Changes in Crystallite Size Distribution During the Isothermal Crystallization of Linear Polyethylene

G.M. Stack, L. Mandelkern* and I.G. Voigt-Martin

Institute of Molecular Biophysics, Florida State University, Tallahassee, FL 32306, USA

Institut für Physikalische Chemie, Johannes-Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany

Summary

    Changes in the crystallite size distribution during the isothermal crystallization of linear polyethylene fractions were studied using low frequency Raman spectroscopy (LAM). Increases in the crystallite size and broadening distributions were observed as a function of time for all molecular weights studied. Large increases in size occurred even after most of the isothermal crystallinity had formed. The rate of increase was faster for higher crystallization temperatures, while the process was retarded for the higher molecular weights. Similar results were obtained for an unfractionated polymer except for complications that are likely due to molecular weight fractionation.

Introduction

    The question as to whether the size distribution of crystallites change during the isothermal crystallization of polymers has been under discussion for some time. Contrary conclusions have been reached by different investigators (HOFFMAN and WEEKS, 1965; KAWAI, 1969; DLUGOSZ et al., 1976; VARNELL et al., 1981). However, a recent electron microscopic study of a linear polyethylene fraction ($M_W = 1.88 \times 10^5$, $M_N = 1.79 \times 10^5$) has shown that after long time isothermal crystallization a very broad distribution of crystallite lamellar sizes is developed. The breadth of the distribution depends on the crystallization temperature (VOIGT-MARTIN and MANDELKERN, 1981). More recent electron microscopic studies have shown that the average crystallite size, and the distribution of sizes, are also molecular weight dependent (VOIGT-MARTIN and MANDELKERN, to be published). These results clearly infer that the lamellar thickness must be increasing during the course of the crystallization. It therefore appeared advisable to examine this problem in a quantitative and comprehensive manner.

Experimental

    Linear polyethylene fractions over a very wide range of molecular weights ($2.7 \times 10^3 - 1.6 \times 10^6$) crystallized under carefully controlled isothermal conditions for predetermined times

---

*Address correspondence to this author

were studied. The crystallization kinetic isotherms were
established from enthalpy of fusion measurements. The crys-
tallite size distributions were obtained from analysis of
Raman low frequency longitudinal acoustical mode (LAM) (SNYDER
et al., 1978; SNYDER et al., 1980; GLOTIN and MANDELKERN, in
press). These measurements are made at room temperature after
quenching the sample from the predetermined isothermal crystal-
lization temperature. The spectral contribution from the
quenching can be easily identified and is deleted from the
subsequent discussion (GLOTIN and MANDELKERN, in press).

Results and Discussion

An example of the ordered sequence distribution (or
lamellar crystallite size distribution, when corrected for
chain tilt) that is obtained for a molecular weight sample
$M_W = 70,000$, $M_N = 65,000$, degree of crystallinity $1 - \lambda$ of 0.61,
is given in Fig. 1. In this case a broad distribution in the
crystallite size is clearly observed. The maximum of the dis-
tribution is centered at around 350Å and crystallite sizes
range from 250 to 500Å. Since broad distributions are quite
common it can be misleading to focus attention solely on the
peak value of the crystallite size. Therefore, for presenta-
tion purposes it is convenient to describe the distribution by
the horizontal line of Fig. 1, which represents the half-width
at half-height. The solid circle indicates the most probable
value of the ordered sequence lengths; the terminus of the
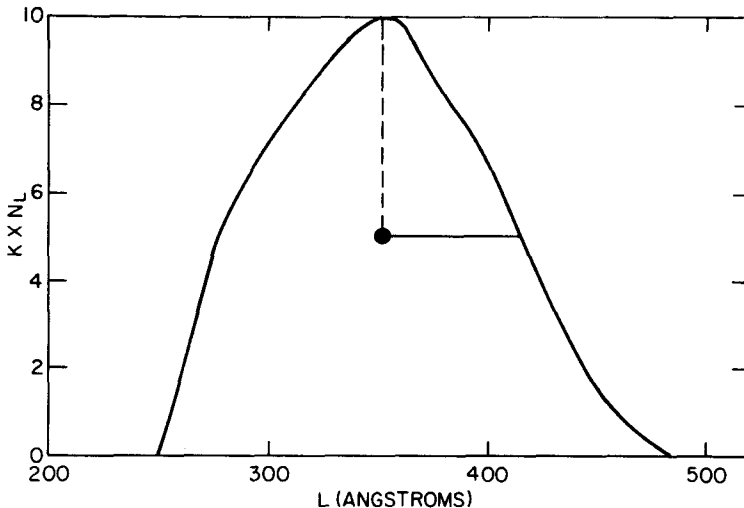horizontal line is the largest crystallite size at half-height.

Figure 1. Plot of normalized number of ordered sequence
lengths against length L in Angstroms. For fraction
($M_W = 70,000$, $M_N = 65,000$) crystallized at 126°C
for 165 min. N_L is number of sequences of length
L; K is normalization constant

    To address the question of whether there is a change in
the distribution with isothermal crystallization time we
present the results in Fig. 2 for a fraction $M_W = 188,000$,
$M_N = 179,000$ isothermally crystallized at 128°C. The levels
of crystallinity for the corresponding times are 0.51, 0.61
and 0.64 respectively. It is clear that over this time span,
although the level of crystallinity is only slightly increas-
ing there are significant changes in both the peak height
and crystallite size distribution. The peak position has
changed from about 350Å to 500Å, while the largest crystallite
size (at half-height) has increased from 425Å to 650Å.* The
results in this figure make clear that the crystallite sizes
increase significantly in the flat portion of the crystalliza-
tion isotherms (ERGOZ et al., 1972). Here, there is only a
slight increase in the level of crystallinity but the time
scale is relatively large. The results shown in Fig. 2 are
typically found in all the fractions studied. However, the
magnitude of the sizes found depends on the molecular weight,
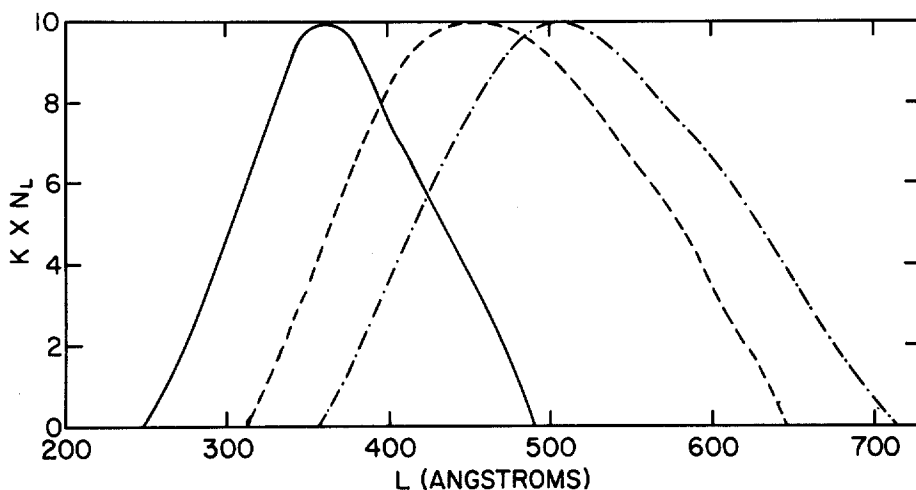and on both the crystallization temperature and time.

Figure 2. Normalized crystallite size distribution for frac-
           tion ($M_W = 188,000$, $M_N = 179,000$) crystallized at
           128°C for different times. —— 135 min.; --- 1140
           min.; ·-·-·· 10,000 min

*Although it has been shown that the method used gives the
proper distribution (GLOTIN and MANDELKERN, submitted), for the
very long time crystallizations that are illustrated in Fig. 2,
the sensitivity of the method does not allow for the detection
of 10 - 20% of crystallite sizes which are the order of 300Å.

Figure 3 describes in detail how the crystallite thickness and distribution change during the course of the crystallization. There are plotted on the same graph both the half-width at half-height and level of crystallinity as a function of the logarithm of time. The results here are for a fraction $M_W = 70,000$, $M_N = 65,000$ crystallized at 128°C. The crystallization isotherm follows the well-established pattern (ERGOZ et al., 1972). In this example the earliest size determination is made at a time which corresponds to a level of crystallinity of about 0.20. This time is thus still in the ascending portion of the isotherm. However, we can again note that the most substantial increase in the crystallite thickness takes place during the time span in which the increase in crystallinity is very small.
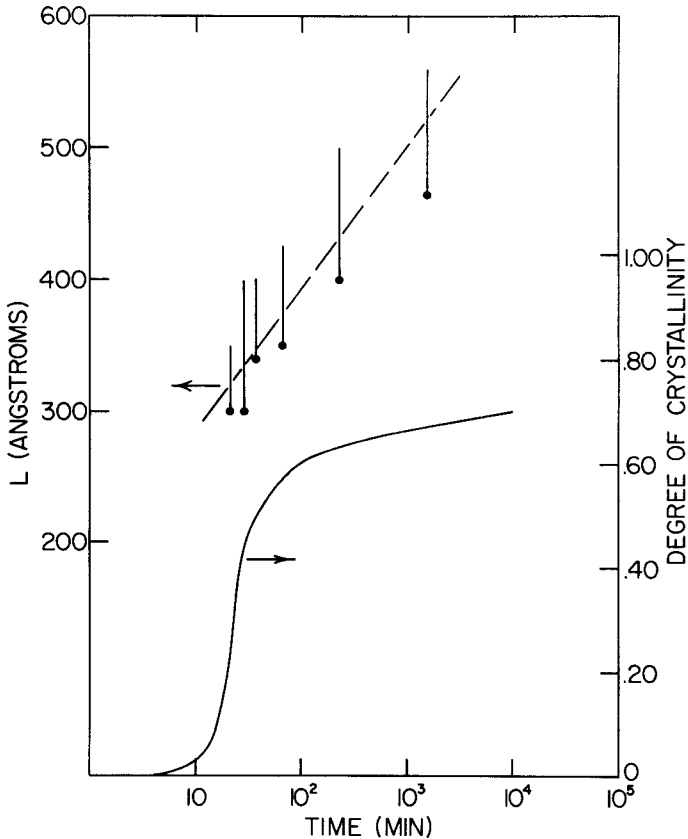

Figure 3. Plot of the representations of the distribution functions and the corresponding crystallization kinetic isotherm as a function of the log time. For fraction ($M_W = 70,000$, $M_N = 65,000$) crystallized at 128°C
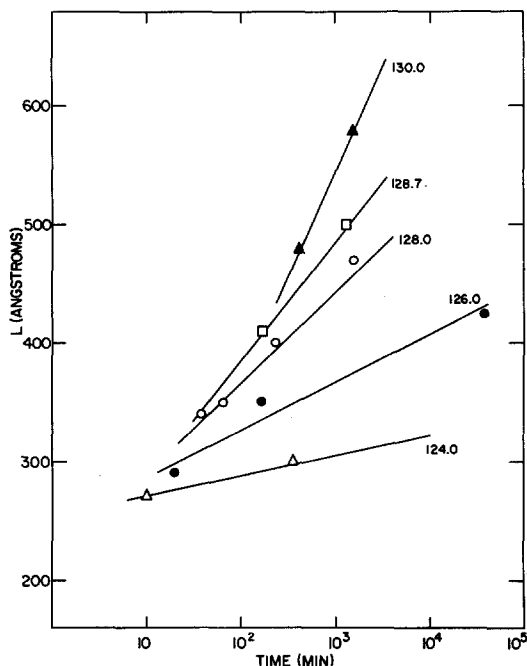
Figure 4. Plot of the most probable thickness (maximum in
distribution function) as a function of log time
for fraction (M_W = 70,000, M_N = 65,000) crystal-
lized at the indicated temperatures

The temperature dependence of the change in the crystal-
lite size distribution is illustrated in Fig. 4. Here the
peak value in the size distribution is plotted as a function
of the crystallization time for the different isothermal
crystallization temperatures for the fraction M_W = 70,000,
M_N = 65,000. These data are only for the flat portion of the
isotherm. The linear relation that can be deduced may just
be coincidental and reflect the limited time scale. Most
important, however, is the fact that the rate at which the
crystallite thickness increases is markedly dependent on the
isothermal crystallization temperature. The slopes of these
lines change by a factor of about eight as the crystallization
temperature increases from 124 to 130°C. The clear implica-
tion of these results is that the crystallite size distribution
must be much broader at the higher crystallization times. This
conclusion is in accord with the electron microscopic studies
previously described. Furthermore, the prediction is made that
for the higher crystallization temperatures, in this molecular
weight range, very large crystallite thicknesses should be
observed after very long time crystallization. Large crystal-
lite thicknesses have been found under these conditions by
both electron microscopy and small angle X-ray scattering

studies (VOIGT-MARTIN and MANDELKERN, 1981; VOIGT-MARTIN and MANDELKERN, to be published; POLLACK et al., 1962).

These results reemphasize the fact that for bulk crystallized polymers, crystallite thicknesses are not limited to the 200-300Å range. This latter concept is a very restrictive one. The data illustrated in Figs. 2-4 show further that the magnitude of the changes in the crystallite sizes that occur during isothermal crystallization can be quite substantial. Increases by factors of at least two to three are easily observed. These facts must be borne in mind when developing a quantitative mechanism for this process. Because of the long time involved the fact that a substantial increase in crystallite thickness occurs in the flat portion of the isotherm is not nearly as apparent when very high isothermal temperatures, such as 130°C, are studied.

For intermediate molecular weights, about 2.7×10^4 to 2×10^5, the observations that have been described are very pronounced and are quite easy to detect. At higher molecular weights, up to 1.6×10^6, the changes in crystallite size slow down considerably. Hence the conclusions reached will be very dependent on the time allotted to a given experiment. However, the same type of experiment indicates that there are still increases in crystallite thickness and size distribution, the magnitude of which is dependent on the crystallization temperature. The results in this range are also in accord with electron microscopic observation (VOIGT-MARTIN and MANDELKERN, to be published). At the lower molecular weights, up to about 14,000, there are complications in the crystallization process because crystallite thicknesses which are comparable to the extended molecular length can be achieved. Theoretical analysis and experimental results pertaining to the low molecular weight range are being presented separately (STACK et al., to be published).

We have also studied this phenomenon in a whole polymer with a very broad molecular weight distribution, $M_W = 1.8 \times 10^5$, $M_N = 7.4 \times 10^3$. The results for isothermal crystallization at 125°C are given in Fig. 5. A substantial increase in the crystallite thickness with the course of time is again observed in the flat region of the isotherm. The results are qualitatively similar to those which have been described for molecular weight fractions. However, an unusual feature appears, in that during the course of the crystallization an additional LAM peak is observed. This peak, which is of much lower wave number and consequently corresponds to a higher crystallite size, is indicated by the dashed vertical line in Fig. 5. With time, this peak merges with the major LAM peak. This observation could be a consequence of the fractionation of the very low molecular weight species that are known to be present in this polymer. These species would crystallize in a more extended form and consequently yield a larger size. With the exception of one experiment, all the earlier works in the literature were conducted with unfractionated polymers. The fact that conflicting conclusions were reached is therefore not surprising.

The typical examples that have been illustrated here demonstrate that increases in crystallite thickness and major
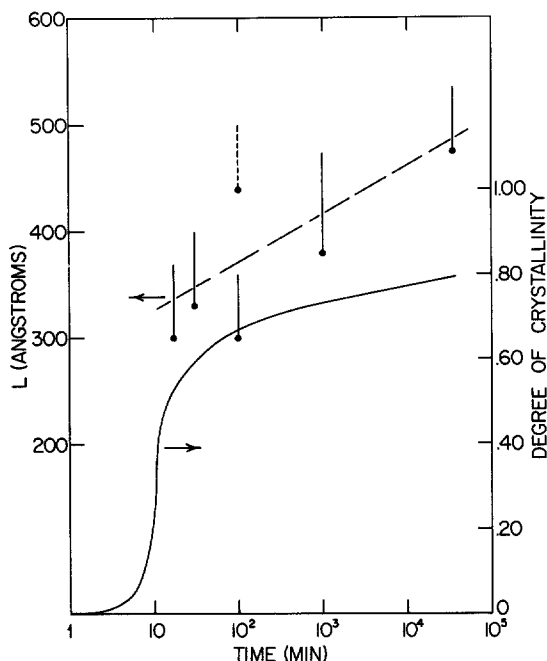
Figure 5. Plot of the representations of the distribution
functions and the corresponding crystallization
kinetic isotherm as a function of the log time.
For unfractionated polymer ($M_W = 1.8 \times 10^5$, $M_N = 7.4 \times 10^3$) crystallized at 125°C. The dashed
vertical line represents the distribution derived
from the lower frequency peak as discussed in text

changes in crystallite size distribution are always observed
during the course of isothermal crystallization. However, it
is apparent that these effects can be missed depending on the
molecular weight, crystallization temperature and the portion
of the isotherm that is being studied. Broad size distributions
develop almost as soon as measurements can be undertaken. This
result makes it important that care be exercised in interpret-
ing other measures of crystallite size such as the maxima in
small angle X-ray scattering patterns. The problems that are
encountered are quite obvious. The fundamental question also
arises as to what thickness is to be assigned to the melting
temperature observed for a given sample. The answer must de-
pend on the details of the distribution and the method used to
determine the melting temperature. Without a detailed analysis
of this problem there could be a very serious error in the in-
terpretation of the measured melting temperature-size relations.
This error will in turn be reflected in the extrapolated equil-
ibrium melting temperature (VARNELL et al., 1981; BASSETT et al.,
1981).

It is important to determine the mechanism by which the crystallite size increases so markedly. At the initial onset of crystallization, there should be a relatively narrow size distribution. One must direct attention to the question as to how the distribution broadens and the average value increases. Cognizance must be taken of the very large changes that can take place. Because of their large magnitude, these changes cannot be attributed, irrespective of the details of the interfacial structure, to the direct growth of the lamellae by internal motion of the ordered chain sequences. Over the course of time a given lamella would have to double or triple in thickness. The size increase can take place by a fluctuation process whereby melting or partial melting, followed by recrystallization occurs. This process becomes highly plausible when it is recognized that polymer crystallites are inherently unstable. Typically, a bulk crystallized polymer will melt only 4-5 degress above its crystallization temperature. A more comprehensive set of data and detailed analysis of the problem will be presented shortly.

Acknowledgement

References

BASSETT, D.C., HODGE, A.M. and OLLEY, R.H.: Proc. R. Soc. Lond. A377 39 (1981)
DLUGOSZ, J., FRASER, C., GRUBB, D., KELLER, A., ODELL, J. and GOGGIN, P.: Polymer 17 471 (1976)
ERGOZ, E., FATOU, J.G. and MANDELKERN, L.: Macromolecules 5 147 (1972)
GLOTIN, M. and MANDELKERN, L.: J. Polym. Sci., Polym. Phys. Ed. (in press)
GLOTIN, M. and MANDELKERN, L.: J. Polym. Sci., Polym. Lett. Ed. (submitted)
HOFFMAN, J.D. and WEEKS, J.J.: J. Chem. Phys. 42 4301 (1965)
KAWAI, T.: Kolloid-Z. u. Z. Polymere 229 116 (1969)
POLLACK, S.S., ROBINSON, R., CHANG, R. and FLORY, P.J.: J. Appl. Phys. 33 237 (1962)
SNYDER, R.G., KRAUSE, S.J. and SCHERER, J.R.: J. Polym. Sci., Polym. Phys. Ed. 16 1593 (1978)
SNYDER, R.G. and SCHERER, J.R.: J. Polym. Sci., Polym. Phys. Ed. 18 1421 (1980)
STACK, G.M., MANDELKERN, L. and VOIGT-MARTIN, I.G.: to be published
VARNELL, W.D., HARRISON, I.R. and WANG, J.I.: J. Polym. Sci., Polym. Phys. Ed. 19 1577 (1981)
VOIGT-MARTIN, I.G. and MANDELKERN, L.: J. Polym. Sci., Polym. Phys. Ed. 19 1769 (1981)
VOIGT-MARTIN, I.G. and MANDELKERN, L.: to be published