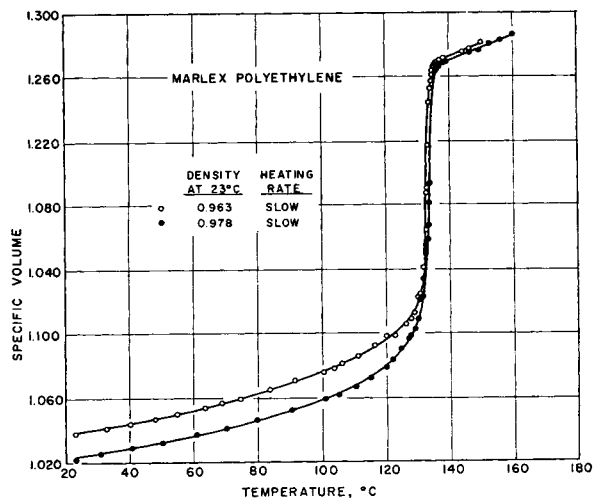


Fig. 4. Specific volume-temperature curves for Marlex: (O) compression-molded sample; (●) pressure-crystallized sample, both by slow heating (1°C./42 hr.).

the thermal expansion coefficient has been compared with the specific heat data obtained for Marlex 50 by Wunderlich and Dole.⁷ The maxima for both occur at very nearly the same temperature. Wunderlich and Dole have attributed the existence of such finite maxima to the branch points or chain ends, but the melting point itself determined in this manner (134.85°C.) is not in agreement with the result presented here.

The same slow rate of heating (1°C./42 hr.) was employed in studying volume change in a pressure-crystallized sample with the density of 0.978 g./cm.³. The sample was pre-

pared by inducing crystallization in the melt at 150°C. under 2000 atm. for 2 hr. and then slowly cooling. The difference in density between the compression-molded and the pressure-crystallized samples seems to persist up to the melting point at the same slow rate of heating (Fig. 4).

Some highly significant observations were made during this experiment. When the temperature was increased from 137 to 150°C. over a 7-hr. period, the pressure-crystallized sample continued to exhibit several small (1–2 mm. in diameter) translucent spots. After an elapsed time of 16 hr., at 150°C. these spots became less defined, and disappeared almost completely when the temperature was further increased to 152°C.

When this experiment was ended at 161°C., the sample was left to cool in the bath and was found to have recrystallized to the original pressure-crystallized density of 0.978 g./cm.³. Since such a high density is not ordinarily obtainable under atmospheric pressure in a short time interval, the result suggests that some "memory" of the previous crystalline state had still persisted for several hours at 10–20°C. above the melting temperature. Dilatometric measurements show that the melting point of this sample is essentially the same ($\pm 0.5^\circ\text{C}$.) as that of the compression-molded sample, but a more sensitive measurement would conceivably have revealed the existence of order in this presumably nonequilibrium melt.

The authors wish to thank Messrs. I. L. Hopkins and C. E. Rogers for various useful discussions concerning the instrumentation.

References

1. Quinn, F. A., Jr., and L. Mandelkern, *J. Am. Chem. Soc.*, **80**, 3178 (1958).
2. Marker, L., R. Early, and S. L. Aggarwal, *J. Polymer Sci.*, **38**, 369 (1959).
3. Bueche, F., *J. Polymer Sci.*, **22**, 113 (1956).
4. Bekkedahl, N., and L. A. Wood, *J. Appl. Phys.*, **17**, 362 (1946).
5. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, Chap. 8, p. 567.
6. Mandelkern, L., *Chem. Revs.*, **56**, 903 (1956).
7. Wunderlich, B., and M. Dole, *J. Polymer Sci.*, **24**, 201 (1957).

S. MATSUOKA
C. J. ALOISIO

Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

Received June 2, 1960

Moisture Permeability of Polymers. Effect of Symmetry of Polymer Structure

In order to be able to correlate water vapor permeability with polymer structure, it is necessary that one be able to measure the permeability of polymeric films as completely amorphous structures or to calculate the permeability of the amorphous regions based on data obtained with partially crystalline films which include a large number of the inter-

esting polymeric structures. In a previous paper,¹ it has been shown for polyethylene terephthalate, nylon 610, and polyethylene (at densities above about 0.94 g./cc.) that the water vapor permeability P for a given polymeric structure varied directly as the square of the amorphous volume fraction X_a , i.e., $P = P_a X_a^2$, in which P_a is the permeability of the film as a completely amorphous structure. This relation also appears to hold for other hydrophilic polymers such as nylon 6 and nylon 66; these data will be reported at a later date. It is the purpose of this letter to show the utility of this relation in the isolation of some interesting effects of short-chain branching on the water vapor permeability of vinyl-type polymers. The water vapor permeabilities were determined as previously reported¹ at a 53-mm. Hg vapor pressure differential at 39.5°C. and reported, for thicknesses of 1.0 mil, in units of grams/100 m.²/hr.; such data are readily converted to more conventionally used permeability units, i.e., cc. (STP)/sec./cm.²(area)/mm. (thickness)/cm. Hg (vapor pressure differential), by multiplying by 0.166×10^{-8} .

The particular polymeric structures of interest are those from 1-substituted and 1,1-disubstituted vinyl monomers in which the substituted group is the nonpolar methyl group in one case and the polar chlorine atom in another case. These polymers are shown in Table I and represent two structural

TABLE I
Effect of Structure on Water Vapor Permeability

Polymer	Water vapor permeability P_a , g./100 m. ² /hr./mil	Comments
Polyethylene	200–220	P_a calculated (see ref. 1)
Polyisobutylene	90	P_a measured*
Polypropylene	420	P_a calculated from film with 2% crystallinity
Polyvinyl chloride	~300	P_a estimated from data as described in this letter
Polyvinylidene chloride	~30	P_a calculated as described in this letter.

* Morgan² reports value of 76 g./100 m.²/hr./mil.

series: (1) polyethylene, polypropylene, and polyisobutylene; and (2) polyethylene, polyvinyl chloride, and polyvinylidene chloride. The value of the water vapor permeability of the linear polyethylene structure is that calculated in a previously reported work.¹ Before considering the data, some comments on the structures *per se* and their water vapor permeabilities should be made. The water vapor permeability of polyisobutylene was determined on a completely amorphous structure and that of polypropylene on structures with less than 10% crystallinity. Also, both structures are linear, having been prepared with coordination-type catalysis in the case of polypropylene and in a low temperature, ionic-catalyzed polymerization in the case of polyisobutylene. In the case of the polyvinyl chloride and polyvinylidene chloride structures, however, the situation is substantially different. Polyvinylidene chloride homopolymer is highly crystalline and insoluble; it was necessary to arrive at the permeability of this homopolymer by extrapola-