

NOTES

*Diffraction Studies of Polyethylene and Polypropylene
Creep Specimens*

INTRODUCTION

X-Ray diffraction studies were performed on polyethylene and polypropylene samples which were elongated in creep tests at very low strain rates. The results of the creep tests were reported earlier.¹ The creep specimens were found to have a preferred orientation similar to that reported by other investigators²⁻¹¹ and, in addition, to have an orientation-dependent change in lattice parameter.

EXPERIMENTAL

Front-reflection Laue photographs and diffractometer tracings were performed on polyethylene and polypropylene sheet samples before and after creep. The steady-state creep rates to which the samples were subjected were in the range from 0.01 to 0.08 hr⁻¹. The tests were done on specimens from the necked-down region of the samples.

The data produced by diffractometer studies are summarized in Figures 1 and 2 for polyethylene before and after creep, and in Figures 3 and 4 for polypropylene before and after creep, respectively. The samples were studied with the long axis of the specimen both perpendicular and parallel to the goniometer plane of the diffractometer, in both cases with the large flat surface of the sheet specimens comprising the diffraction sample. The tests were performed with a Norelco diffractometer, using a copper target x-ray tube and a nickel filter to obtain $\text{CuK}\alpha$ radiation.

The diffractometer tracings with the sample in the perpendicular and parallel positions are nearly identical for each of the unstretched materials, indicating that no preferred orientation is detectable by this method. After stretching, relative peak intensities are either increased or decreased, indicating the presence of a preferred orientation.

In the perpendicular position, there is no change in d -spacings after stretching; but in the parallel position, all the peaks except one at a d -spacing of 8.8 Å are shifted toward higher d -spacings in polyethylene, as shown in Figures 1 and 2. Clearly there is not only an orientation effect but also a selective change in lattice parameter. A similar change in d -spacings in polypropylene in the parallel position only is also present, as shown in Figures 3 and 4.

Line broadening was also observed (Figs. 1 to 4) in the stretched specimens, an effect that is consistent with a reduction in crystallite size, or with the introduction of lattice defects which disturb the structural order of the materials.

The Laue photographs for unstretched and stretched polyethylene are shown in Figures 5 and 6, respectively. The corresponding photographs for polypropylene are shown in Figures 7 and 8. The resulting diffraction circles are complete, with little difference in photographic density about the circles of the unstretched specimens, while the photographs of the stretched specimens show discrete, intense spots on the circles. This evidence of preferred orientation is consistent with the published data of Keller⁶ and Andrews and Ward.¹¹

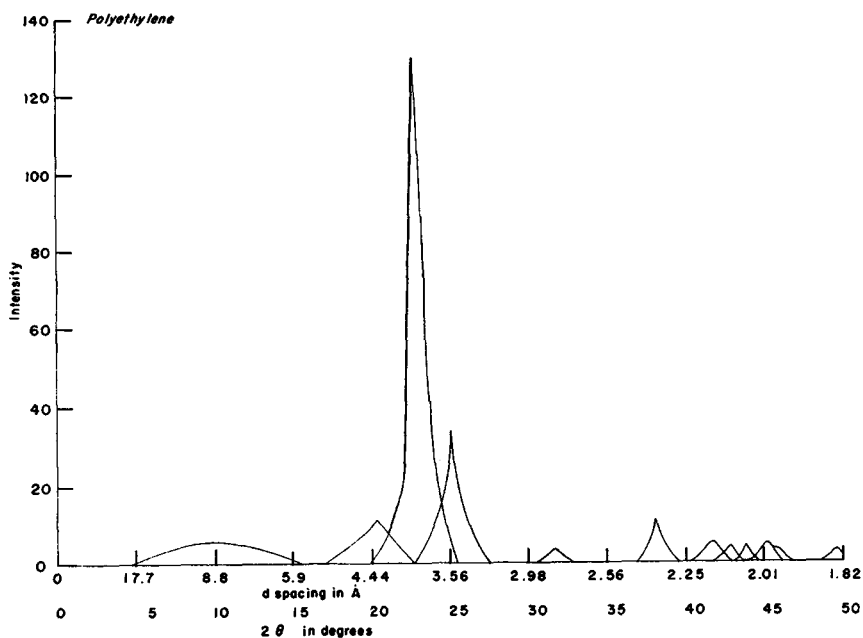


Fig. 1. Diffractometer tracings for unstretched polyethylene: (—) parallel and perpendicular positions.

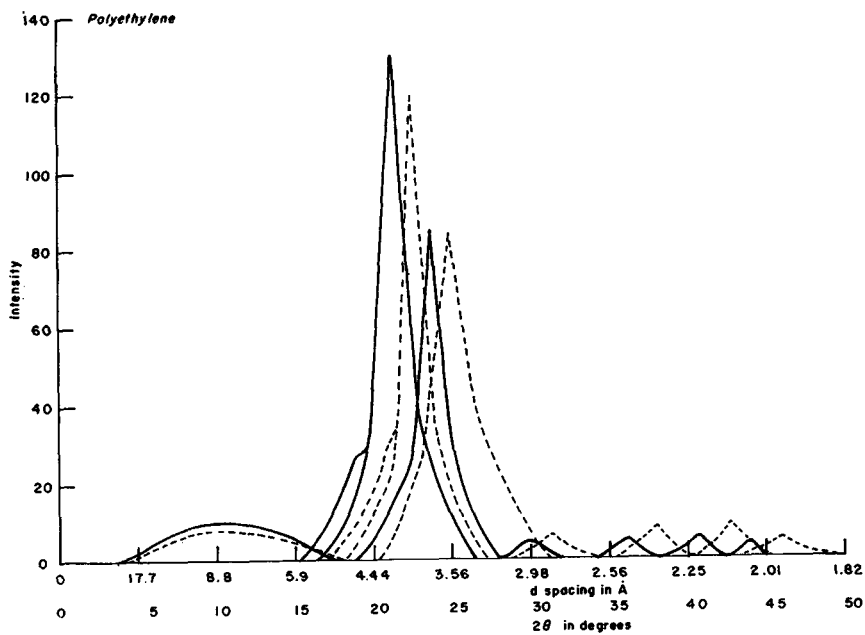


Fig. 2. Diffractometer tracings for stretched polyethylene: (—) parallel and (---) perpendicular.

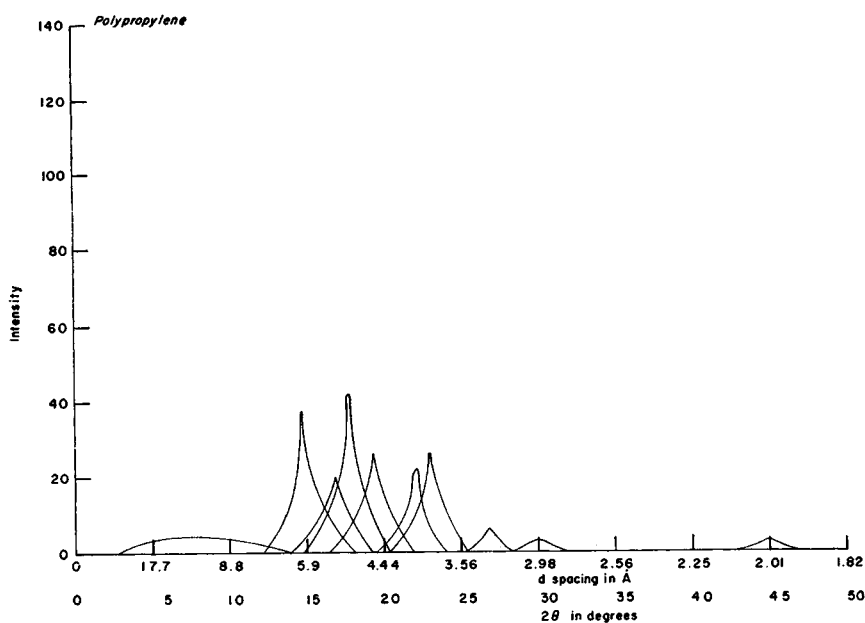


Fig. 3. Diffractometer tracings for unstretched polypropylene: (—) parallel and perpendicular positions.

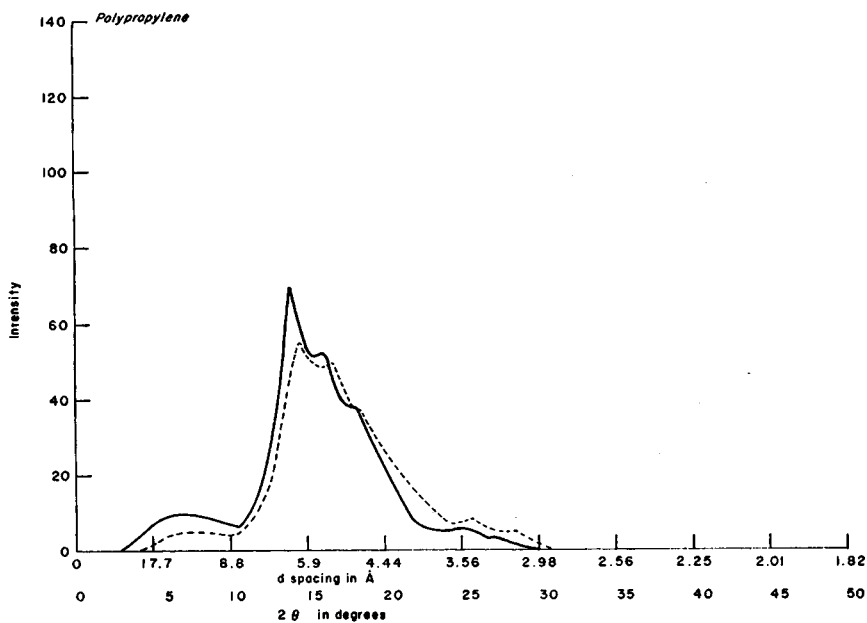


Fig. 4. Diffractometer tracings for stretched polypropylene: (—) parallel and (---) perpendicular.

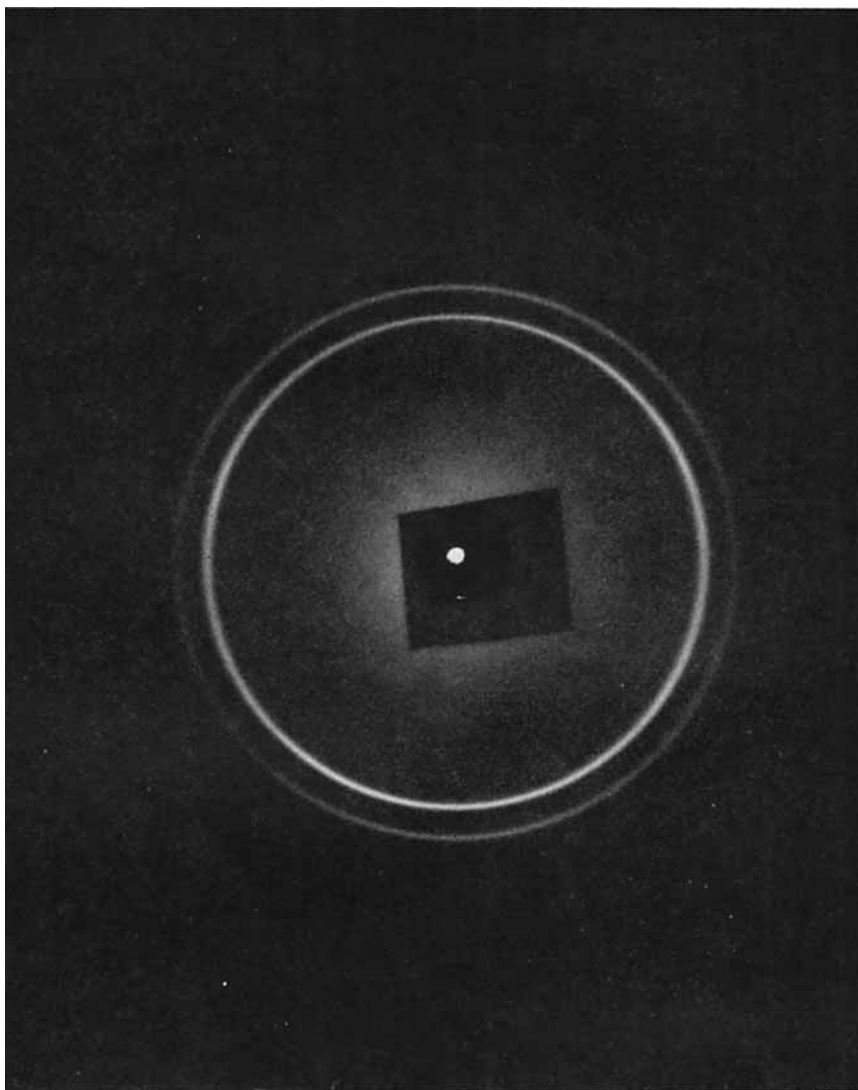


Fig. 5. Unstretched polyethylene.

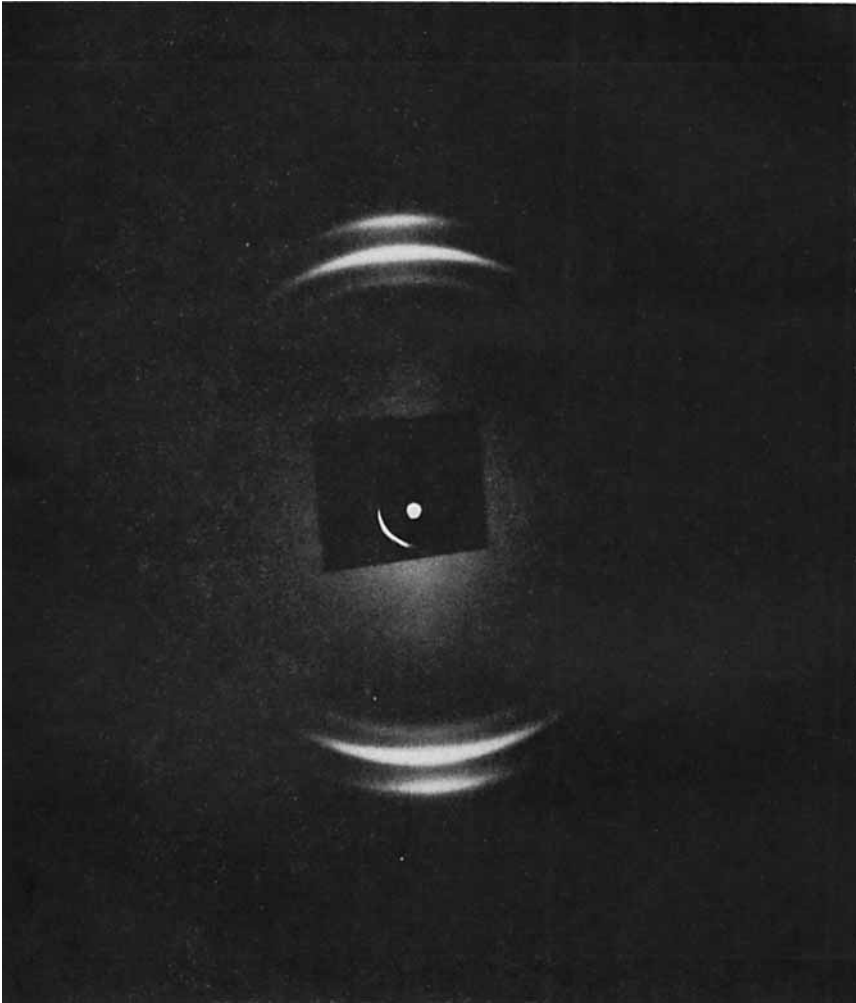


Fig. 6. Stretched polyethylene.

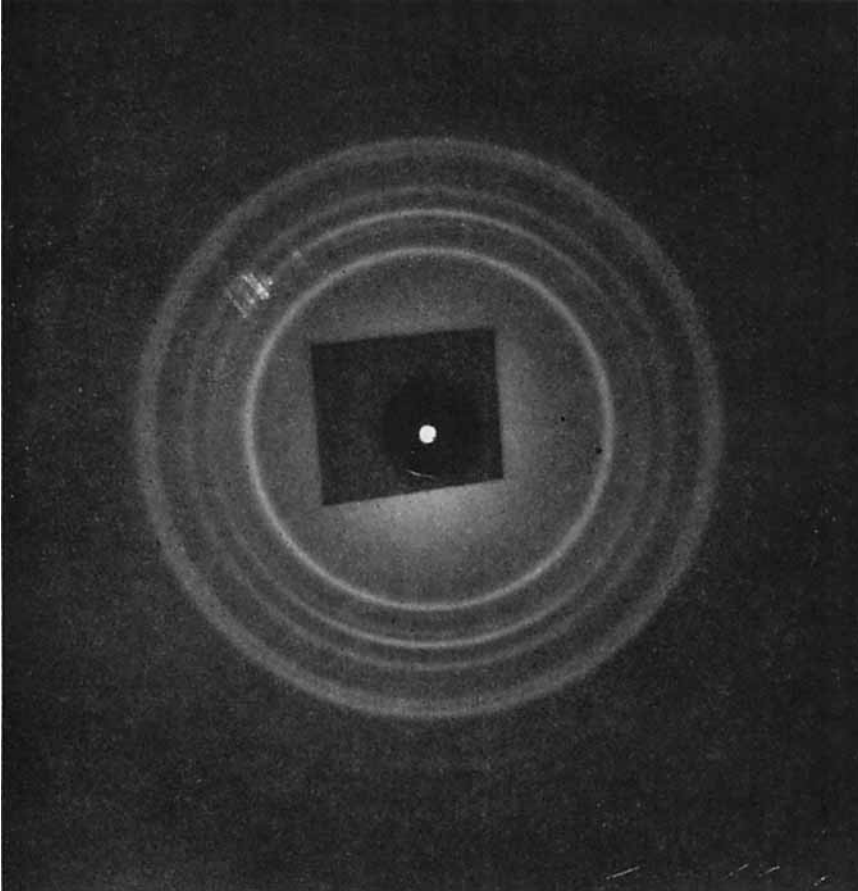


Fig. 7. Unstretched polyethylene.

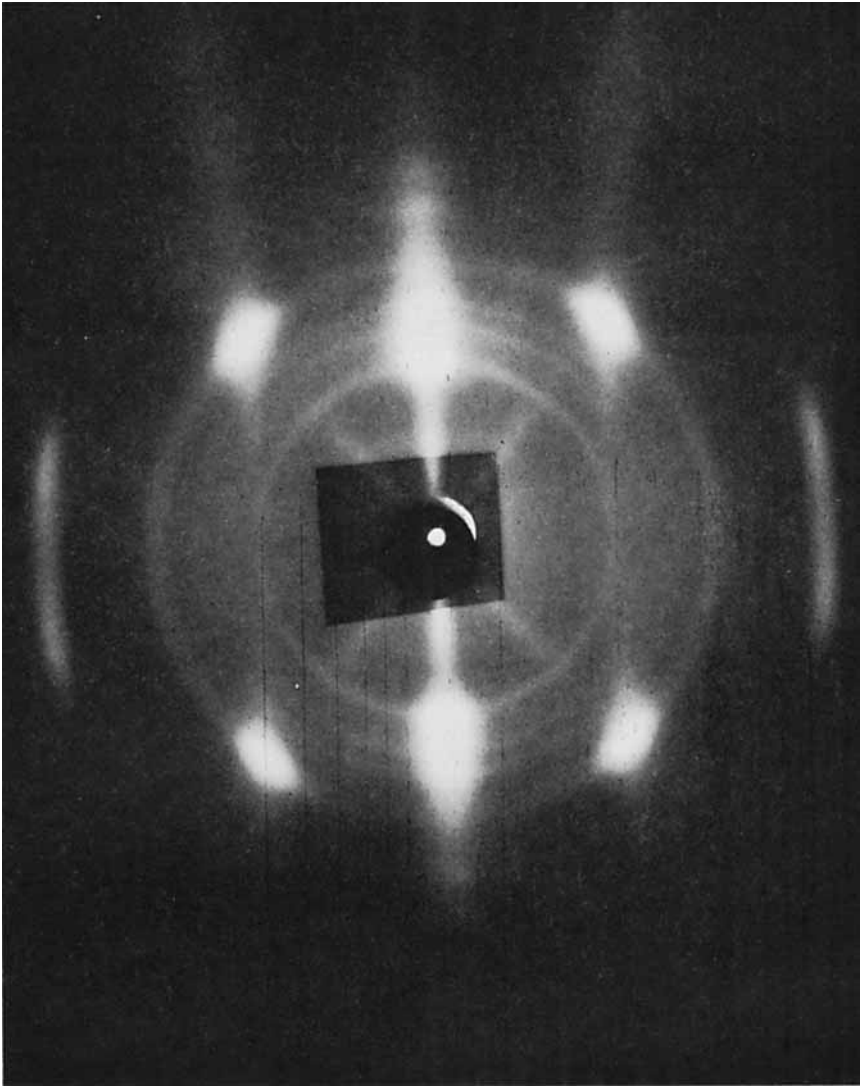


Fig. 8. Stretched polyethylene.

DISCUSSION

The above mentioned line broadening, because of reduced crystallite size, has been used with the well-known Scherrer formula¹² to obtain the crystallite sizes of unstretched and stretched polyethylene and polypropylene. The results are presented in Table I. The line broadening was not determined for all lines because of instances of line overlap or other sources of uncertainty. The crystallite size is approximately halved in stretching polyethylene. The crystallite size of polypropylene is reduced to about one third the original size.

TABLE I
Particle Size

	Polypropylene	Polyethylene
Unstretched, parallel	~100 Å	~100 Å
Unstretched, perpendicular	~100 Å	~100 Å
Stretched, parallel	~40 Å	~50 Å
Stretched, perpendicular	~33 Å	~40 Å

The change in *d*-spacing found upon stretching may be caused by a minor ordering change in the structure, by residual stresses, or by increases in defect concentrations in certain positions in the crystal structure. There is insufficient evidence to support any one of the three suggested explanations to the exclusion of the others. But the change in *d*-spacing is consistent with an increase in the number of interlamellar ties which are, in effect, defects in certain positions in the crystal structure.

Andrews and Ward¹¹ suggest that lower strain rates result in a lower degree of orientation of stretched specimens of polyethylene. Thus, the creep specimens used in this study should have less preferred orientation than specimens that were stretched at a higher strain rate. The substantial amount of disorientation remaining in the creep specimen of Figure 6 is consistent with the above relationship proposed by Andrews and Ward.

References

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