

How temperature varies with depth in the deep ocean depends on the ratio, z^* , of the vertical eddy diffusivity to the upwelling rate (23, 24), and temperature-depth relationships have been used to calculate z^* . The z^* value can, in fact, be calculated from the depth dependence of any conservative tracer in a region where only two water masses are mixing. The $\delta^{18}\text{O}$ of calcite precipitating in isotopic equilibrium with seawater is a function of temperature and of the seawater $\delta^{18}\text{O}$, and therefore is, to a first approximation, a suitable conservative tracer (25). The $\delta^{18}\text{O}$ -depth trend in the early Pliocene (Fig. 1) is adequately fit by a curve having a z^* value equal to the present Pacific value of about 1 km (23, 24). Today, the area of the Pacific studied here is marked by mixing of more than two water masses, and thus cannot be strictly treated by the diffusion-advection model. Furthermore, temperature-depth relationships may be influenced by lateral mixing as well as vertical advection and diffusion. The calculated z^* value must thus be considered with caution; we simply wish to point out that it is indistinguishable from the present-day value.

In summary, early Pliocene oxygen isotope data from Pacific Ocean benthonic foraminifera reflect a relative paleotemperature change of about 3.5°C between 1 and 4.5 km. The structure of the early Pliocene Pacific deep-water column is similar to the modern structure. This result is consistent with the fact that the early Pliocene has been compared with interglacial episodes during the Quaternary, when the most significant Northern Hemisphere continental ice was restricted to Greenland. The approach used in this study may be useful for other problems in deep-water paleoceanography.

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5. The notation $\delta^{18}\text{O}$ is defined by

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{reference}}} - 1 \right] \times 10^3$$

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10. *Globocassidulina subglobosa* (7, 8) and *Oridorsalis* sp. (8) are thought to deposit their calcite close to equilibrium with the $\delta^{18}\text{O}$ of seawater.
11. The results of Shackleton and co-workers (6, 7) are converted to B-1 from PDB by subtracting 0.29 per mil from the published values.
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13. Open circles in Figs. 1 and 2 show results at sites 158 and 208 including the two "glacial" samples. Including these two samples raises the average standard deviation for all sites from 0.12 to 0.14 per mil.
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16. We neglect horizontal plate motions because small changes in latitude and longitude since the early Pliocene are not likely to affect bottom-water temperatures within the study area.
17. Site 158 was drilled on the aseismic Cocos Ridge.
18. The remaining sites all lie on oceanic crust that is estimated to be at least 50 million years old.
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20. Water about 212 m shallower in the vicinity of site 83A has the same temperature. Water about 240 m shallower in the vicinity of site 84 is warmer by 0.02°C.
21. We interpolated temperature from hydrocast stations typical of those within a 5° square of each site from the National Oceanographic Data Center (NODC) file. The reference number (Table 2) uniquely identified each hydrocast in the NODC file. Sea floor at sites 83A and V28-179 is deeper than stations listed by NODC. We estimated the temperature at these sites from results obtained by Scripps Institution of Oceanography cruises Step-1 (station 87) and Monsoon VIII-11, respectively.
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25. We ignore the very small effects of nonlinearity in $d\delta/dT$ for equilibrium calcite precipitation, and the difference between in situ and potential temperatures.
26. We thank the National Science Foundation for making samples available through the Deep Sea Drilling Project. This research was funded by NSF Cenozoic Paleooceanography (CENOP) grant OCE76-81489.

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Single Crystals of Linear Polyethylene Crystallized from the Glass

Abstract. *Isolated single crystals of polyethylene have been crystallized from the glassy state by annealing uniformly thick films of amorphous linear polyethylene just above their glass transition temperature. In agreement with previous results for polycarbonate, substantial molecular mobility at the glass transition temperature is implied.*

Recent reports from our laboratory described a reproducible method of quenching linear polyethylene (LPE) to the glassy state (1, 2). Electron diffraction and differential scanning calorimetry showed that crystallization from the glass occurs on warming, at about 190 K. This is in agreement with the value reported previously by Hendra *et al.* (3) based on infrared measurements. More recently, we replaced the liquid nitrogen slurry quenchant with isopentane at its melting point and performed dynamic mechanical spectroscopy studies which indicate that the glass transition temperature (T_g) is ~ 190 K (4, 5). A large peak in $\tan \delta$ (loss angle) is observed at this temperature, as well as a rise in rigidity. This peak is not observed on cooling and reheating the sample or in normally crystallized samples. In agreement with Boyer (6) we define it as $T_g(L)$, the T_g of unconstrained amorphous LPE, whereas the large β peak (~ 260 K) observed in these samples would be $T_g(U)$, the T_g of molecules constrained by crystallites.

The effect of annealing the samples above and below $T_g(L)$ on the dynamic mechanical spectra and the morphology has been examined (4). We have shown that it is possible to grow isolated single crystals from uniformly thick, amorphous films of polycarbonate (PC) by

annealing just above $T_g(L)$ (7). Here we report similar results for amorphous LPE. In addition to their intrinsic interest, the results have implications for the current controversy over the degree of molecular mobility during crystallization from the melt (8-10).

Thin-film samples of LPE (Dow HBPE; melt index, 1.2; density, 0.955 g/cm³) mounted on electron microscope grids were prepared as previously described (1, 2). These films are of essentially uniform thickness, displaying a nodular surface structure ~ 100 Å in diameter when shadowed cold. Rapid heating through T_g results in the development of a microcrystalline texture, the crystals being 100 Å or less in size and the surface resembling that observed in the amorphous state (2). The sample shown in Fig. 1 was annealed for 5 hours at ~ 200 K in a test tube immersed in an acetone-Dry Ice bath. It was then warmed rapidly to room temperature and shadowed with Pt/C before being placed in the microscope.

In various regions of the samples we observed numerous structures that were ~ 0.15 μm in diameter, frequently more or less hexagonal in outline, and interconnected with fibrils ~ 100 Å in diameter. No polymer remained between the fibrils, indicating that the molecules from at least these regions had moved dis-

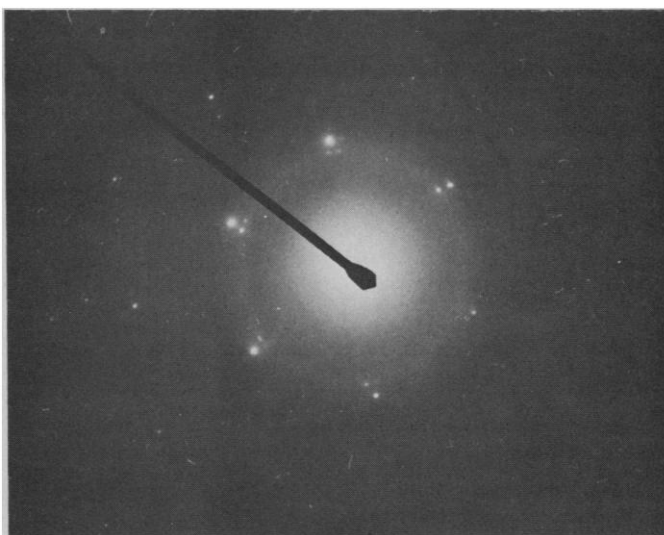
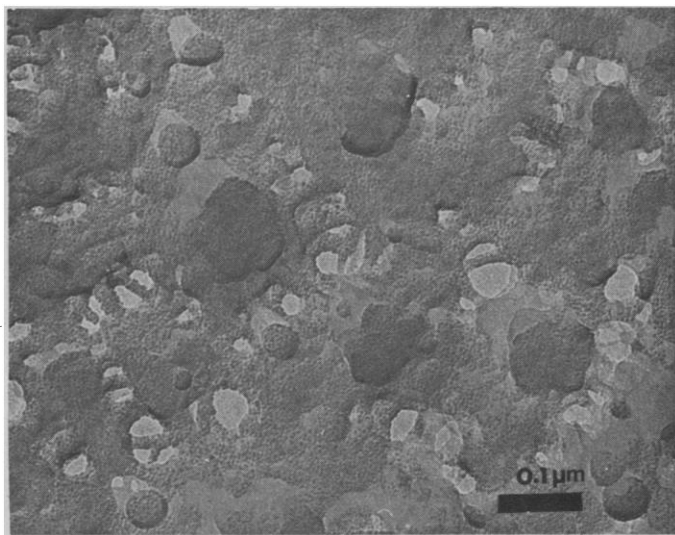


Fig. 1 (left). Portion of a thin film of uniform thickness of amorphous polyethylene crystallized from the glass at 200 K. Fig. 2 (right). Microbeam electron-diffraction pattern from an area similar to that in Fig. 1.

tances greater than several hundred angstroms during the crystallization. [In the PC samples no fibrils were seen and the voids were micrometers in lateral size (7). There is some possibility of degradation in the thin-film PC samples at 145°C, but degradation cannot explain the absence of LPE molecules at -75°C.] In other regions of these samples spherulites were observed, apparently composed of poorly defined lamellae, and again interconnected with fibrils (4).

Figure 2 shows a microbeam (diameter ~ 1200 Å) electron-diffraction pattern from an area in a sample such as that in Fig. 1. Although it has not yet been possible to clearly localize the region giving rise to such a pattern, similar microbeam patterns have been obtained from numerous areas of samples such as that in Fig. 1 and even from spherulitic samples. As in the case of the PC samples, where clearly defined lamellae were observed in both single crystals and spherulites, these patterns are single crystal in nature, with the molecular axes oriented normal to the plane of the film.

Although the platelets in Fig. 1 are not well enough defined to be described even as stacks of lamellae (their thickness appears to be about 150 to 200 Å, somewhat thicker than we expect for individual lamellae grown at this temperature), we suggest that further annealing at this temperature will result in perfection of these structures. This was the case for PC, for which 1 to 2 days of annealing at T_g was required to permit observation of clearly defined lamellae (7). Undoubtedly, however, it is these platelets that are giving rise to the single-crystal patterns, with domains of commonly orient-

ed lamellae in the spherulites giving rise to similar patterns.

Even without clearly defined lamellae the concept of chain folding must be invoked, since the overall thickness is less than the extended molecular length. No conclusions can be drawn about the regularity of the folding or the number of "tie chains." However, if the PC molecules can move distances of micrometers at T_g , as we have shown before (7), and considering the large-scale motion that occurs in the crystal lattice when crystals thicken during annealing (near the melting point, T_m), then the development of some degree of regularity of folding in these PE crystals during both growth and subsequent warming to room temperature is not inconceivable.

We note that the diffraction pattern has pseudohexagonal symmetry, consisting of three orthorhombic patterns at 120° angles to each other. This was found frequently, and the three patterns had varying ratios of intensity. We suggest that the crystals develop with a hexagonal crystal structure and undergo a randomly nucleated phase change to the orthorhombic phase either at the crystallization temperature or, more likely, during warming to room temperature. A similar phase change from order-disorder hexagonal to hexagonally twinned monoclinic has been observed in multilayer films of vinyl stearate during crystal growth (11).

In summary, the electron micrographs and diffraction patterns clearly indicate the growth of polyethylene single crystals from the glassy amorphous state when it is annealed just above $T_g(L)$. It is anticipated that longer annealing times will result in further perfection of these

crystals. In addition, regardless of theoretical calculations to the contrary (8, 9), we claim that polymer molecules can and do undergo substantial motion during crystallization not only at T_m but also at T_g . This is clearly shown by the isolated single crystals of polyethylene reported here and the previous description of crystallization of PC at its T_g . We suggest that the difficulty in the theoretical predictions lies in attempts to correlate the molecular motions involved in viscosity effects with those involved in crystallization.

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