SAXS — Isothermal annealing and swelling studies on polyethylene from dilute solution

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(*Received* 29 *April* 1981; *revised* 26 *June* 1981)

INTRODUCTION

Crystallization theories incorporating the concept of isothermal annealing have been reported by several authors[1–3]. These theories attempt to provide mechanisms for a Gibb's type of monomolecular nucleation which supports either a decrease in the interfacial free energy as the crystallite develops from the nucleus or growth in the chain direction after nucleation[4]. It has been suggested[5] that a decrease in the interfacial free energy of the crystallite is highly unlikely. These theories therefore require growth in the chain direction at the crystallization temperature. In one postulate[2] an increase of as much as 10 Å is proposed from the time of initial nucleation to mature crystal formation. It is this general postulate of a change in lamellar thickness with time at the crystallization temperature (isothermal) that we refer to as isothermal annealing.

A number of studies[2,6–8] produced experimental results which apparently support these theories. However, it has been noted[5] that these studies contain questionable experimental techniques, especially with regard to testing isothermal annealing at the crystallization temperature. In contrast, other authors have grown crystals from dilute solution using fractionated polyethylene and obtained results[5,9,10] which seem inconsistent with past nucleation theories.

In our present studies of single crystals prepared from whole polyethylene (Marlex 6001), we have also made observations differing from these past theories. These studies were undertaken to obtain further experimental evidence concerning the relationship between the time of isothermal crystallization, lamellar thickness, melting point behaviour, and the longitudinal acoustic mode (*LAM*) of solution grown polyethylene. In addition we have explored the effects which potential solvents (swelling agents) have on these isothermally grown crystals.

EXPERIMENTAL

The polyethylene single crystals used in our studies were grown from a 0.12% solution of the whole polymer (Marlex 6001) in xylene. The solution was pre-crystallized at 93°C and washed several times with xylene heated to 93°C to remove lower molecular weight chains. The crystals were then reheated (self-seeded) and finally recrystallized in a bath with a constant temperature of 90°C. The system was carefully purged with nitrogen during the entire experiment to prevent oxidation. Samples were taken at various time intervals (2, 10, 24, 72, and 168 h), washed at the crystallization temperature, sedimented, and dried to form oriented mats.

The lamellar thickness was measured using a Kratky small angle X-ray scattering system (SAXS). Data was corrected for sample absorption, background, and the Lorentz factor using the $(2\theta)^2$ method[11]. The Bragg equation was applied to the first peak position to determine the reported lamellar thicknesses. The data are precise to within ±2 Å. Fold periods were also determined for mats swollen with xylene. In this case the mats were immersed in xylene for approximately 30 min. During the course of the SAXS experiments, xylene was added dropwise to the mats in order to prevent them from drying out. Melting points were determined using a Perkin–Elmer d.s.c.-2 at a heating rate of 20°C min^{-1} with ~0.5 mg samples. The reported melting points are accurate to within ±0.3°C. The *LAM* studies were performed using small pieces of the appropriate SAXS mats. The *LA* modes were recorded with a Jobin–Yvon Ramanor HG2S Raman spectrometer at a resolution of 1 cn^{-1}. An argon-ion laser was used as the energy source.

0032-3861/81/111590-03$02.00

RESULTS AND DISCUSSION

At 90°C the precipitate became visible and crystallization was essentially complete after 2 h[12]. The scattering data for the 2, 24, and 168 h samples are shown in *Figure 1*. The

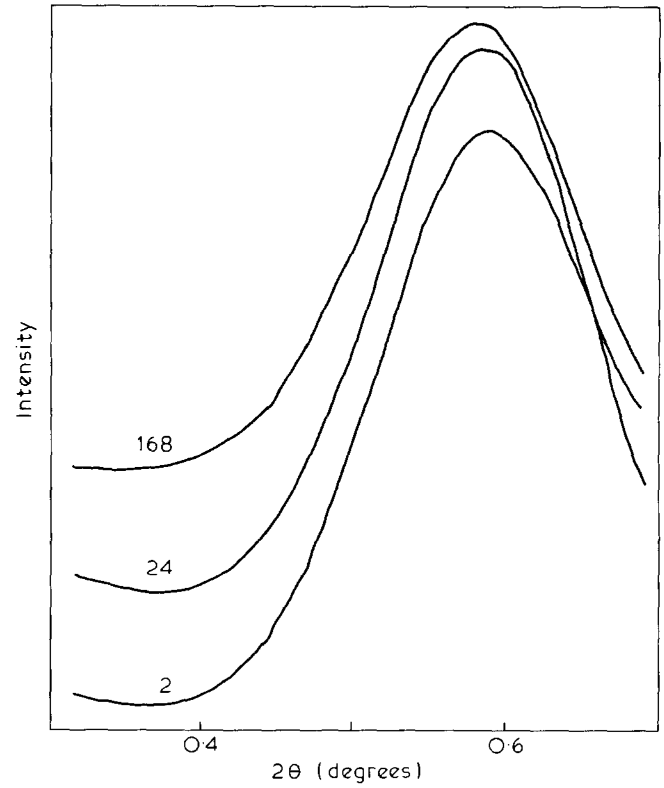

Figure 1 Plot of Lorentz corrected intensity *versus* scattering angle (2θ) in degrees. Crystals kept in the crystallization bath for the time shown in hours

curves for the 10 and 72 h samples resembled those shown, but were omitted for clarity. The 2θ angles in *Figure 1* correspond to lamellae thicknesses of 153 ± 2 Å. Clearly, lamellae thickness shows no significant change with time. Our results are similar to those of Mandelkern[5], however they are much more consistent over a similar time range of isothermal crystallization conditions. This is possibly due to differences in our experimental methods. While we used whole polymer, our experimental procedure included a pre-crystallization procedure as well as washings at the crystallization temperature.

The melting point behaviour for the dried crystals is seen in *Figure 2*. Again, the curves for the 10 and 72 h samples were omitted for clarity; the results being similar to those shown. Melting points for all samples do not differ significantly within experimental error. A change of 10 Å in lamellar thickness for polyethylene corresponds to a melting point change of about 1°C. This was determined using the Hoffman–Weeks equation and differs somewhat from Mandelkern's predictions[5]. The lack of significant change in melting point temperature is further evidence against theories predicting isothermal annealing at the crystallization temperature. We have observed a slight broadening of the isotherms with increasing time in the crystallization bath. This could be due to a broadening of the distribution of lamellae thicknesses or possible reorganizations of the crystals.

There did appear to be a reproducible trend to slightly higher values of heat of fusion with increasing crystallization time. However this increase was within the error range of this technique (±1%).

The *LAM* results are seen in *Figure 3*. Once again, the curves for the 10 and 72 h samples have been omitted for clarity; the results being the same as those shown. The peak positions for the samples are in the range of 20–20.5 cm^{-1}. Applying these frequencies to the appropriate equations the range of variation in lamellar thickness is no greater than 4 Å. This data clearly supports the SAXS and melting point data as evidence against past theories predicting isothermal annealing.

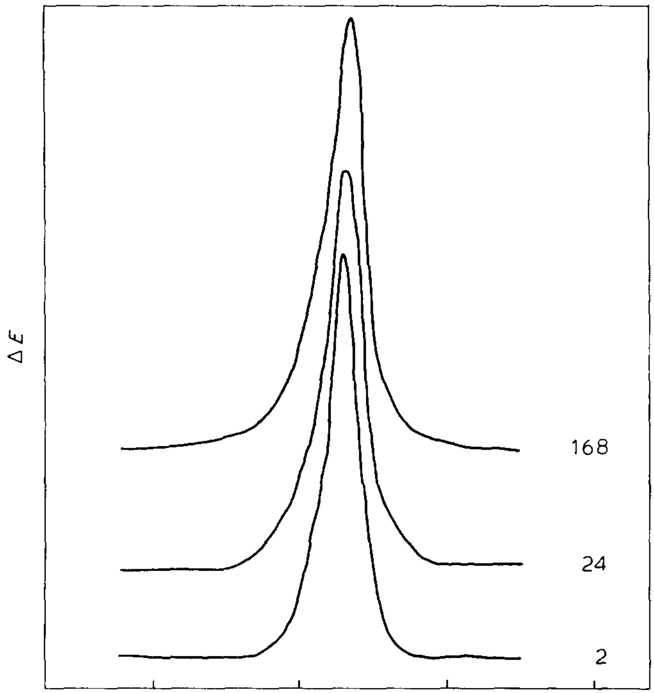

Figure 2 D.s.c. traces for crystals kept in the crystallization bath for the time shown in hours

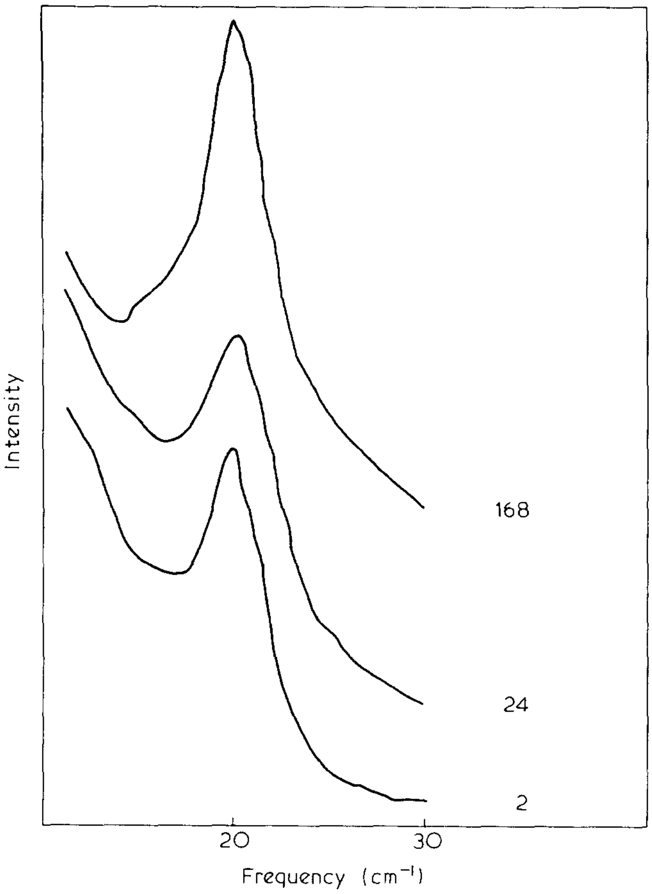

Figure 3 Intensity *versus* frequency (cm^{-1}) for crystals kept in the crystallization bath for the time shown in hours

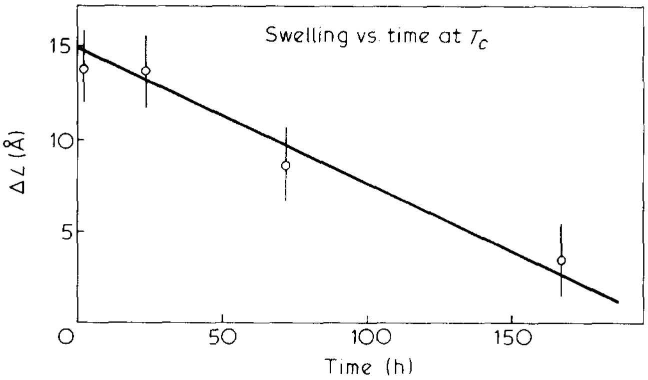

Figure 4 Plot of the difference in fold period (in Å) between dry mats and the same mat swollen in xylene (ΔL) *versus* the time the original crystals were kept in the crystallization bath

Up to this point we have examined only the dried mats. On the basis of the data so far, we would have to say that there are no detectable differences in the crystals. One would therefore be tempted to conclude that isothermal annealing at the crystallization temperature simply does not occur for crystals grown from dilute solution. However our results on swollen mats leads us to slightly different conclusions.

If we plot the difference between the fold period of the dry mats and the period in the swollen mats (ΔL) as a function of crystallization time we find significant differences as a function of crystallization time (*Figure 4*). At short times ΔL is maximum and approximately 15 Å for our system. With longer times ΔL decreases to approximately 4 Å. Note that the time variable is the time the crystals were held in the crystallization bath. All other times are approximately the same, i.e. time to form a mat, time to swell, time in the beam, etc.

A number of explanations are possible. However one must keep in mind that all explanations must also be consistent with the observations reported for dry mats. One could speculate that there is some reorganization from 'loose-loop' to 'tight loop' folding with time in the bath. Keeping in mind the data on dry mats this also implies that the length of cilia should increase with crystallization time. This would be required to maintain the all-*trans* length constant (*LAM*) and the fold period unchanged in dry mats. This also postulates that swelling is due to folds (more for 'loose-loop', less for 'tight-loop') and cilia play no role. It further implies that the reorganization occurs *via* a reptation process.

It is possible to rationalize the data on the basis of an adsorbed surface layer[13]. Here we envisage a layer of adsorbed material on a crystal surface (tight or loose loops). As crystallization time increases the adsorbed layer becomes held by more and more attachment points and is less likely to swell. Swelling is ascribed in this case primarily to the adsorbed surface layer.

Finally a similar argument can be applied to cilia. One can picture that at short crystallization times cilia are only attached at one point to the surface, their exit point. As crystallization time increases one can postulate that the cilia itself becomes attached to the surface at various points along its length. Here swelling is assumed to be due primarily to cilia. It is also worth recalling the work of Bank and Krimm[14] in which it was shown that simple physical mixtures of polyethylene and perdeuteropolyethylene showed splitting of CH_2 or CD_2 bending and rocking modes which were smaller than those for the pure species. This was supposedly due to the penetration of a $-\!(CH_2)\!-$ cilia into the lattice of an adjacent $-\!(CD_2)\!-$ crystal. Presumably a cilia is also able to penetrate the lattice from which it originally emerged. In passing, it is also worth recalling that cilia can account for a large percentage of the total amorphous component in single crystals. Therefore one does not need to assume the absence of regular folding to explain observed density deficiencies.

Incidentally if the latter model is the correct explanation for the observed swelling behaviour one would predict that swelling is a function of cilia concentration. This in turn leads to the prediction that the degree of swelling should depend on molecular weight and would be expected to decrease as molecular weight increases. (This assumes a crystallization model in which some constant fraction of stem length is rejected from the growing crystal). Experimentally just the reverse has been reported[15,16], however, questionable experimental methods were used on these studies. We are currently re-examining this molecular weight effect. Although our results are preliminary they do indicate that the degree of swelling does indeed decrease as molecular weight increases. This work will be reported in detail in a later paper. Clearly further studies on the mechanism of crystallization need to be researched while applications using these past studies as a basis need to be re-evaluated.

CONCLUSIONS

(1) Using dry mats there appears to be no effect on single crystals from dilute solution due to isothermal annealing at the crystallization temperature. There are no measurable differences in the lamellar thicknesses, melting points or longitudinal acoustic modes of these crystals.

(2) There are however differences in these crystals which manifest themselves on swelling. These differences can be rationalized using a variety of postulated models. We are in the process of evaluating experiments which could differentiate between proposed mechanisms.

ACKNOWLEDGEMENTS

The authors would like to thank the National Science Foundation, Materials Research Division (Polymers) for support through grant DMR-78 25233. The authors would also like to thank Dr J. P. Runt for a number of helpful discussions.

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