EFFECT OF ANNEALING AND TEMPERATURE ON THE MORPHOLOGICAL STRUCTURE OF POLYMERS

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ABSTRACT

During heat treatment of a semicrystalline polymer, various alterations of the morphological structure can occur. Two special cases are treated in more detail: the irreversible thickening of the polymer crystals during annealing and the reversible premelting effects occurring during heating of a well annealed sample.

With regard to the thickening process, two mechanisms have to be taken into account: melting and recrystallization on the one hand and refolding in the solid state due to the high mobility of the chain molecules on the other. Which type of process predominates depends on crystallization conditions, heating rate and molecular weight.

The changes in the morphological structure due to premelting can be analysed by x-ray small angle scattering studies. It is shown that the decrease of crystallinity within the so-called melting range is due to an increase of the thickness of the disordered surface layer.

I. INTRODUCTION

It is well known that semicrystalline polymers generally change their physical properties when they are heated to elevated temperatures far below the melting point. These changes are related to alterations of the morphological structure and they indicate that in most cases the polymeric sample is not in a state of thermodynamic equilibrium. Therefore the heat treatment results in a reorganization of the structure leading to a state of order with a lower free energy.

It is well established that two types of structure alterations can occur: irreversible and quasi-reversible changes. The first group of phenomena embraces numerous kinds of 'annealing effects' and generally the accompanying changes of morphology depend not only on temperature but also on annealing time. In the other case the measured quantities show a reversible behaviour with regard to temperature if the time of passing through the temperature cycle is sufficiently short. Very often a combination of both types of processes is observed.

In this paper we will deal firstly with an important effect of the first kind,

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the irreversible increase of the thickness of the polymer crystal; and secondly we will treat the quasi-reversible structure changes occuring during pre-melting.

II. THICKENING OF CRYSTALS DURING ANNEALING

One of the most important annealing effects is the increase of the thickness of the crystals in the chain direction when semicrystalline polymers are heated above a certain temperature. These changes can be measured by electron microscopy and small angle x-ray scattering and have been observed for numerous polymers and for various kinds of sample preparations. The thickening process was first observed on solution grown crystals of poly-ethylene[1,2] but it also occurs in bulk, melt crystallized and in highly drawn samples[3].

The general features of lamellar thickening measured by the large increase in long spacing are well established. Two different points of view have been assumed to explain this phenomenon. On the one hand the thickening process is believed to occur in the solid state by means of special diffusion mechanisms which make possible the translation of molecule sequences through the lattice. On the other hand it has been proposed that the increase of lamellar thickness is due to a melting of either whole crystals or parts of the crystals followed by a recrystallization from the melt. In our opinion the question is by no means settled and the mechanism of thickening is not understood properly. In the following this will be demonstrated by some experimental observations.

The assumption of a solid state diffusion mechanism for isothermal thickening is mainly based on two observations. (i) It has been observed repeatedly by electron microscopy of single lamellae that the orientation of the chains remains constant[2,4]. An example of the structure of an annealed polyethylene single crystal is given in *Figure 1*. Maintainance of molecular
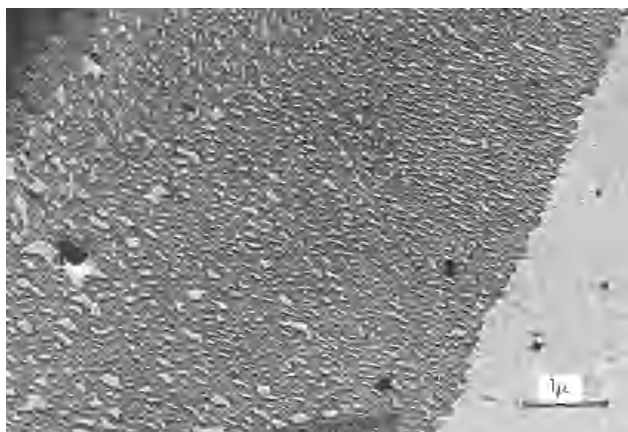
Figure 1. Electron micrograph of an annealed polyethylene single crystal[5]. The chain orientation is still perpendicular to the plane of the lamella.

orientation during thickening has also been observed macroscopically in oriented samples[3] and suggests that a completely molten phase is not formed during annealing. (ii) In many cases it was found that the long spacing after annealing depends not only on temperature but also on annealing time[2] as demonstrated in *Figure 2*. If the long spacing *L* is supposed to represent the
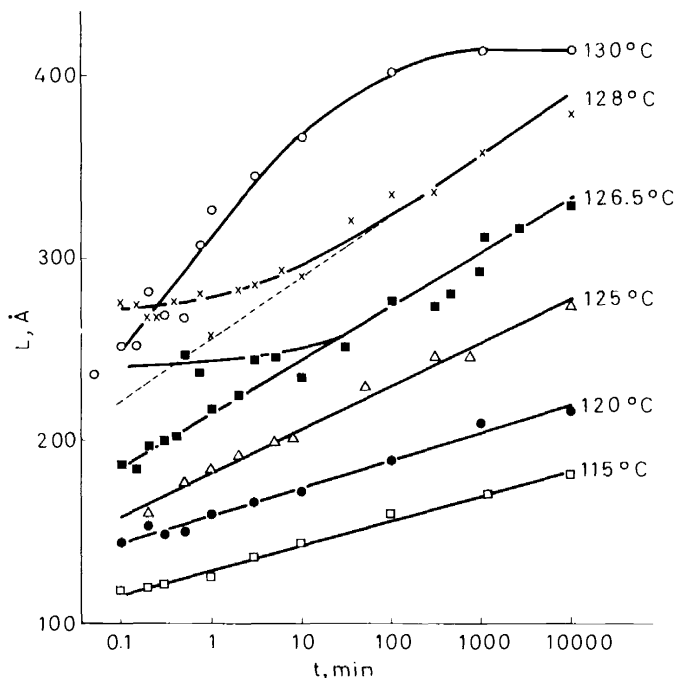
Figure 2. Dependence of long spacings of polyethylene single crystals on annealing time for various annealing temperatures[7,8]. The original spacing was 116 Å.

average thickness of the crystals, then the assumption of continuously occuring melting and recrystallization seems to be unreasonable.

The experimental results plotted in *Figure 2* reveal some interesting features of the thickening process. Within a certain temperature range the time dependence can be described in good approximation by

$$L = L_0 + B(T)\log\left(\frac{t}{t_0} + 1\right) \qquad (1)$$

where $B(T)$ is a proportionality constant. Remarkably the very first jump in long spacing after the shortest experimentally accessible times fits the logarithmic line well, at least for lower temperatures. Further it is noticeable that above 125°C some deviations from relationship (1) are observed. Especially at short times a large scattering of the values occurs which we could not overcome by variation of the experimental conditions. We have already explained this observation by the assumption of small unavoidable

differences in heating rate[8]. Faster heating rates lead to melting and re-crystallization, whereas with slightly smaller heating rates thickening occurs which stabilizes the crystals against melting. So one may draw the conclusion that the increase of long spacing is not due to a uniform process, but that both mechanisms can occur: thickening by a sliding diffusion and melting followed by recrystallization. Some electron microscopical observations show indeed, that the annealing behaviour of the polyethylene lamella is of a nonuniform and complicated nature. For example, *Figure 3* reveals clearly
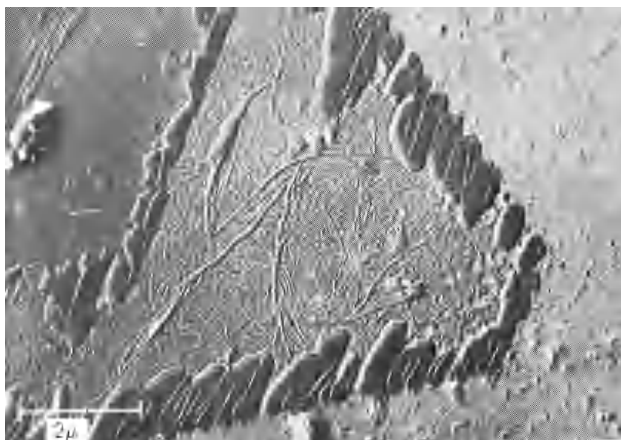
Figure 3. Electron micrograph of a polyethylene single crystal annealed at 125°C for 6 min and subsequently quenched[7, 8].

three different regions of one and the same crystal: a central unaffected area; a middle area exhibiting fibrillar structure supposedly crystallized from the melt during quenching of the crystal, and an outer region thickened during annealing.

There is a variety of additional evidence for the role of melting during annealing treatment. Before we deal with those experiments, some models for the thickening process may be considered. The change of the overall structure can be described adequately by the scheme of *Figure 4* proposed by Statton[9]. At the molecular level different mechanisms for chain refolding have been proposed by Reneker[10], Peterlin[11] and Hoffman[12], where the last two proposals take into account the time and temperature dependence of the thickening process described by equation 1. More recently Keller *et al.*[13] suggested a refolding mechanism according to *Figure 5*, taking into account some experimental results on polyamides.

The discussion of these models is of great interest, since it may stimulate new experiments. But first of all we have to try to decide the basic question involved in these models: is the thickening process appropriately described by the assumption of a solid state transition? Obviously the answer to this question is closely associated with the problem of the melting temperature of the original crystals, since by definition, such a transition takes place without
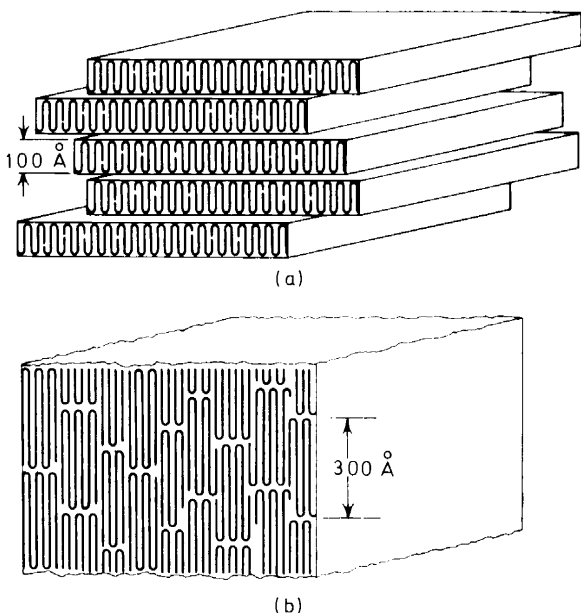
Figure 4. The arrangements of chains in sections of a lamellar aggregate. (*a*) Before annealing (*b*) After annealing. According to Stratton[9].

transforming the material to the molten state. Unfortunately the melting behaviours of polymer crystals is very complicated as well. We will see later especially that the effect of partial melting and the influence of molecular weight distribution will give rise to serious difficulties in the definition of the fusion point of a semicrystalline polymer. Nevertheless, according to Mandelkern *et al.*[14] there is strong evidence that in the case of fractions of polyethylene the temperature T^*, at which the increase of the long spacing starts, can be identified with the melting temperature of the crystals. The authors studied this critical annealing temperature T^* as a function of the
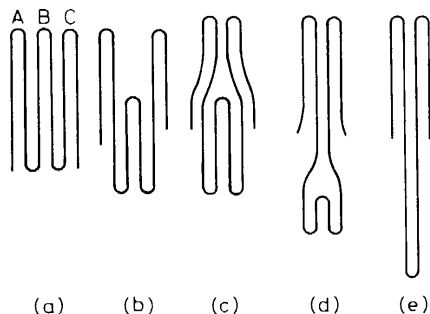

Figure 5. Schematic representation of a refolding mechanism proposed by Dreyfus and Keller[13].

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initial crystallite thickness and showed that T^* obeyed the well known equation of the melting point T_ζ of a crystal of the small size ζ in the chain direction:

$$T^* = T_\zeta = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta H \zeta} \right) \qquad (2)$$

Reasonable values of the equilibrium melting point T_m^0, the interfacial free energy σ_e and the enthalpy of fusion ΔH have been obtained using the identity $T^* = T_\zeta$.

In the case of unfractionated polyethylene the situation is more difficult. For example, in *Figure 6* the change in long spacing L as a function of anneal-
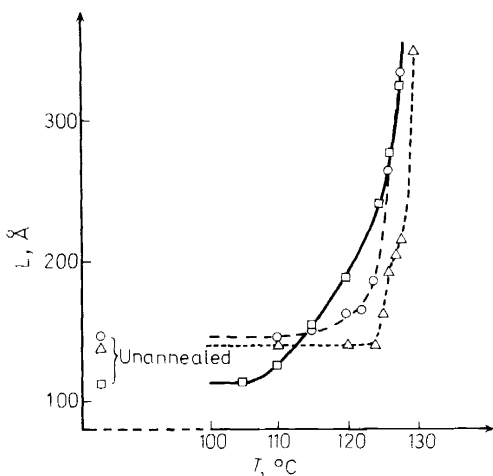
Figure 6. Dependence of long spacing of solution grown polyethylene crystals on annealing temperature after annealing for 1 hour[15]. (——▢——) PE crystallized at 80°C; (— ·· - O — ··—) PE crystallized at 90°C; (— — △ — — —) fractionated PE ($\overline{M}_\eta = 40\,000$), crystallized at 90°C

ing temperature is plotted for various samples of polyethylene grown from dilute solution[15]. In the case of a fraction $\overline{M}_\eta = 40000$, L remains constant up to 124°C in agreement with the results of Mandelkern *et al.*[14]. The unfractionated material†, however, shows thickening at 110°C and 115°C respectively, depending on crystallization temperature.

The remarkable differences between fractionated and unfractionated samples are also reflected in the shape of the differential thermoanalysis curves, see *Figure 7a*. The crystals of unfractionated polyethylene show only one endothermal maximum at about 132°C, whereas the fractionated sample yields two peaks as already found by other authors[16, 17]. The first peak can be interpreted as due to the melting of the original crystals, the second peak is supposed to be caused by the recrystallized material. This

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† The crystals were filtered at the crystallization temperature, so the very low molecular components have been removed.
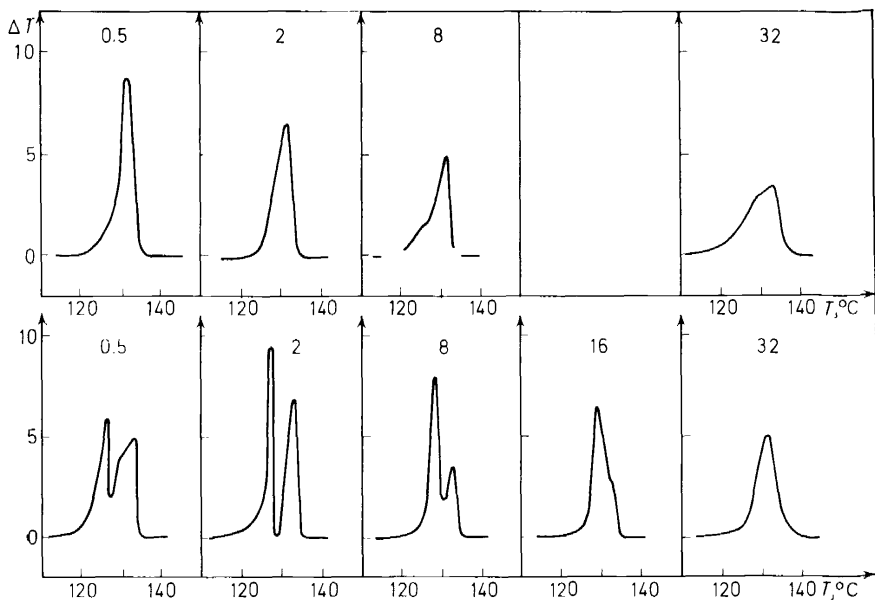
Figure 7a. DSC curves of solution grown polyethylene crystals recorded with the indicated heating rates in °C/min[15]. Upper row: Unfractionated Marlex 50; Bottom row: fractionated PE, $\bar{M}_n = 40\ 000$, crystallization temperature 90°C.
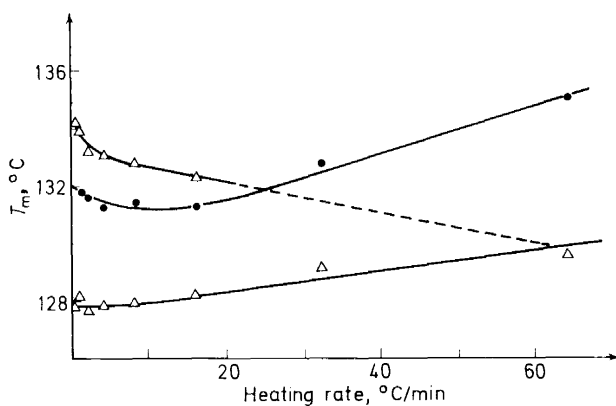

Figure 7b. The temperature position of the endothermal maxima of the DSC curves depending on heating rate[15]. ● Marlex 50, ▲ fractionated PE.

interpretation is supported by the dependence of the shape of the melting curves on the heating rate, see *Figures 7a* and *b*. In the case of the fractionated sample, only one endotherm maximum is observed when high heating rates are applied. Obviously recrystallization from the melt is avoided by fast heating.

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So far the interpretation of the increase of long spacing as caused by melting and recrystallization seems to be fully confirmed. One has to keep in mind, however, two other observations. Firstly, the appearance of two endotherm maxima in the melting curves of the fractionated samples also depends on the crystallization temperature as shown in *Figure 8*. At low
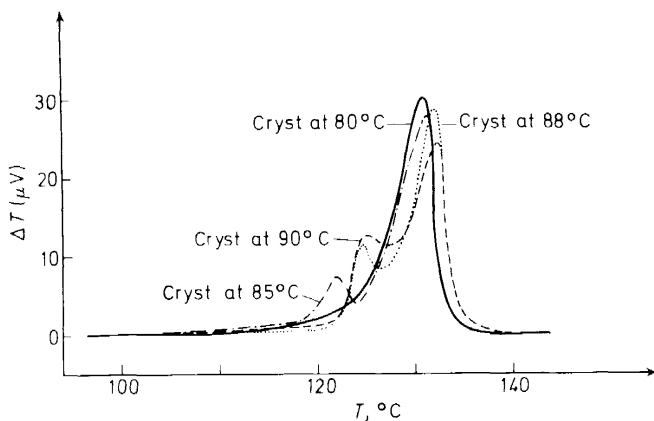
Figure 8. DSC curves of a polyethylene fraction ($\bar{M}_\eta = 40\,000$) crystallized from dilute solution at the indicated temperatures[15]. Heating rate 1 C/min.

crystallization temperature (80°C) only one maximum appears. Secondly, the temperature position of the second peak depends not only on annealing temperature but also on annealing time, as demonstrated in *Figure 9*. During annealing at temperatures above the melting point of the original crystals, the melting peak due to the recrystallized material still shifts to higher temperatures with increased time. Accordingly small angle x-ray measurements showed that the long spacing of crystals obtained from the fraction increases from 160 Å to 240 Å when the annealing time is increased
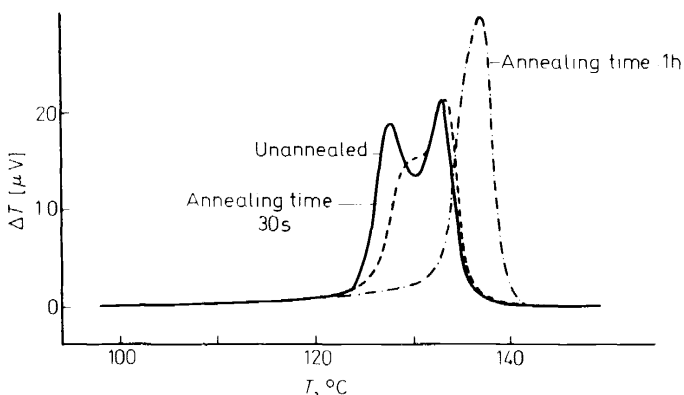

Figure 9. DSC curves of a solution crystallized PE fraction annealed at 128 C for various times[15].

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from 1 min to 1000 min at a constant temperature of 128°C. These results indicate that in addition to melting and recrystallization another process is going on, which results in a continuously changing long spacing.

The same conclusion could already be drawn from the results obtained with unfractionated samples which are plotted in *Figure 2*. Even if the solution grown crystals melt at annealing temperatures beyond 125°C, it is observed that subsequently the long spacing of the recrystallized mat increases continously with time.

In this connection it may be interesting to look at the annealing behaviour of solution grown crystals of polymers different from polyethylene. It is known that polyethylene oxide (PEO) crystals also undergo a drastic alteration of morphology during annealing[18]. Our own studies were performed using PEO of $\overline{M}_n = 32\,000$ crystallized from 0·1 % xylene solutions[19]. The dependence of long spacings on annealing temperature are plotted in *Figure 10*. There is a clear break in the curve at 57°–58°C. On the other hand,
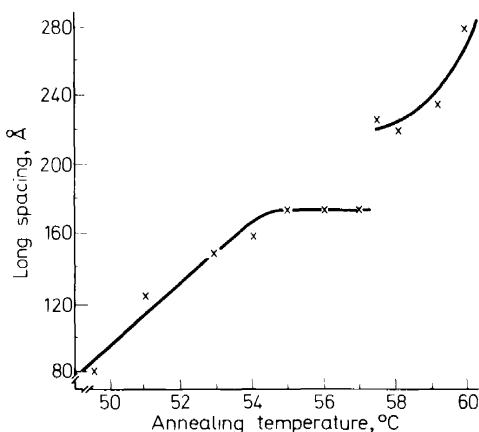
Figure 10. Dependence of long spacing of solution grown polyethyleneoxide crystals on annealing temperature after annealing for 10 min[19].

in the DSC melting curves of the same crystals, the first indication of melting is observed at about 58°–59°C with a temperature position of the endothermal maximum of 62.5°C. Taking into account the fact that during the DSC run some reorganisation has already taken place, it may be reasonable to assume that the break in the curve in *Figure 10* is caused by the melting of the original crystals. Then the increase of long spacing at annealing temperatures below 57°C is probably due to a thickening mechanism which is different from melting and recrystallization. Remarkably, in the $L(T)$ plot of *Figure 10* a plateau at about 170 Å is observed. This value agrees rather well with the twofold value of the original long spacing. This observation may be considered as additional evidence for the model proposed by Keller *et al.*[13] which was pictured in *Figure 3*.

The described results of small angle x-ray scattering studies give rise to the

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intriguing question whether there is sufficient mobility of the chain molecules within the crystal lattice. In order to allow for a complete reorganization of the structure without melting. a coordinated translational motion has to be assumed. The mobility of the chains in the lattice can be studied by means of the motional narrowing of the broad component in the nmr spectra. *Figure 11* shows the temperature dependence of the second moment and of
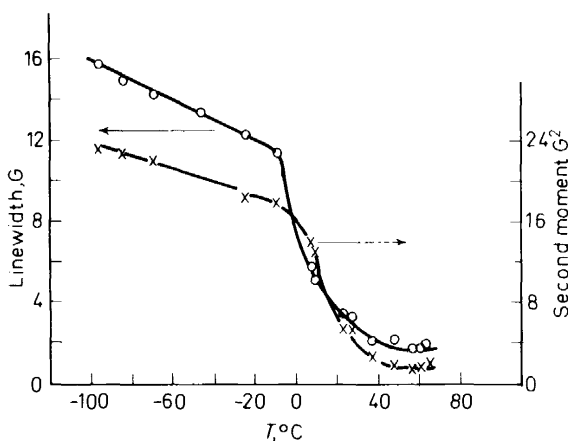

Figure 11. Linewidth and second moment of the nmr broad line spectra of PEO solution grown crystals as a function of temperature[19].

the line width in the case of PEO solution grown crystals[19]. A drastic decrease of these quantities is observed and rather low values are obtained at temperatures beyond 50°C, where the thickening process starts. In this connection we refer also to the extremely interesting results of Kovacs[20], who observed thickening during the crystallization of PEO single crystals from the melt.

Summarizing the results about the effect of annealing on the change of morphological structure one may conclude that two competitive processes occur. On the one hand, whole crystallites or parts of them may melt and new crystallites develop from the molten phase. On the other hand there is evidence for a thickening process occuring continuously and involving parts of the original crystals. Which mechanism predominates depends on molecular weight distribution, crystallization temperature, heating rate and annealing temperature.

The distinction between a melting–recrystallization process and continuous thickening does not mean that in the latter case no molten material is involved. As we will show in the next section, many experimental results indicate that during heating a partial melting at the surface of the crystal takes place which we call boundary premelting. This process seems to play an important role in the thickening mechanism.

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III. THE BOUNDARY PREMELTING OF POLYMER CRYSTALS

It is well known that semicrystalline polymers generally exhibit the phenomenon of partial melting; this means that the degree of crystallinity decreases continuously with temperature within the so-called melting range. This behaviour can be studied easily by measuring the heat capacity or the specific volume of the sample. The temperature of melting as well as the extension of the melting range depend on the crystallization conditions, on the molecular weight distribution and on the chemical homogeneity.

The important question arises: how does the morphological structure change during partial melting? This effect is as complex as thickening by annealing. The trivial explanation is based on the assumption that some of the crystals melt completely below the melting point of the majority of the crystals. There is no doubt that this effect occurs as a result of distributions in molecular weight, the lengths of homopolymer sequences, and size and perfection of the crystals. On the other hand, there is evidence for an additional process which we call boundary premelting and which can be proved directly by analysis of the temperature dependence of the small angle x-ray scattering.

Before we deal with that subject two other experimental results obtained by dilatometry may be mentioned. Firstly, it is well known that during crystallization from the melt, within a finite time, generally an ultimate
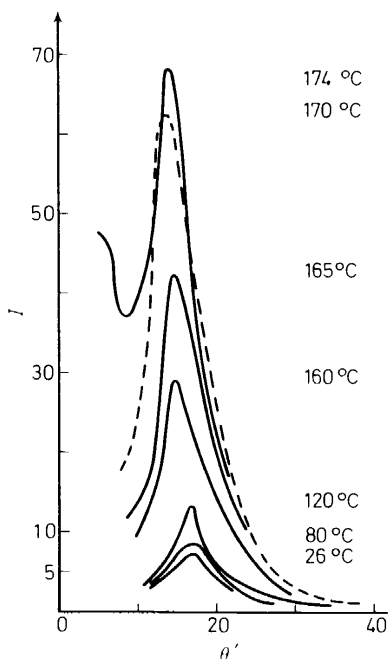

Figure 12. Slit-corrected small angle x-ray scattering curves of melt crystallized polyoxymethylene (Delrin) measured at the indicated temperatures[31].

degree of crystallinity is obtained which decreases with increasing crystallization temperature. Cooling the sample after crystallization leads to an increase in crystallinity. It is important that this effect is also observed using fractionated polymers[21]. Secondly, by heating the sample to temperatures below the original crystallization or annealing temperature, the decrease in crystallinity is reversible depending on heating and cooling rates. So the polymer samples behave like metastable systems, where the crystallinity is a function of temperature.

The reversibility in the degree of crystallinity is correlated to the reversibility of small angle x-ray scattering curves[8]. There is a tremendous change in intensity as well as shape of the scattering curves as demonstrated by *Figure 12*. A similar behaviour is observed for many other polymers.

The increase in the intensity or scattering power of the sample is due to an increase in the electron density fluctuation, which is caused by the changes of the morphological structure. The mean square density fluctuation $\langle \eta^2 \rangle$ can be evaluated from measurements on an absolute scale. On the other hand this quantity can easily be calculated from the results of dilatometric or calorimetric measurements if a two-phase structure of the partially molten polymer is assumed. In this way one can prove that the changes in the scattering pattern are due to the melting process[22]. In a second step the shape in the scattering curve can be analysed in terms of the changes in the morphological structures.

The analysis of the scattering curve can be accomplished by calculating theoretical scattering curves of a suitable model and by subsequent determination of the model parameters from comparison with the measured scattering curves. It has been shown previously[22,23] that the generally observed changes in the scattering curves cannot be explained by the assumption that some statistically distributed crystallites melt when the temperature increases. With this model the peak intensity of the long spacing reflection decreases drastically whereas the background intensity increases. Just the
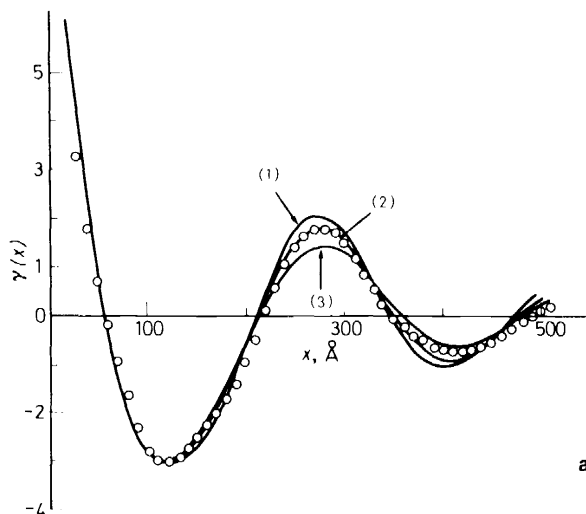
Figure 13. Comparison between the calculated correlation functions $\gamma(x)$ of a layer structure and
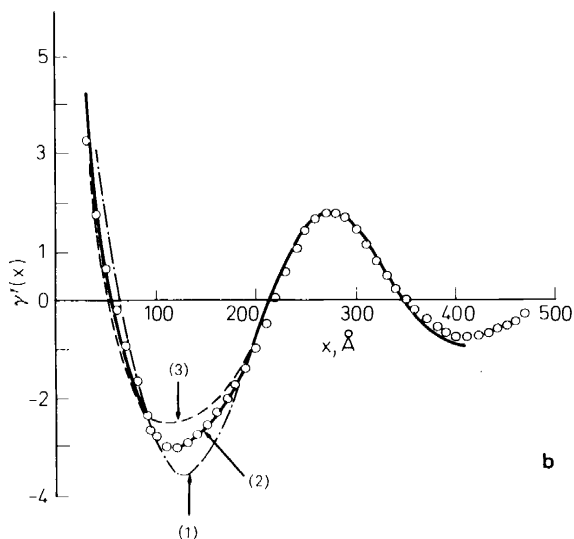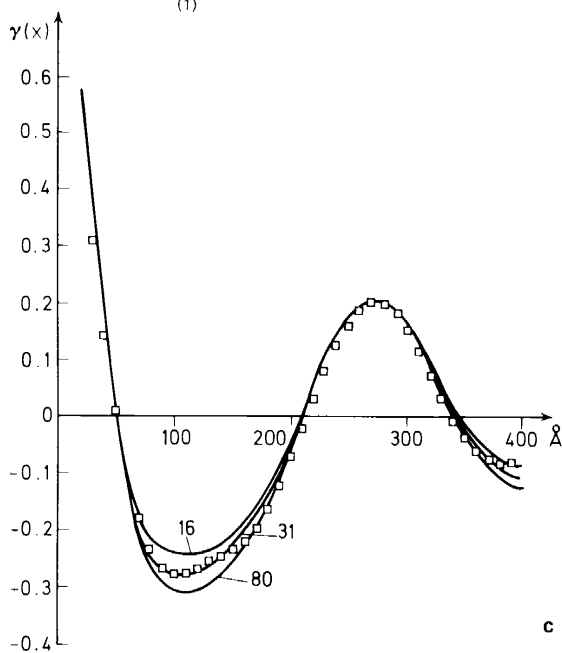
the experimentally obtained correlation function for a melt crystallized polyoxymethylene sample[31]. The open circles are the experimental values. (a) The effect of variation of the width of the distribution function of the interlamellar distance. 1) 25% 2) 27% 3) 31%. (b) The effect of variation of the degree of crystallinity w_c, where the width of the distribution function has been adjusted to fit the height of the maximum. 1) $w_c = 0.80$ 2) $w_c = 0.76$ 3) $w_c = 0.70$. (c) The effect of variation of the number N of layers in the coherent scattering layer structure, where the widths of the distribution function and the degree of crystallinity have been adjusted to fit the height of the maximum and the first intersection $\gamma(x) = 0$, respectively.

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opposite behaviour is observed, see for example *Figure 12*; it can be explained easily by scattering-models characterized by a temperature dependent thickness of the intercrystalline layers. The thickness of the disordered regions between the crystalline cores increases continuously with temperature. This model of boundary premelting has been proposed on the basis of the small angle scattering studies of polyethylene single crystals[3, 24] and in the meantime several authors drew similar conclusions from the results of their measurements with other polymers and samples[25, 28].

For a quantitative interpretation of the scattering behaviour, a second way of analysing the scattering curves offers some advantages. From the scattering data, the correlation function $\gamma(x)$ can be obtained by Fourier transformation. This function is defined[29] by

$$\gamma(x) = \frac{\langle \eta_A \eta_B \rangle_{av}}{\langle \eta^2 \rangle_{av}} \tag{3}$$

where η_A and η_B are the local fluctuations

$$\eta = \rho - \langle \rho \rangle$$

of the densities at points A and B a distance x apart. Equation 3 enables the correlation function to be calculated for any model of the scattering sample. Since the electron microscope studies have shown that semicrystalline polymers of the type discussed here have a layer-like structure, one can use a one-dimensional model according to Vonk and Kortleve[30].

One advantage of this procedure is that by comparison between calculated and experimental correlation functions, the structure parameters of the model can be more easily obtained than by the use of the scattering curve itself. This is demonstrated by *Figures 13a, b* and *c*, where calculated functions $\gamma(x)$ are compared with the experimental values indicated by open circles[31]. It can be seen that rather small variations in the model parameters yield definite deviations from the experimental curves. A more detailed description of this approach will be published elsewhere[31].

By a computer program it is possible to determine five model parameters with a step by step approximation: the average distance between crystallites, the widths of the distribution functions of the crystalline and amorphous regions, the degree of crystallinity and the average number N of coherent scattering lamellae. The results of such a calculation are demonstrated in *Figure 14*. There the distribution functions $P_c(x)$ and $P_a(x)$ of the crystalline and amorphous regions are plotted for the case of scattering curves obtained at various temperatures from melt crystallized polyoxymethylene. Clearly this analysis yields a quantitative proof for the model of boundary melting described above. With increasing temperatures the average thickness of the disordered intercrystalline layers increases considerably (about a factor of two), and the average thickness of the crystals shows a small decrease. These results are in qualitative agreement with the observations of other authors who studied the temperature dependence of small x-ray scattering of polyoxymethylene[26, 28].

The described analysis is rather laborious, since the numerical fit between the calculated and experimental correlation function needs many approxima-
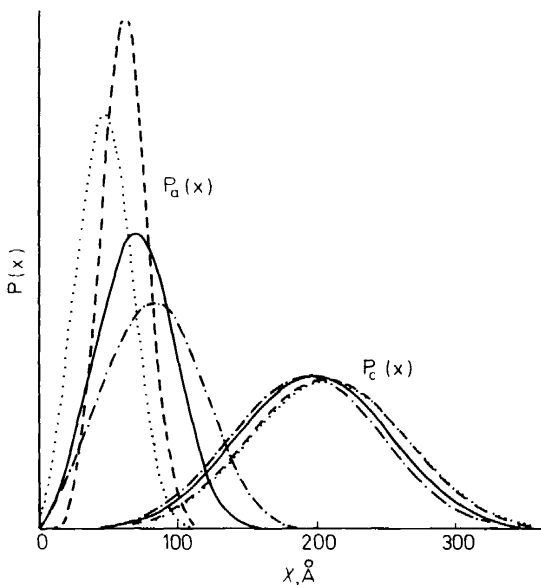
Figure 14. Distributions $P_c(x)$ and $P_a(x)$ of the thicknesses of the crystalline and amorphous regions of polyoxymethylene in dependence on temperature[31] ····· 26°C; – – – – 160°C; ——— 165°C; –·–·–· 170°C.

tion steps. Fortunately it is very easy to observe the boundary premelting just by measuring the peak intensity of the long spacing reflection. It follows from the basic principles of scattering theory, that in a two phase structure the scattered intensity is proportional to the square of the electron density difference. So in a temperature range in which no structure changes occur by premelting, the temperature dependence of the scattered intensity is only due to the difference in thermal expansion coefficients of the two phases. One obtains easily[32]

$$\frac{J(T)}{J(T_0)} = 1 + \frac{\alpha_a - \alpha_c}{\Delta \rho_0}(T - T_0) \tag{4}$$

where α_c and α_a are the thermal expansion coefficients†, T_0 is an arbitrary reference temperature, $\Delta\rho_0$ is the density difference at T_0. Equation 4 yields a straight line, if the expansion coefficients do not suddenly change as is the case, for example, at the glass transition of the amorphous phase. By application of this relationship, it was possible to prove the existence of the glass transition in the surface layers of polymer single crystals[32].

Equation 4 is no longer valid if the degree of crystallinity changes with temperature. Then both the particle factor of the crystalline layers and the lattice factor resulting from the interlamellar interference may change with

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† For convenience they are defined as change of density per °C, deviating from thermodynamic definition.

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temperature. Starting with a highly crystalline sample, one obtains an increase in intensity of the long spacing reflection which is larger than the increase due to the difference in the thermal expansion coefficients. This effect was shown several years ago for the case of polyethylene single crystals[24]: a similar behaviour is demonstrated by *Figure 15*, where the square
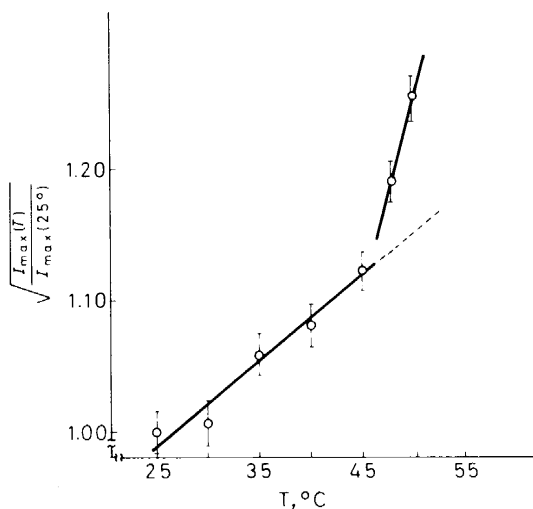
Figure 15. The square root of the relative peak intensity of the long spacing reflection of polyethyleneoxide crystals as a function of temperature[19].

root of the relative intensity is plotted *versus* temperature for the case of solution grown polyethylene oxide crystals[19]. There is a break in the curve at about 45°C, indicating a change in the particle factor in addition to the thermal expansion effect below this temperature.
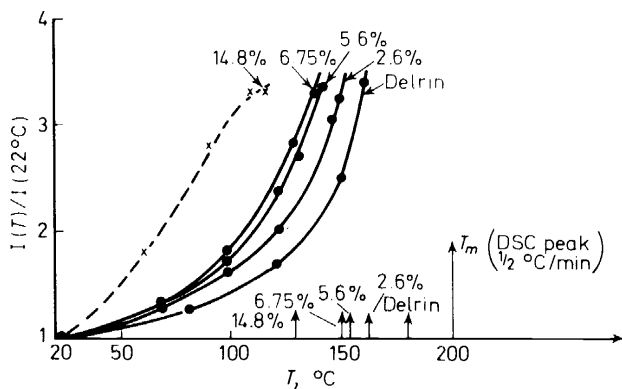

Figure 16. Dependence of relative peak intensity of the small angle reflection of trioxane-dioxolane copolymers on temperature. The arrows represent the DSC melting points of the various copolymers with the indicated mol percentage of dioxolane[33].

The relationship between the increase in the intensity of the small angle reflection and the partial melting also manifests itself in studies of the melting behaviour of copolymers. In *Figure 16* the corresponding results are plotted for trioxane–dioxolane copolymers[33]. The melting temperature measured by the peak position of the DSC curves is reduced by the copolymer content as generally observed. Accordingly the intensity increase is shifted to lower temperatures. This observation clearly demonstrates that the intensity changes are due to the partial melting of the polymers.

The described method of detecting partial melting effects is more sensitive than any other technique especially in the case of high crystallinity. So one may ask what this method reveals about the beginning of the partial melting. Preliminary studies of polyethylene single crystals have shown that melting may already start at 70°–80°C, since in this temperature range the first deviation from the straight line according to equation 4 is observed[34]. The problem is not yet completely solved, however, because there is some evidence of changes of the expansion coefficients of the amorphous and crystalline polyethylene near these temperatures[35,36]. On the other hand our measurements showed that the intensity changes depend strongly on molecular weight, see *Figure 17*, which cannot be understood on the basis of
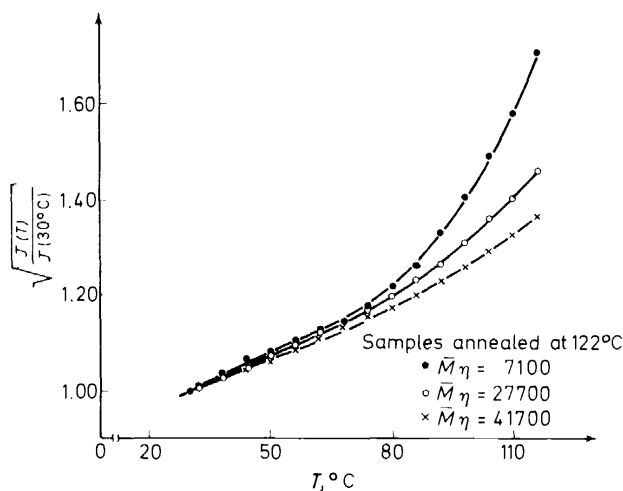
Figure 17. The square root of the relative peak intensity of polyethylene single crystals as a function of temperature. The crystals have been prepared from various fractions and annealed at 122°C before measuring[34].

thermal expansion. A complete analysis of the whole scattering curve and especially a comparison of the temperature dependence of the intensities of the first and second order reflections will answer this question.

The results of the small angle scattering studies mentioned above show that in many cases partial melting of polymers is due to the creation of additional disorder at the surface of the crystallites. Similar behaviour has been observed in the case of *n*-paraffins, where the scattered intensities

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of the long spacing reflections also increase strongly with temperature[37, 38, 22]. In polymers and oligomers the intensity variations are reversible under suitable conditions, therefore these premelting effects can be treated by a theory based on the assumption of a hindered thermodynamic equilibrium. Evidently the increase in entropy due to the additional disorder at the surfaces minimizes the free energy of the lamellae.

A theoretical explanation of the premelting on a molecular level has to proceed on certain assumptions regarding the structure of the disordered surface layers. For the special case of the model of 'loose loops', such theories have been developed in the past and it has been shown that the thickness of the disordered surface layer is governed by an equilibrium length of the noncrystallized sequences[39, 40]. The theoretical results agree qualitatively with the experimental observations. In the case of 'adjacent reentry' of the folds, surface premelting effects have been also predicted theoretically[41]. Additional measurements for analysis of the structure of the disordered surface will have to be made, however, in order to allow a more refined theoretical treatment, which has to take into account the similarity between the behaviour of polymers and oligomers.

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