Modelling 'melting' in macromolecules

Ian R. Harrison

Polymer Science Program, Material Science and Engineering Department, The Pennsylvania State University, University Park, PA 16802, USA
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The melting behaviour of polymers was modelled using polyethylene parameters. The model was based on the idea of melting followed by recrystallization and remelting, which can lead to multiple melting peaks. Experimental data is qualitatively fit by the model for changes in heating rate and original lamellar thickness. In addition one can use the model to predict less well documented changes in other parameters. For example predicted changes in the thermograms with changes in thickness distribution follow the kind of behaviour that one would anticipate. Theoretical melting curves often show exothermic types of responses, however these exotherms are effectively eliminated from the observed thermogram when the theoretical curve is convoluted with an instrumental broadening function.

(Keywords: melting; polyethylene; recrystallization; modelling; multiple melting endotherms; polymers)

INTRODUCTION

The phenomenon of multiple melting endotherms (and associated exotherms) exists for most polymers. A variety of explanations have been proposed and encompass a range of molecular level mechanisms[1-8]. Undoubtedly for specific cases one particular mechanism will be favoured. However, there is a general feature of polymer crystals, namely their lamella-like nature, which plays a role in establishing the thermogram of the material. For example these platelets 'melt' below the equilibrium melting point of the polymer, and they can reorganize to thicker lamella, all of which can lead to complex thermograms with different melting points. The reorganizational processes are characterized by two extremes[9], part of the lamellar sample may thicken or 'perfect itself' by annealing while being heated to the melting temperature, and eventually show a higher melting point characteristic of a perfected crystal. Alternatively, one can picture the lamellae melting, then recrystallizing, since it is below the equilibrium melting point, and finally remelting.

Distinguishing between these two possibilities is not an easy task, indeed the reality of the situation may be a combination of both effects. Many thermal analysts implicitly recognize this problem and talk of 'reorganizational' processes near the melting point. As a first effort to elucidate these processes a computer program has been written which models the recrystallization scheme. This is not meant to imply that this is the only, or indeed the preferred route to reorganization, but rather reflects the fact that more data is available on melt crystallization than exists for annealing. This paper describes the parameters and assumptions of the model and discusses the agreement between theoretical curves and experimental observations.

MODEL DEVELOPMENT

Because of the availability of data, the parameters chosen for this scheme are those of polyethylene (PE). However, the model is general enough that, if the data is available, other polymers can be readily examined. As a starting point it is assumed that we have a Gaussian weight distribution of crystal thicknesses whose mean is L_{Ave} and sigma value L_{Half}. There are no lengths permitted to be greater or less than L_{Ave} plus or minus three times L_{Half}. The sigma value, L_{Half} is normally input directly as a distance, however unless otherwise specified it is kept at 10% of the value of L_{Ave}.

The melting points for the individual crystal thicknesses are calculated using the Hoffman–Weeks expression:

$$T_m = T_m^\circ (1 - 2\sigma e / \Delta H_f \cdot L) \qquad (1)$$

T_m° is taken as 414 K, σe as 80 ergs cm^{-2} and ΔH_f as 70 cals cm^{-3}; i.e. the density of PE is assumed to be 1 g cm. The endotherm produced by melting an individual lamellar thickness is a function of the weight of the amount of material. Summing the endotherms from the individual lamellar thicknesses produces the melting endotherm for the original thickness distribution, as a function of temperature. This endotherm represents the melting behaviour if no reorganization takes place and will be termed the 'original' melting curve.

Before attempting to compute any 'reorganizational' changes two parameters must be estimated; recrystallization rates as a function of temperature, and the melting point of those recrystallized materials. Wunderlich[10], using a variety of data, has constructed plots of the reciprocal of time to reach one per cent crystallization, as a function of temperature and molecular weight. As a simplification it is assumed that such plots go through zero at 402 K, have a value of 1 min^{-1} at 396 K and are linear with temperature. That is, at 396 K it takes approximately 1 min for a 1% increase in overall crystallinty; molecular weight effects are not addressed. In practice the overall rate of crystallization does not increase indefinitely as temperature decreases, due to viscosity effects, however in the temperature range of interest the assumption of a linear increase with decreasing temperature appears to be reasonable. For reasons

Table 1 Default values for the melting model

L-$_{Ave}$	= 125 Å	ΔH_f	= 70 cals cm^{-3}
L-$_{Half}$	= 13 Å	β	= 1
T_m	= 414 K	CT (crystallization term)	
			= 10
σ_e	= 80 ergs/cm^2	HR (heating rate)	
			= 20 K min^{-1}

which will be addressed in the discussion section the actual rates used in model calculations are ten times those calculated by the above method.

Once recrystallized, the melting point of the polymer is given by:

$$T_m = [T_m^{\circ}(2\beta - 1) + T_c]/(2\beta) \qquad (2)$$

where β indicates the fold length in multiples of the primary homogeneous nucleus[11]. Some variation in β is listed in the literature, but it is usually close to one for PE; a value which is used in the model. The program also requests a heating rate, from this one can calculate the time a sample resides in a particular temperature interval. For ease of computation the temperature is stepped in 0.25 K intervals through the appropriate range.

The actual computation of the 'reorganized' melting trace starts with the 'original' curve. For each temperature increment the amount of sample melted is obtained from the original curve. Using recrystallization rate data one can compute how much of this molten material will recrystallize in this particular time interval. For a typical temperature increment, one can also visualize that some of the material which did not recrystallize in earlier time/temperature increments can now recrystallize. That is, although the temperature has increased (the recrystallization rate decreased) the polymer that melted earlier has experienced those conditions for a longer time and may now recrystallize. Once the total recrystallized material for a particular increment has been determined, by summing over earlier temperature increments, one can now calculate its new melting point, using equation (2) since the T_c is known.

The endotherms and the exotherm from melting and recrystallization can now be summed to give the 'reorganized' melting curve. This should be similar to the trace that a d.t.a. or d.s.c. instrument would give. There are two other factors that should be kept in mind. The program only permits one recrystallization cycle for a polymer, i.e. once melted, recrystallized and remelted the polymer is not allowed to further recrystallize and remelt. In addition, at this stage the program contains no 'instrumental broadening', i.e. even a high purity low molecular weight organic or inorganic when run on any existing instrument has a finite width peak. This presumably arises from 'thermal resistance' types of problems. Its effect will be to smear out the curves produced by the existing program, which was written in 'Basic' on an Apple II+ computer.

RESULTS AND DISCUSSION

Many of the parameters used in the model have been described previously and their default values given. For convenience we have listd these again in *Table 1*. One of the input variables which we have examined is heating

rate (HR). The effect of heating rates ranging from 1–80 K min^{-1} are shown in *Figure 1*. These are qualitatively the same as many experimental curves shown in the literature[9,12]. The main feature is a reduction in what is sometimes called the 'annealing' peak, as heating rate increases. That is, on increasing heating rate the high temperature peak due to the melting of recrystallized material will show a marked decrease in size. At higher heating rates there is only a short time to recrystallize before the temperature increases. Incidentally, in this and subsequent Figures, no attempt was made to normalize the curves on the basis of area. Rather, I have followed the thermal analyst's intuition to make the peaks 'about the same size'.

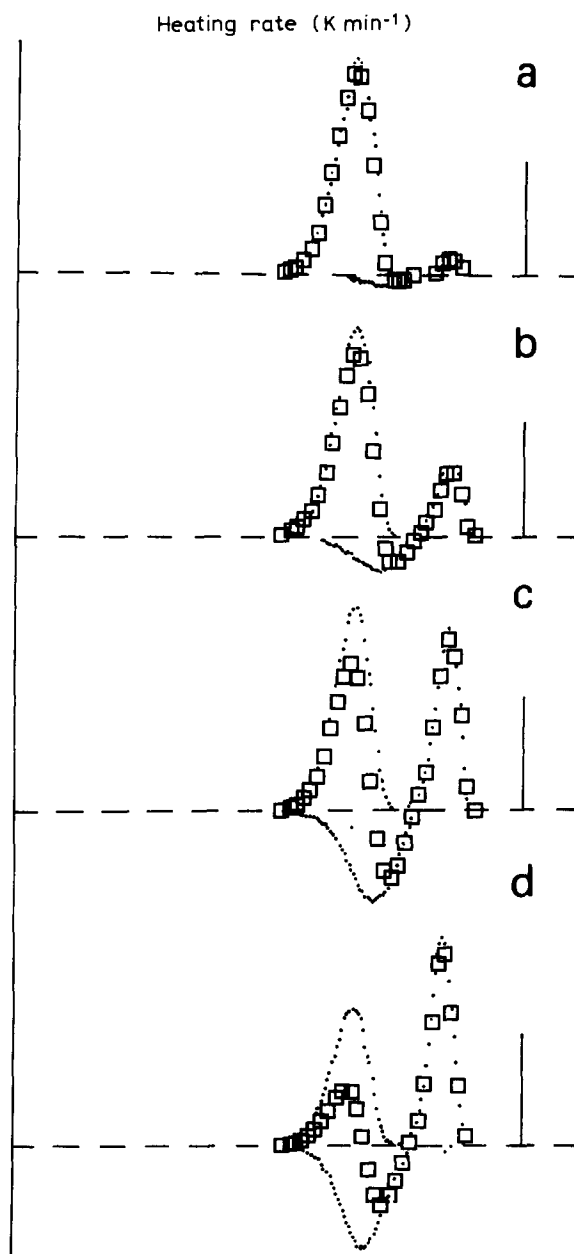Changes in thermograms with changes in original crystallization temperature are shown in *Figure 2*. If the

Figure 1 Model thermograms showing the effect of heating rate, with the appropriate plots. In this and subsequent plots (□) represent the summation of endotherms and exotherms. The short vertical line indicates $T_m^{\circ} = 414$ K, the left hand axis is at approximately 358 K. a) 80 K min^{-1} b) 20 K min^{-1} c) 5 K min^{-1} d) 1 K min^{-1}
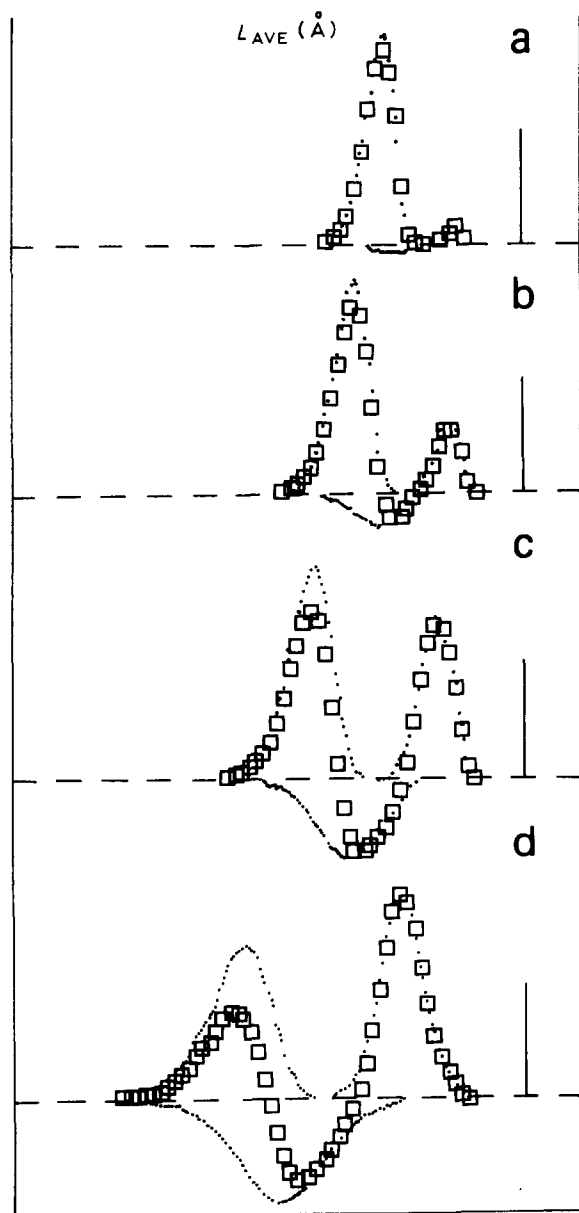
A *CT* value of 10 was chosen for the model since this appears to offer the best qualitative fit to existing data. It should not be too surprising that the overall crystallization rate in this type of sample is higher than in classic studies. In the latter case, almost invariably, care is taken to ensure that homogeneous nucleation of the sample is obtained. In any real sample undergoing melting and recrystallization there will be ample opportunity for surface nucleation. This will occur not only on the as yet unmelted sample, but also on the walls/surfaces of the d.t.a./d.s.c. cell. In a d.s.c. cell the optimum sample geometry is one in which the sample is thinly and evenly dispersed over the pan[14]. This geometry gives the least 'smearing' due to thermal conductivity effects. It is also the geometry which offers the greatest opportunity for surface nucleation on the sample pans.

The model apparently gives a good qualitative fit with existing data. It should therefore be possible to utilize the model to predict changes in the thermograms when other, less characterized, parameters are modified. For example

Figure 2 Model thermograms showing the effect of lamellar thickness in Å. See text for appropriate crystallization temperatures. a) 150 Å b) 125 Å c) 100 Å d) 75 Å

original crystals are formed at different temperatures their lamellar thickness changes. So PE crystals grown from a dilute xylene solution at 75°C are ~100 Å thick; if T_c were 90°C then the crystals would be ~150 Å. Again the theoretical curves are qualitatively identical with experimental data[13]. The lower temperature peak which is primarily associated with the 'original' curve moves to higher temperatures with increasing original lamellar thickness; or increasing original crystallization temperature. At the same time as L_{Ave} increases, evidence for recrystallization and remelting becomes less apparent. Since the original lamellae will initially melt at higher and higher temperatures the average rates of recrystallization will be substantially smaller. This leads to the near absence of a high temperature 'reorganizational' peak in samples which originally contained thicker lamella.

In the previous examples we have allowed the polymer to recrystallize at a rate ten times that calculated using the process described earlier. The effect of this crystallization term (*CT*), which is just a multiplier, is shown in *Figure 3*.

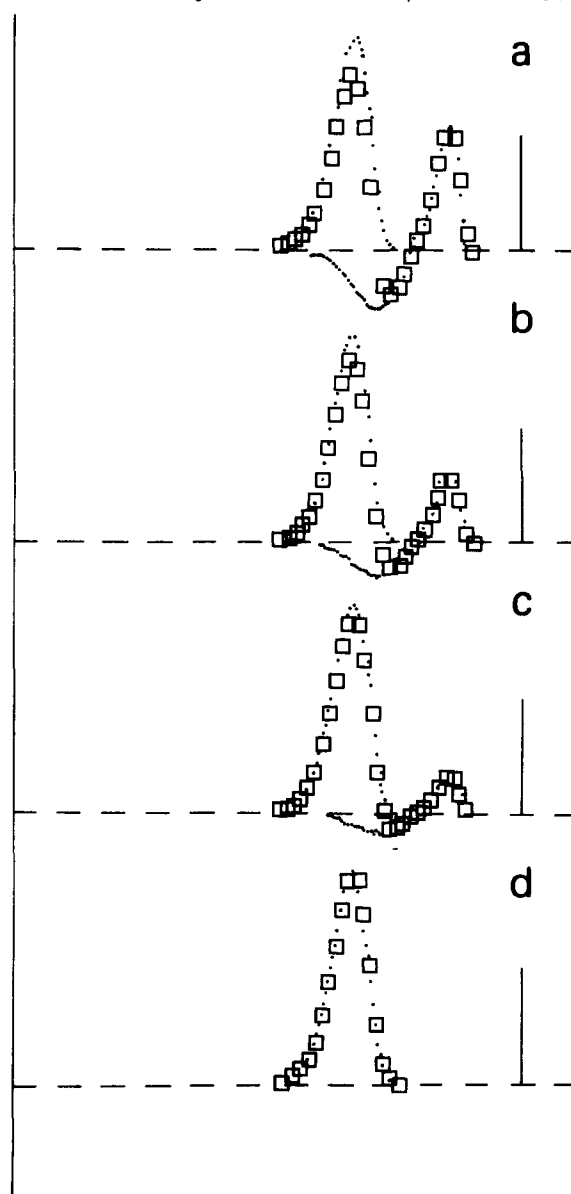**Figure 3** Model thermograms showing the effect of the isothermal crystallization multiplier term, *CT*. a) 20 × b) 10 × c) 5 × d) 1 ×
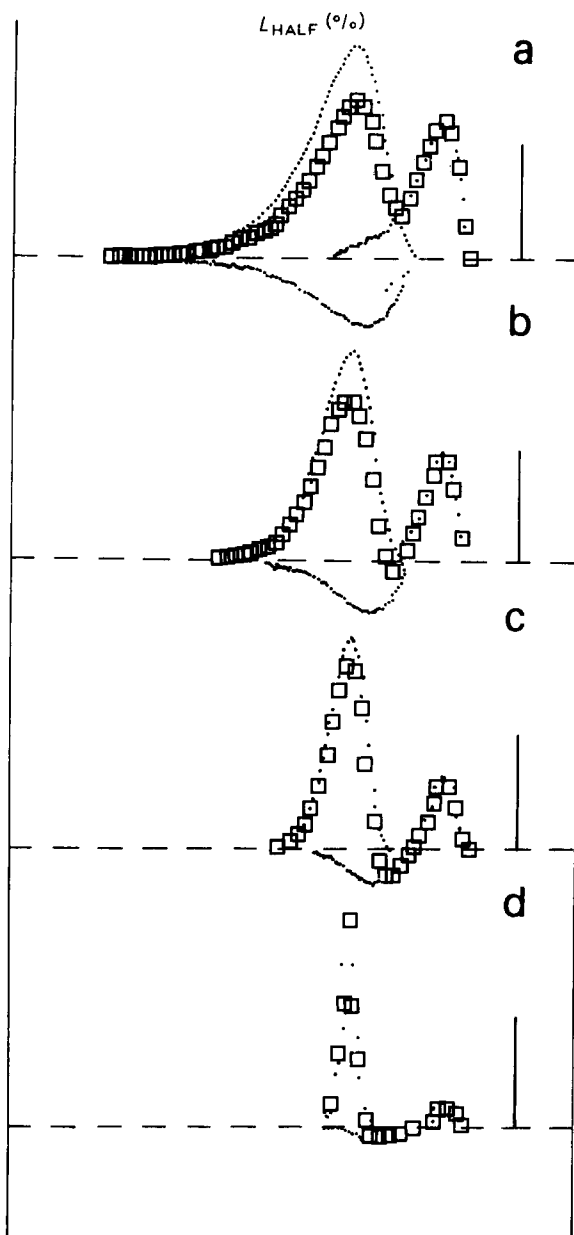
L_{HALF} (%)

a

b

c

d

Figure 4 Model thermograms showing the effect of changes in
L Half. These changes are expressed as a percentage of the
default value of L_{Ave} (125 Å). a) 20% b) 15% c) 10% d) 5%

Figure 5 Model thermograms showing the effect of
convolution with an indium type peak. The indium is shown
schematically on the left. △ represents the convolution product
with the original peaks

in *Figure 4* we see the thermograms that the model
predicts for changes in thickness distribution (L_{Half}).
Intuitively one believes that as the breadth of the thick-
ness distribution increases, the thermogram should get
broader. This is certainly consistent with model pre-
dictions. The low temperature 'original' peak increases in
width, with an increase in the thickness distribution. It is
not as obvious, intuitively, that the 'reorganization' peak
should also increase in size as the thickness distribution
increases. However, on reflection, this would certainly
seem to be a valid prediction. With a broader thickness
distribution more of the material will melt, at lower
temperatures than the average 'original' melting point. As
a result this lower melting material has a longer time to
recrystallize and will experience higher recrystallization
rates at these lower temperatures. The net result will be
qualitatively as predicted by the model.

The model is qualitatively similar in many respects to
observed thermograms. One somewhat disquietening
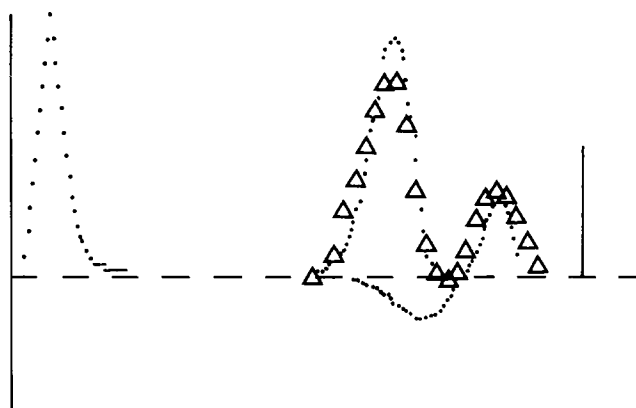feature is the observation that with the default values, one

observes signs of a crystallization exotherm between the
melting endotherms. Such exotherms have been reported,
but usually at lower heating rates than 20 K min^{-1}. In the
model, this exotherm will all but disappear with a
decrease in β or an increase in the value of L_{Half}. However a
more probable cause for the slight exotherm was alluded
to in the section of 'Model Development', namely, the
model contains no attempt to accommodate 'instrumen-
tal broadening'. That is, one normally observes thermo-
grams which have been 'smeared out' to various amounts
by the particular instrument used. In an attempt to mimic
the smearing behaviour, I have folded or convoluted the
model data with a curve based on a typical d.s.c. trace
from an indium sample. The indium trace has a width at
half-height of approximately 2K and is 10K wide at the
base. The particular indium sample weighed approx-
imately 2 mg and was run at 20K min^{-1}. The results of
convolution are shown in *Figure 5* together with the
indium based curve that was used to convolute the model
data. Such folding or convolution effectively smears out
the peaks and the exotherm has all but disappeared from
this trace.

CONCLUSIONS

A model has been developed which qualitatively describes
many features of the multiple melting behaviour of
polymers. The program is easily modified to accom-
modate a variety of polymers whose parameters are
known or can be estimated. Convolution of model peaks
is possible by appropriate functions which describe
'instrumental broadening', this leads to thermograms
which are effectively free of exotherms under default
conditions. This program is based entirely on a melt/crys-
tallize/remelt scheme and within the range of heating rates
and other parameters used, appears to adequately de-
scribe multiple melting in PE. This does not negate the
idea that annealing will affect melting behaviour, parti-
cularly at lower heating rates. Subsequent programs will
attempt to model this annealing behaviour and its effect
on melting.

REFERENCES

1   Mandelkern, L., Fatou, L. J., Denison, R. and Justin, J. *J. Polym.
     Sci. B.* 1965, **3**, 803
2   Holden, H. W. *J. Polym. Sci. C* 1964, **6**, 53

3   Bell, J. P., Slade, D. E. and Dumbleton, J. H. *J. Polym. Sci.* 1968, **6**, 1773
4   Bair, H. E., Salovey, R. and Huseby, T. W. *Polymer* 1967, **8**, 9
5   Mandelkern, L. and Allou, A. L. Jr. *Polym. Lett.* 1966, **4**, 447
6   Hoashi, K. and Machizuki, T. *Macromol. Chem.* 1967, **100**, 78
7   Bell, J. P. and Dumbleton, J. H. *J. Polym. Sci. A-2* 1969, **7**, 1033
8   Harland, W. G., Khadr, M. M. and Peters, R. H. *Polymer* 1972, **13**, 13

9   Jaffe, M. and Wunderlich, B. *Kolloid Z. Z. Polym.* 1967, **216–217**, 203
10   Wunderlich, B. *Macromol. Phys.* 1976, **2**, 233
11   Wunderlich, B. *Macromol. Phys.* 1980, **3**, 33
12   Harrison, I. R. and Runt, J. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 321
13   Harrison, I. R. *J. Macromol. Sci.-Chem.* 1974, **A8(1)**, 43
14   Harrison, I. R. and Varnell, W. D. *J. Therm. Anal.* 1982, **25**, 391