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MELTING POINT VARIATIONS IN LINEAR HIGH POLYMERS*†

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ABSTRACT

The melting is analyzed for folded chain, fringed micelle, and extended chain crystals of linear high polymers which crystallize in lamellar, isometric, fibrillar and dendritic morphology. Time-dependent differential thermal analysis or differential scanning calorimetry are the best techniques usable for such investigations. After detailed analysis of polymer crystals, it seems feasible that this method of time-dependent thermal analysis can be transferred to the analysis of other materials.

INTRODUCTION

In discussing the melting of linear high polymers by differential thermal analysis (DTA) or differential scanning calorimetry (DSC), it is of importance to recognize that these thermal analysis methods are ideally suited for the study of slow melting, or reorganizing metastable crystals. Transition temperatures, heats of transition, and heat capacities can be measured more accurately (although with more effort) by adiabatic calorimetry than by differential thermal analysis. The added feature of differential thermal analysis is, besides a wider temperature range, the possible use of time as an experimental variable. It is at present easily possible to vary the experimental heating time scale from 0.1 °C/min to 1000 °C/min, five orders of magnitude. It should be possible with only little added effort to extend this to heating rates as fast as 10^6 °C/min‡. While in the study of polymer melting heating rate dependent DTA and DSC played an important role, not many other materials have been analyzed to date in this way. There is considerable evidence, however, that a second look at the melting and general transition behavior of organic and inorganic compounds with time dependent techniques will give added information.

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‡For a general discussion of the technique and instrumentation of DTA see: B. Wunderlich, *Differential Thermal Analysis*, in Weissberger and Rossiter (Eds.), *Physical Methods of Chemistry*, Vol. I, Part V, Chap. 8, J. Wiley and Sons, New York, 1971.

The special nature of polymer melting is best revealed when one compares the melting of a typical polymer like polyethylene $(CH_2-)_x$ with a typical low molecular weight material like water (H_2O). If one asks the question at what temperature does pure ice melt, the precise answer is: 273.15 K or 0 °C. If one asks at what temperature does pure polyethylene melt, I can, after having studied this problem for about 15 years*, give the following answer: "There is evidence that polyethylene may start melting at −10 °C. Mostly it melts between 80 and 135 °C. The equilibrium melting point seems to be at 141.4 °C. However, I have seen polyethylene still only partially molten at temperatures of 160 °C and higher." These seemingly contradictory facts will be analyzed in this paper.

DISCUSSION

Thermodynamics of melting

Melting is the transformation of a fully or partially crystallized substance into the liquid state, the melt. In the crystalline state polymer chains are largely immobile, while in the liquid state frequent conformational changes occur. A crystal has a low enthalpy and entropy. This is achieved microscopically by a maximum of van der Waals interaction in the dense atomic packing. If in addition, stronger interactions like dipole-dipole or H-bonds are possible, they are maximized by alignment such that pratically all of these bonds are made. Finally, the chain conformation in the crystalline state is such that it gives an overall minimum energy. Experimentally the crystallization order can be analyzed by X-ray diffraction. Thermodynamically the crystalline state can be characterized by the free energy:

$$G_c = H_c - TS_c \tag{1}$$

The melt, in contrast, is a state of higher enthalpy with no long range order and accordingly with much higher entropy. Analogous to Eqn. 1, the free energy of the melt is

$$G_l = H_l - TS_l \tag{2}$$

The lowest temperature where melting is possible is the point of equal free energies

$$G_l = G_c \tag{3}$$

These three equations allow us to discuss the melting temperature T_m

$$T_m = \frac{H_l - H_c}{S_l - S_c} = \Delta H/\Delta S \tag{4}$$

It is to be noted that Eqns. 1–4 apply to systems in equilibrium as well as to metastable systems.

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*A list of pertinent references from our laboratory is given at the end of this discussion.

Comparison of monomer and polymer melting temperatures

For monatomic elements ΔS is nearly constant, as illustrated in Table I. This fact is known as Richard's rule, which places S between 1.8 and 3.4 cal deg^{-1} mole^{-1}.

TABLE I

MOLAR HEATS OF FUSION (ΔH_f), MELTING POINTS (T_m), AND ENTROPIES OF FUSION (ΔS_f) OF ELEMENTS

Element	ΔH_f (*cal/mole*)	T_m (*K*)	ΔS_f (*cal/deg mole*)	*Element*	ΔH_f (*cal/mole*)	T_m (*K*)	ΔS_f (*cal/deg mole*)
Ne	80	24.5	3.26	Cd	1500	594	2.53
Ar	281	83.5	3.35	Zn	1800	692	2.60
Kr	390	116	3.36	Al	2500	930	2.70
Rb	520	312	1.70	Ag	2700	1234	2.18
Hg	560	234	2.40	Cu	2700	1356	1.99
Na	610	371	1.64				

If S changes only little for a group of crystals, the melting temperatures are fixed by the enthalpy change. Furthermore, if the gain in disorder is similar for a series of substances, the number of "broken bonds" at any time in the liquid is often similar, so that the melting points are nearly proportional to the bond strength in the crystal (or the cohesive energy density). Table I shows that for example argon, with van der Waals bonds only, melts low, while gold with strong metallic bonds melts high. Similar data for linear high polymers are collected in Table II.

TABLE II

HEATS OF FUSION (ΔH_f), MELTING POINTS (T_m, t_m), AND ENTROPIES OF FUSION (ΔS_f) OF POLYMERS PER MOLE OF CHAIN ATOM

Polymer	ΔH_f (*cal/mole*)	T_m (*K*)	t_m (*C*)	ΔS_f (*cal/deg mole*)
Polyethylene	925	414.6	141.4	2.23
Polypropylene	737	449	176	1.64
Polystyrene[a]	1200	512	239	(2.34)
Poly(vinyl fluoride)	900	470	197	1.91
Polytetrafluoroethylene	730	600	327	1.22
Polyethylene oxide	660	339	66	1.94
Polymethylene oxide	795	453	180	1.76
Polyacrylonitrile	600	590	317	1.02
Poly(ethylene terephthalate)	785	540	267	1.45
Poly(ethylene sebacate)	571	349	76	1.64
Nylon 6.6	736	540	267	1.36
Nylon 6.10	666	499	226	1.33
Nylon 6	728	498	225	1.46

[a] In the case of polystyrene, the ΔH_f and ΔS_f should be compared not per chain atom. The C_6H_5 side group is so big that it should be taken as a separate unit, reducing ΔS_f to 1.56.

The ΔH and ΔS values are calculated per mole of backbone atoms. The very flexible polymers, for example polyethylene, have a ΔS similar to that of the monatomic elements. None of these polymers melts very high since the heat of fusion is relatively low. If, on the other hand, the polymer chains become less flexible, as for example in polytetrafluoroethylene, ΔS decreases and despite a small ΔH, the melting temperature increases. High melting points can be caused in linear high polymers by stiff backbone chains.

Complications in melting experiments

The simple description of melting offered by Eqn. 3 is often complicated by one or more of the following situations. *1.* The transition from crystal to melt is not instantaneous, but needs a certain amount of time. If one heats a crystal faster than it can melt, the interior superheats temporarily. Experimentally, a melting range which broadens to higher temperatures on faster heating is observed. *2.* Small crystals have a large surface free energy so that

$$G_c = G_c^\circ + G_s \tag{5}$$

where G_s represents the surface free energy per mole of substance. The point of equal free energy of melt and small crystal is thus at a lower temperature. In addition, small crystals are, because of higher free energy, metastable with respect to larger crystals. Whenever the time scale allows, the small crystals will reorganize to bigger crystals with smaller free energy. Defect crystals behave similarly to small crystals. *3.* Impure melts have a lower free energy due to the entropy of mixing of the impurities with the crystallizable component. The change in free energy is represented by the change in chemical potential

$$\mu_p = (\delta G_1)/(\delta n) \tag{6}$$

The temperature of equal chemical potential of crystal and crystallizing component in the melt is changed according to the following equation

$$(1/T_m) - (1/T_m^\circ) = (R/\Delta H)[-\ln v_p + (x-1)v_i - x^2 v_i^2 \chi], \tag{7}$$

where T_m is the observed equilibrium melting point of the polymer dissolving into a melt of volume fraction v_p; T_m° is the equilibrium melting point of the same polymer into its pure melt; ΔH is the heat of fusion of one mole of polymer; x is the ratio of molar volume of polymer to that of the second component i; and χ is an appropriate interaction parameter defined per mole of the second component, which may also be polymeric.

It turns out that polymer crystals are often slow melting, form frequently notoriously small crystals, and are mostly impure. Experiments on melting must then be interpreted by taking into account the time scale of the experiment, the crystal sizes, and the purity.

Polymer crystals

Polymer crystals vary widely in morphology*. On crystallization of the already polymerized molecules each molecule must go through an intermediate "folded conformation" to overcome molecular nucleation. Very often the final crystals are not much thicker in the molecular chain direction as the initial fold length of 50–500 Å. On careful crystallization regularly folded thin lamellae result on growth from dilute solution or also from the melt. On faster crystallization, or on crystallization at relatively low mobility of polymer chains, chain folding becomes more irregular and increasing tie molecules which run from one crystal to the other appear. This crystal morphology will be called the "fringed micelle" type. Little is known about the detailed structure of the fringed micelles despite the fact that it may represent the commercially most important crystal morphology. On crystallization of the monomer directly to the polymer, chain folding is not a necessary intermediate. In these cases "extended chain crystals" with much larger dimensions in the molecular chain direction may be grown. The folded chain, fringed micelle, and extended chain crystals represent the three basic macroconformations a crystallizable linear macromolecule may assume. Besides changes in the chain conformation which is linked to crystal perfection in one dimension only, there may be the usual morphology changes in the other two dimensions. Isometric or lamellar crystals grow naturally only at slow rates (see Fig. 1 a). On fast crystallization, extended chain crystals yield fibrous crystals, and folded chain crystals, dendrites (see Fig. 1 b). Both macroconformations may in addition give rise to spherical aggregates of crystals, called spherulites (see Fig. 1 c). Below some of these crystal morphologies are briefly characterized.

(*1*) Extended chain crystal lamellae represent the polymer crystals closest to equilibrium. Their free energy is the lowest of all analyzed materials. The molecular chains in these crystals are extended to such a degree that chain folding becomes unimportant as a free energy reducing cause. In general, polymer crystals which are more than 2,000 Å in the molecular chain direction can be considered extended. For such long distances between chain ends or folds, the temperature of equal free energy of crystal and melt (Eqn. 5) has usually increased to within less than one degree of the equilibrium melting temperature. This arbitrarily chosen length agrees approximately with the definition of the lower limit of a polymer molecule as having at least 10,000 molecular weight.

At present, melting of extended chain crystals has been analyzed for polyethylene, polyoxymethylene, polytetrafluoroethylene, selenium, and polycaprolactam. The polyethylene for these analyses was made by crystallization under hydrostatic pressure of 4000 atm. The other polymers were obtained by simultaneous polymerization and crystallization, which removes the *a priori* reason for chain folding.

(*2*) Spherulites of polymers consist of many small ribbon- or fiber-like polymer crystals radiating out of a common center, giving a spherical appearance under low

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*For a detailed discussion of polymer crystal morphology see: B. Wunderlich, *Crystals of Linear Macromolecules*, Academic Press, New York, 1972–73.

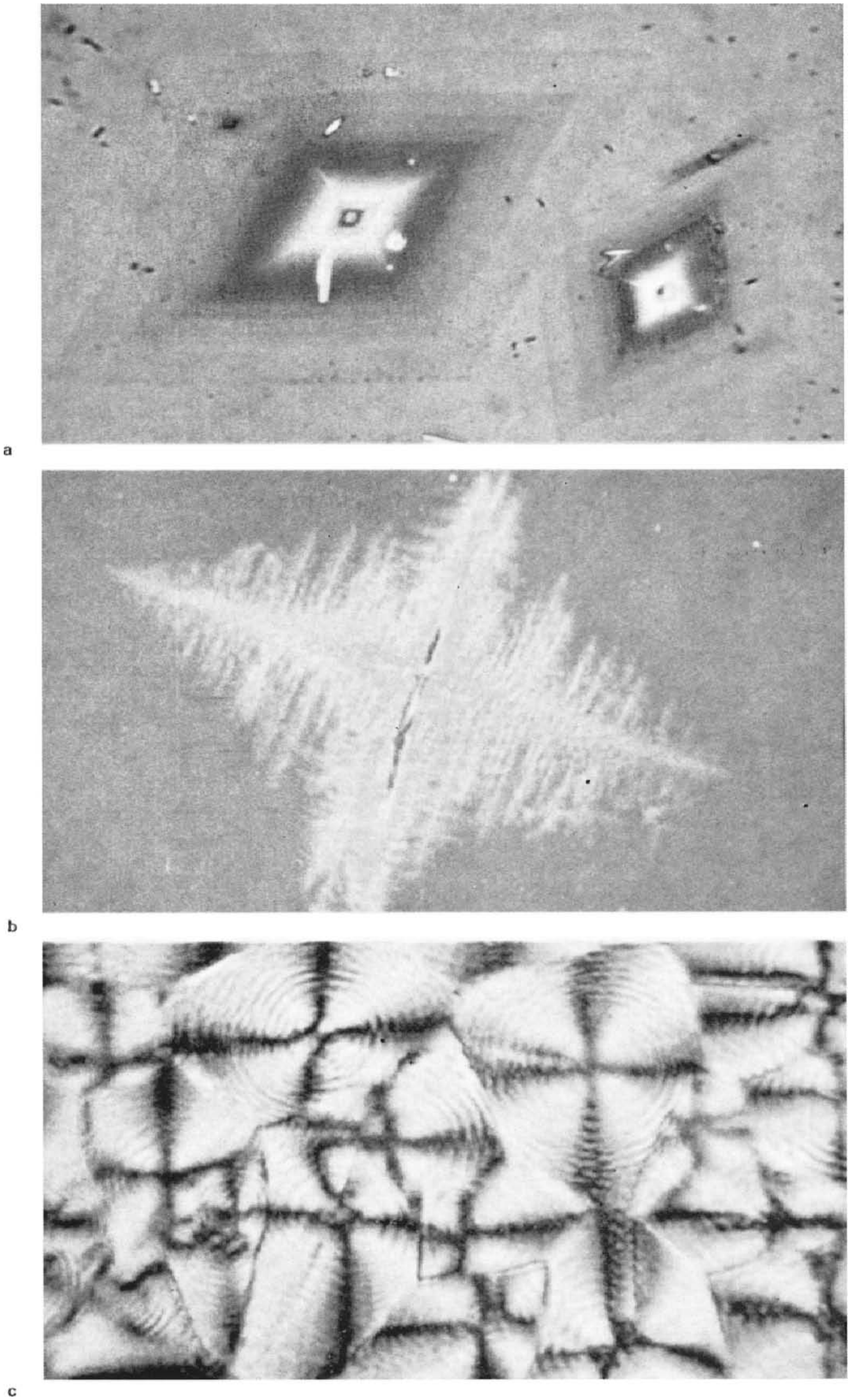

Fig. 1. a. Lamellar polyethylene grown from dilute solution. b. Dendritic polyethylene grown by fast cooling of a dilute solution. c. Spherulitic polyethylene grown from the melt. All three micrographs were taken with interference optics. The largest crystal dimensions are 0.1 mm [*J. Polym. Sci., Part C,* 1 (1963) 41].

magnification (see Fig. 1c). Usually these crystals are grown from the melt so that the polymer chains in these crystals are folded in the ribbon-like morphology. The spherulitic arrangement of crystal lamellae of polymers is general. Spherulitic character can also be found for lamellar crystals of folded chain molecules and even in extended chain crystal aggregates of fibrillar or lamellar morphology.

(*3*) Folded chain single crystals is the term most frequently applied to the perfectly shaped polymer crystals grown from dilute solution (see Fig. 1a). Their macroscopic faces correspond to low-index crystallographic planes. The fold center in these crystals is usually only between 50 and 200 Å. Although these crystals may reach lateral dimensions up to 0.1 cm or more, due to the thin lamellar morphology, their surface area is usually enormous. Typical surface areas are 10^5–10^7 $\mathrm{cm^2 g^{-1}}$. The weight of such single crystals is between 10^{-14} and 10^{-10} g.

(*4*) Dendritic polymer crystals are produced by a skeleton type growth as is known, for example, from snow flakes. Fast crystallization from solution leads to such crystal morphology (see Fig. 1b). The fold length is similar to that of the folded chain single crystals. Dendritic crystals are even less stable than folded chain single crystals because of their appreciable side surface. They have many polymer chains located on surface sites which accounts for a higher mobility. Dendrites can reorganize fast if they are heated above their crystallization temperature.

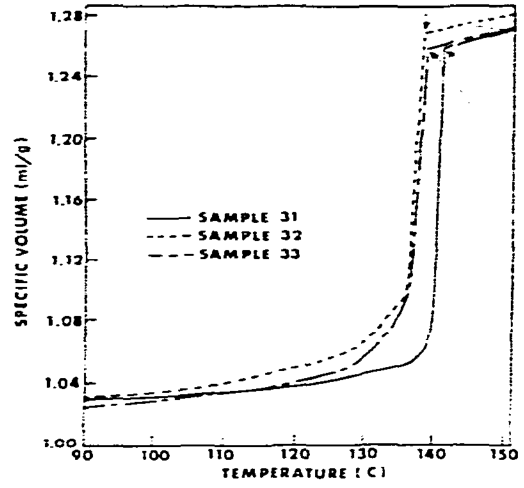

Fig. 2. Melting of extended chain crystals of polyethylene. Curve 31 illustrates the sharp melting of high molecular weight polyethylene. The curves 32 and 33 are of broad molecular weight distribution and show lower and wider melting regions. Data obtained by dilatometry [*J. Polym. Sci., Part C*, 16 (1967) 653].

Melting of extended chain crystals

Extended chain crystals are close to thermodynamic equilibrium such that on very slow heating a sharp thermodynamic equilibrium melting point can be achieved. This melting point will be lowered and broadened as soon as a molecular weight distribution is present (impurity effect). These effects are shown in Fig. 2. Table III lists results of melting point on extended chain crystal determinations. The first four polymer melting points are probably close to the equilibrium melting point for infinite molecular weight, while the last may be somewhat too low because of insufficiently high molecular weight.

TABLE III
MELTING POINTS OF EXTENDED CHAIN POLYMER CRYSTALS

Polymer	*Melting point (°C)*
Selenium	220.5
Polyethylene	141.4
Polytetrafluoroethylene	327.0
Polyoxymethylene	182.5
Polycaprolactam	228

These melting point experiments are distinguished from many monomer melting points by the fact they can only be measured in the heating mode. A polymer chain, once removed from the crystal, will not recrystallize into the same crystal morphology at the melting temperature. Considerable supercooling and often special crystallization conditions (for example high hydrostatic pressure or crystallization from the monomer) may be necessary to reverse the melting process.

A broad molecular weight distribution of polyethylene was also analyzed (curves 32 and 33 in Fig. 2). It was crystallized into an extended chain conformation by the use of about 4000 atm. pressure. The resulting extended chain lamellae showed a broad distribution in length parallel to the molecular chains. The lower portion of the dilatometric melting curves (crystallinity *vs.* temperature), up to about 135°C,

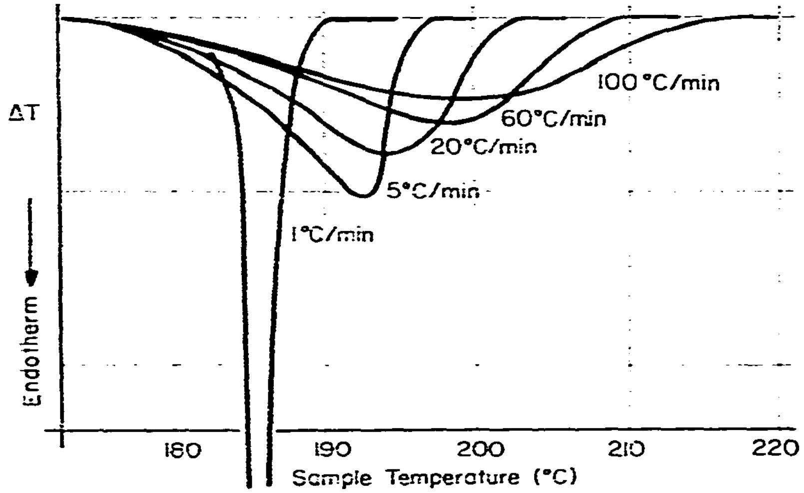

Fig. 3. DTA traces of extended chain crystals of polyoxymethylene as a function of heating rate. All curves are normalized to equal areas. The equilibrium melting point is 182.5°C [*Kolloid Z.Z. Polym.*, 203 (1967) 216–217].

could be perfectly matched using Eqns. 7 and 3. This indicates that here separation occurred into different molecular weights according to a eutectic phase diagram. At the higher temperatures the sample melted sharper than calculated. This can be taken as an indication that the polymer chains in the remaining crystals were cocrystallizing in a common lamella. In agreement with the idea of cocrystallization, no lamellar thicknesses corresponding to the largest molecular weight fractions were observed. The lowering of the maximum experimental melting point from the high molecular weight value in Table III can be attributed to mixed crystal formation of the different molecular weights.

Such a simple melting behavior is found only on slow heating. All extended chain polymers analyzed superheated as soon as the heating rates were increased. The crystals could be heated faster than the melt–crystal boundary could progress toward the interior. The remaining inner portion of the crystal thus superheats temporarily and melts at a much higher temperature. Table IV lists some typical values of superheating for the last crystal trace melting. All values were obtained by differential thermal analysis. Fig. 3 illustrates the DTA traces on fast melting of extended chain polyoxymethylene.

TABLE IV

ESTIMATED MELTING TEMPERATURE (°C) OF THE LAST TRACE OF EXTENDED CHAIN CRYSTALS FOR DIFFERENT HEATING RATES

Polymer	*Heating rates (°C/min)*				
	1	*5*	*10*	*50*	*100*
Polyethylene	151	154	157	165	
Polyoxymethylene	191	196	201	206	216
Polytetrafluoroethylene	332	337	340	350	
Selenium	223	225	226	231	236

For most of the analyzed samples the isothermal melting kinetics could be expressed mathematically as follows:

$$c_w = \exp(-t/\tau) \tag{8}$$

where c_w is the weight fraction of crystals which remain unmolten at time t, τ is a constant which has formally the appearance of a relaxation time. A comparison of values for τ at different degrees of superheating above the equilibrium melting point is listed in Table V.

At present, the melting of extended chain polymer crystals can be summarized by saying that these crystals follow equilibrium thermodynamics. On faster heating, as is experienced in almost all experimental techniques, superheating can be expected. In fact, measuring the superheating gives at present the only experimental tool for discovery of extended chain crystals in an unknown sample.

TABLE V

RELAXATION TIMES (sec^{-1}) FOR ISOTHERMAL MELTING AT THE GIVEN DEGREES OF SUPERHEATING

Polymer	*Superheating (°C)*	
	5	*10*
Polymethylene (high molecular weight)	55	17
Polyethylene	34	10
Polyoxymethylene	86	22
Polytetrafluoroethylene	65	13
Selenium	3	0.9

Melting of spherulites

Spherulites grown from the melt are metastable with respect to the extended chain crystals. The temperature at which the free energy of these crystals equals that of the melt is usually 5–10 °C below that of the extended chain crystals. Frequently these crystals also contain large portions of ill-crystallized polymer which extends the melting range to very low temperatures. For cooling rates from the melt between 1 °C h^{-1} and 1 °C sec^{-1}, which encompass most actual situations, the melting peak temperature of the resulting spherulite crystals, as measured by differential thermal analysis, varies only little with heating rate. Many of the resulting crystals have large enough fold lengths to be metastable up to temperatures close to the melting point. If it is possible to transform a metastable crystal without reorganization on heating directly into the supercooled melt, a path of zero entropy production melting is followed. No irreversible process has occurred during this experiment. In such case melting occurs where the free energy of the metastable crystal (which can be analyzed by X-ray diffraction, microscopy etc. at low temperatures) is equal to the free energy of the supercooled melt (whose properties can be extrapolated from the stable melt). Zero entropy production melting points are important for a thermodynamic characterization of defect crystals. Only a small amount of superheating is discovered in these crystals.

It must not be overlooked, however, that by careful annealing all intermediate stages to the extended crystals can be produced. Also, on excessive quenching, dendritic spherulites may be produced. Such crystallite distributions will behave similar to the solution grown dendrites to be described below. Besides experimental time scale variation, polymers of different inherent crystallization, melting, and reorganization rates will produce varying effects. The region of zero entropy production is limited at low heating rates by reorganization or recrystallization, at high heating rates by superheating. The region where at least approximate zero entropy production melting can be achieved is dictated by the chemical nature of the polymer and the detailed crystal structure on hand. If the thermal behavior of a polymer is quite well known, again, observation of melting as a function of heating rate can be used as an analytical tool. At present, detailed studies have been performed on the polymers listed in Table III.

Melting of folded chain single crystals

The morphology of folded chain single crystals, in particular, can be easily analyzed. Interference microscopy (as shown in Fig. 1), electron microscopy, and X-ray diffraction enable a complete description of unit cell, crystal shape and dimensions, chain length between folds, and also possibly the internal defects. Because of their usually very small fold length even for laterally large lamellae, reorganization, mainly by fold length increase, occurs on heating. The actual process is different for different polymers. Polyethylene, for example can, over a range of heating rates, be caused to increase smoothly in fold thickness via a solid-state thickening mechanism. As a result, the microscopically observable melting point of solution-grown, folded-chain lamellae decreased smoothly from 130°C, for 0.5 °C sec^{-1} heating rate, to a constant 120°C for heating rates above 20°C sec^{-1} up to 3000°C min^{-1}. Zero entropy production is reached only above 20°C sec^{-1}. Polyoxymethylene and polycaprolactam, in contrast, showed thickening mainly by recrystallization. In the latter case, differential thermal analysis shows two or more melting peaks on slow heating, often separated by a clearly visible recrystallization exotherm (see Fig. 4). In all cases a zero entropy production melting region could be established with reasonable certainty. Superheating is of no concern in these extremely thin crystals. Eqn. 5 allows us to calculate a surface free energy if we assume no other defects contribute to the melting point lowering from the equilibrium value. The melting point lowering calculation for thin lamellae is based on the Thomson equation (1871) and has first

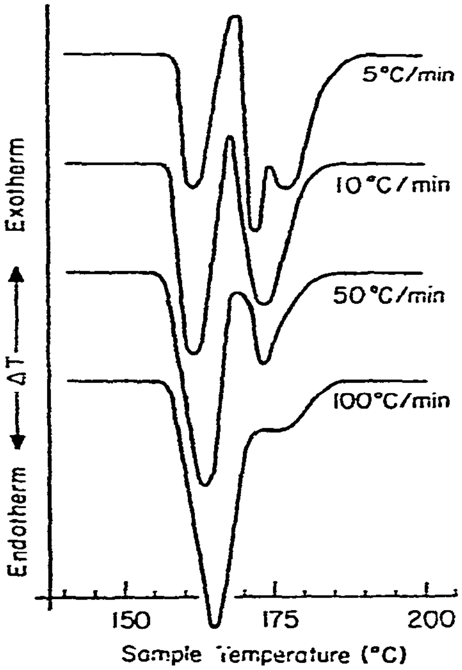

Fig. 4. DTA traces of solution crystallized polyoxymethylene as a function of heating rate. Multiple peaks have developed due to reorganization and recrystallization at the slower heating rates.

been applied to lamellar crystals by Tammann (1920)

$$\Delta T = (2\sigma T_0)/(\Delta H_f l) \tag{9}$$

ΔH_f is the heat of fusion per cm^3, σ is the specific surface free energy, while l is the fold length in cm. For polyethylene, polyoxymethylene, and polycaprolactam, specific surface free energies of about 80, 50, and 30 ergs cm^{-2} have been calculated from fold length determination and melting point data on the assumption that all melting point lowering is caused by the surface free energy.

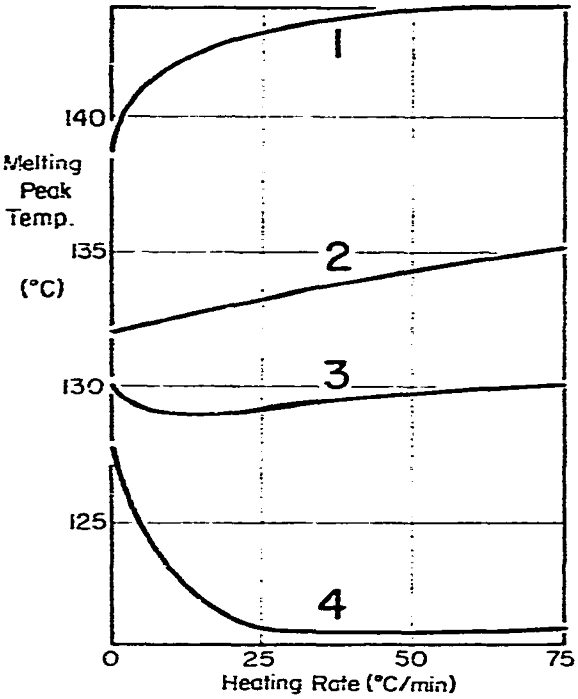

Fig. 5. DTA melting peak temperature of chemically identical polyethylenes of different morphology as a function of heating rate. Curve 1, extended chain crystals; curves 2 and 3, slowly and fast cooled melt crystallized spherulites; curve 4, solution grown folded chain single crystals.

In summary, folded chain single crystals melt about 20°C lower than the equilibrium melting points when heated fast enough for zero entropy production melting. On slower heating, reorganization and recrystallization occurs. In combination with fold length determinations, surface free energies of the fold surface can be determined. A summary of DTA melting peak temperatures for differently crystallized polyethylenes is given in Fig. 5.

Melting of dendrites

Dendrites are the least stable of the "good crystals" described above. Their zero entropy production melting point is frequently difficult to assess. It is as much as

30 °C below the equilibrium melting point. The difficulty of measurement arises from the large mobility of the polymer chains on the skeletal side-surfaces of the dendrite. The microscopic melting point for polyethylene dendrites could be changed only insignificantly from the reorganized polymer value of 128 °C even with heating rates as fast as 3000 °C min^{-1}. Polyoxymethylene, again, showed recrystallization. At the slowest heating rates two recrystallizations could be observed, so that the differential thermogram showed three melting peaks. The amount of polymer molten in each melting region varied with the heating rate. At 100 °C min^{-1} it was still possible for 60% of the dendrites to recrystallize. Quantitative analyses of the portions at each temperature are necessary to establish the processes occurring during dendrite melting. Even more involved seems to be the polycaprolactam melting. In this case as many as four recrystallization steps have been observed.

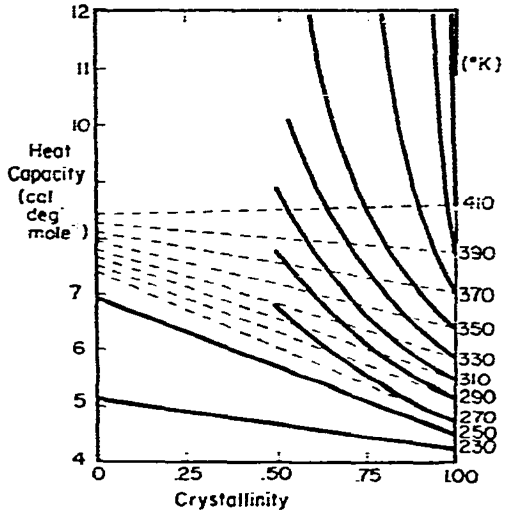

Fig. 6. Heat capacity of polyethylene as a function of crystallinity at different temperatures. The contribution by the heat of fusion (or reorganization of crystals) is indicated by the deviations of the curves from linearity.

Pseudo equilibrium melting

Little is known about fringed micelle melting. From analysis of heat capacities as a function of crystallinities, Fig. 6 shows that increments to the heat capacity appear for partially crystalline polymers as low as 5–10 °C above the glass transition temperature of the polymer. These added amounts of heat necessary to raise the temperature are initially reversible. They have been interpreted as premelting or as growth or reorganization of defect subsystems. Such reversibility indicates a pseudo equilibrium of molecules which is restrained perhaps by partial crystallization on several crystal surfaces. Only when the crystals melt to which they are attached, is the reversibility destroyed. Zachmann (1965) has calculated the increase in entropy on increasing the amorphous portion of such "tie molecules" and shown that ΔS may be much higher in this case. According to Eqn. 4 this could lead to the observed lowering of the melting temperature. When such crystal morphology is produced under strain, superheating is also possible because of restriction of mobility of the molten molecular portion due to the remaining crystalline portion.

CONCLUSION

It is thus quite possible to have strained tie molecules, in "poorly crystallized" polyethylene, which melt at −10°C. Most of the folded chain morphologies melt between 80 and 135°C, depending on fold-length and on defects. High molecular weight extended chain crystals of polyethylene have an equilibrium melting point of 141.4°C. On faster heating the interior of extended chain polyethylene crystals may superheat to 160°C or higher. All these "melting temperatures" are not contradictory, but indicate special morphologies and heating conditions. They may be used as valuable information for structure determinations in polymers. DTA and DSC is the only technique available for evaluation of the time dependent melting points.

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