'EFFECT OF VARIATION IN THE CHEMICAL STRUCTURE ON THE RATE OF CRYSTALLISATION OF POLYMERS'.

by

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SUMMARY.

Seven linear polyesters having similar molecular weights and closely related structures were prepared. The crystallisation rates of these polyesters were measured by using the Du Pont thermal analyzer and DSC cell. Additional rate measurements were made using dilatometry. The relative merits of the two techniques are discussed.

The results obtained by DSC and dilatometry were analysed in terms of the Avrami equation using a computer program. The variation in the Avrami integer n and its possible significance are considered in detail.

Parameters which represented the readiness of a polymer to crystallise, and the maximum crystallisation rates obtainable were selected. These were used to compare the crystallisation behaviour of the different polyesters. Chain flexibility was found to be an important factor governing nucleation. Crystallisation was inhibited by the presence of bulky groups restricting chain movement.

Melting temperatures of the polymers were measured using optical microscopy. An estimate of their thermodynamic melting temperatures was made using crystallisation half times. The effect of polymer structure on melting temperature is discussed.

Spherulite growth measurements were made wherever possible. These results are related to the overall crystallisation rates.

X-ray powder photographs and fibre diagrams were obtained. Results showed that crystallisation rates were not

SUMMARY (Cont.)

affected by crystal structure.

The degree of crystallinity of samples of some of the polyesters was obtained from measurement of heats of fusion. An explanation of the crystallinities obtainable in the different polyesters is given.

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CHAPTER 1.

INTRODUCTION.

1.1. The problem.

Although the technological significance of polymer crystallisation is well known, many of the chemical aspects of the process are still to be investigated.

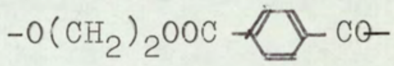
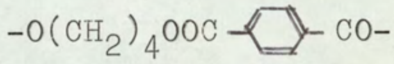
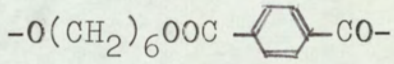
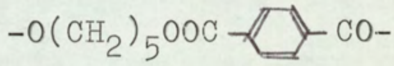
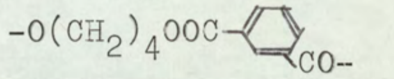
Much work has been published concerning crystallisation kinetics of different polymers. While various workers [1-3,15] have discussed the factors which promote crystallisation, there are few detailed considerations of the effect of chemical structure on polymer crystallisation kinetics and morphology. The aim of this work is the study of this problem.

Initially a survey of the literature was made to select suitable polymers for this investigation. A series of linear polyesters was chosen. Within this series variations in structure could be introduced while still retaining a measurable degree of crystallinity, and producing polymers which melted without severe degradation. Polymers actually prepared are listed in Table 1.1.

Structural changes in this series include change of aliphatic chain length, the introduction of m- and p-substituted benzene rings, and introduction of an odd number of - CH_2- groups into an aliphatic chain. Variation was deliberately restricted so that the effect of individual changes could be observed.

A Du Pont Thermal Analyzer fitted with a DSC cell was used to measure polymer crystallisation rates. Dilatometry was used as a complementary technique. X-ray diffraction gave an indication of crystal structures within the polymers, and a polarising microscope fitted with a hot stage was used to study polymer morphology.

Table 1.1. Polyesters studied.

Polymer	Notation*	Repeat unit.
polytetramethylene adipate	46	$-O(CH_2)_4OOC(CH_2)_4CO-$
polyhexamethylene adipate	66	$-O(CH_2)_6OOC(CH_2)_4CO-$
polyethylene terephthalate	2T	
polytetramethylene terephthalate	4T	
polyhexamethylene terephthalate	6T	
polypentamethylene terephthalate	5T	
polytetramethylene isophthalate	4I	

(*Note- the first digit indicates the number of C atoms in the glycol unit; the second the number in the acid unit. T represents terephthalic acid; I represents isophthalic acid. Thus '46 polyester' is polytetramethylene adipate. This notation will be used throughout.)

1.2. Literature review.

After macromolecules were established as covalently bonded entities of very high molecular weight, it was realised that like monomers these were capable of existing in liquid, or amorphous and crystalline states. Considerable attention was then given to the concept of polymer crystallisation.

~~crystallisation~~. This interest was concentrated in several areas. Relevant features will be reviewed.

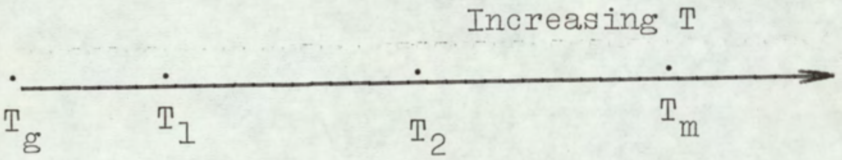
1.2.1 Structural factors affecting crystallisation.

A polymer referred to as crystalline will contain regions of three dimensional order similar to crystalline monomeric substances in many respects. Certain structural factors or combinations of factors are necessary for the existence of such regions. Chain regularity (chemical and stereochemical), symmetry, and polarity can all increase crystallinity. Various workers have commented on the relative importance of such features but it appears that this will depend on the particular system under consideration. In 1954 Bunn[2] suggested that geometrical regularity was more important than symmetry in promoting crystallinity, although Hill and Walker[1] had shown that symmetrically substituted polymers were crystalline while analogous unsymmetrical polymers were amorphous. Bunn commented that packing considerations were only valid when molecules did not form localised strong bonds such as hydrogen bonds, as in the latter case a stable open structure can be formed.

In many cases structural properties resulting in highly crystalline polymers also give high melting temperatures.

However introduction of aromatic groups into a chain will increase the polymer melting temperature but can decrease crystallinity as the bulky groups make chain packing more difficult. Bunn has suggested a theoretical approach that accounts for this behaviour.. He considered the temperature range (T_2-T_1) in which a polymer could crystallise to be between T_g, the glass transition temperature and T_m the melting temperature of the polymer. (Fig. 1.1).

Figure 1.1 The temperature dependence of crystallisation.



If (T_2-T_1) is large crystallisation proceeds readily, but may be inhibited if

1) T_m-T_g is small
2) T_1-T_g is large
3) T_m- T_2 is large

Therefore factors which decrease T_m decrease (T_m-T_g), so such polymers will be more difficult to crystallise. T_g may also be decreased but normally to a lesser extent. (T_1-T_g) depends on molecular mobility, which decreases with increasing chain length. Thus a polymer having a long molecular chain repeat distance may crystallise slowly. This could explain the rapid crystallisation of simple molecules such as polyethylene and polytetrafluoroethylene.

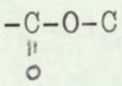
Bunn[4] claimed that the principal factors controlling melting temperatures were molecular flexibility, molecular shape effects, and molar cohesion. While the concepts of molecular flexibility and molecular geometry influence have been widely confirmed, [5-8], that of molar cohesion has been superseded, and thermodynamic quantities are considered. Polymer fusion is classified as a first order phase transition[5,9,10] governed by the equation

$$T_m = \frac{\Delta H}{\Delta S} \qquad (1)$$

ΔH and ΔS are respectively the enthalpy and entropy of fusion of the substance. T_m therefore depends on the polymer heat of fusion, on the amount of disorder in the solid state, and also the amount of freedom which can be achieved in the molten state, and structural effects may be considered in these terms.

T_g is not associated with phase change, but is related to the freezing and liberation of local molecular motions in the amorphous regions[10]. Like T_m it depends on intermolecular forces, chain stiffness and geometry, possibly to a lesser extent[8].

Theories discussed above have been applied to many classes of crystalline polymers. Historically the linear aliphatic polyesters were particularly significant. These materials were used by W.H.Carothers[11] in the elucidation of fibre structure. While the polymers are low melting and have no commercial value, these theories led to the discovery of nylon 66.

Homologous series of linear polyesters and polyamides have the required regularity and polarity to crystallise readily, so have been used to demonstrate various structural effects on melting temperature. As a general rule it has been observed[1,4,9,10] that chains having even numbers of CH_2groups between polar groups have higher melting points than those with odd numbers of CH_2groups present. Melting points of polyamides are higher than polyethylene while those of polyesters are lower. It was thought that the ester group was more flexible than a C-C chain, while the amide group less flexible due to H-bonding and that melting point differences were merely due to flexibility.[4]. Further work has shown that this is an over simplification. Differences are not due to heats of fusion as these are larger for polyesters than the analogous polyamides[13]. High melting points of polyamides have been attributed to low entropies of fusion resulting from low liquid state entropies rather than high solid state entropies. Dole and Wunderlich[5] have made calculations of absolute entropy values from specific heat measurements to confirm this view. Thus the entropy of fusion in polyamides is far more significant than the enthalpy in determining the melting point, compared with the case for polyesters. The same workers claimed that polyesters melted lower than polyethylene due to their lower heat of fusion. It is true that on a weight basis the heat of fusion of polyethylene is twice that for polyesters[9], although no reason for this behaviour has been suggested Previously it had been suggested[4] that the low melting temperatures of polyesters were due to greater flexibility of the ester linkage but it has been shown[14] that the  $-\underset{\underset{O}{\|}}{C}-O-C$ bond is actually stiffer than a C-C-C link which may be expected to result in lower entropies of fusion in the former case. This appears true if the concentration of ester groups is high enough, but it is not the critical factor affecting the melting point value.

Izard[15] has shown that for a homologous series of polyesters the melting points decrease, pass through a minimum, then increase. Initially as the number of CH_2 groups increases the melting point tends to decrease, due to increasing chain flexibility[12]. As the concentration of ester groups decreases however, the structure approaches polyethylene and there is a corresponding increase in melting point.

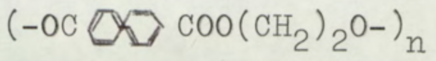
The introduction of aromatic groups into a chain increases the melting temperature considerably, as entropies of fusion are lower for polymers containing aromatic groups than for aliphatic compounds containing the corresponding number of C atoms between end groups[9]. This is due to rigid phenyl groups which allow a lesser degree of disorder in the molten state. However the degree of crystallinity may be reduced in such a case, as increased chain rigidity makes crystallisation more difficult. Shulken et al [16] have observed that polytetramethylene terephthalate crystallises more readily than polyethylene terephthalate, although the latter has a higher melting point. Melting points obtained by DTA[17] for a series of polymethylene terephthalates are shown in Table 1.2.

Table 1.2. Melting temperatures of polymethylene terephthalates.

Polyester	2T	3T	4T	5T	6T	7T	8T	9T	10T
Melting temperature °C	256	227	224	134	148	98	132	90	131

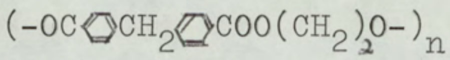
The fall in melting temperature after the first three members of the series is notable. It appears that the aliphatic content of the chain has a significant effect at this level.

The higher melting points of aromatic polyesters compared to aliphatic polyesters may be partly due to resonance between C=O and the benzene ring. The decrease in melting point[1] from



346°C

to



220°C

demonstrates this effect.

Polyisophthalates have lower crystal melting points than polyterephthalates due to larger entropies of melting. The reason for these larger entropies is not immediately obvious, but indications may be obtained from crystallisation behaviour. Polyesters containing p-substituted benzene rings are known to crystallise more readily than those containing o- or m-substituted rings[1,3,9]. Hill and Walker[1] observed that o-phthalates, and polyethylene isophthalate (2I) were non-crystalline. However other workers[3,18] were able to crystallise 2I and certain other isothphalates under conditions which facilitated mobility of the polymer chains. The kinetic dependence of crystallisation is introduced here. Materials may be capable of crystallising, but the time factor may be prohibitive. Conix and Van Kerpel[3] concluded that m-substituted compounds are difficult to crystallise as the bulk of the benzene nucleus projects from the main chain so that its rotations require more space and are hindered by neighbouring molecules. The reduced symmetry existing in 2I compared to 2T did not appear to have a significant effect. This reduction in symmetry assumed a planar molecule in both cases. Such a configuration is known to be present in 2T, but different heats of fusion for the two polymers indicate that 2I may well crystallise in a different configuration(section 1.2.3). Structure differences could in turn account for different entropies of fusion.

Symmetry undoubtedly affects the ability of a polymer to crystallise. Hill and Walker[1] studied substituents in polymer chains. They observed that aliphatic side chains decrease crystallinity generally by introducing linear and lateral disorder, although symmetrical substitution can give crystalline polymers. Polyesters prepared by Holmer[19] from homoterephthalic acid, $HOOCCH_2$COOH were reported to be amorphous due to lack of symmetry. The fact that analogous polyamides were found crystalline demonstrates another important point. For the formation of a three dimensional crystal structure, there must be a degree of interchain cohesion. H-bonding is a relatively strong force, and causes crystallisation in the polyamides described above. In other cases interchain cohesion may be due to polarity (polyesters) or merely to Van der Waal's forces, made effective by ready chain packing (polyethylene).

Thus factors affecting polymer crystallisation and melting temperature are mainly independent and additive. Within a class of polymers a very wide range of properties can be achieved by using a suitably balanced structure. Despite investigation of many hundreds of linear polyesters, polyethylene terephthalate originally discovered by Whinfield and Dickson[20] in 1941 has remained the major commercial linear polyester. The short aliphatic chain and aromatic ring result in a high melting polymer obtainable with vaious degrees of crystallinity. These features give a material with a wide range of mechanical properties, good thermal stability, and considerable inertness to water.

1.2.2. Polymer fusion, Crystallinity determination.

Mandelkern[9] has shown that polymer fusion may be treated as a first order phase transition. Theoretically such a transition should result in infinitely sharp melting; however this assumesan almost perfect arrangement of the crystalline phase, and the presence of large crystals. Transitions over 1-2°C may be obtained for monomeric substances. For polymers considerable deviations from ideal conditions result in broadening of the melting region, which in some cases may cover as much as 100°C[21].A broad melting range is correlated with excessive contributions to the free energy due to surfaces between the crystalline and amorphous phases, when compared to the free energy of fusion, i.e. it occurs when the crystalline regions are small. From the magnitude of the melting range crystallites present in polymers must have dimensions of the order of 100A°.

The wide melting range described causes difficulty in determining polymer melting temperatures, and many values initially recorded may be as much as 10°C too low. To obtain accurate values attention must be give to the method of measurement and to the thermal history of the polymer. Schulken et al[16] have observed that polymers with abnormally high melting points can be obtained by annealing and heating slowly. The theoretical melting point of a polymer may be defined as that temperature at which perfect crystallites would melt at equilibrium, but it has been concluded that even under carefully controlled conditions the observed melting temperature will be a few degrees lower than this. More readily explained crystallisation data has been obtained in several cases by adding 2 or 3°C to the observed temperature [9,22,25,26,28] and this estimated value may be considered to be the thermodynamic melting temperature. McLaren[22] has used a kinetic method proposed by Frank (see Ref.27) to calculate the equilibrium melting temperature of nylon 66. To obtain the best possible melting temperature experimentally it is necessary to maintain the polymer in equilibrium. To achieve this heating rates must be sufficiently slow. Mandelkern[9] concluded that by using appropriate experimental conditions, involving either very slow crystallisation or very slow fusion, or a combination of both, there exists a well-defined temperature T_m at which the last traces of crystallinity disappear. Specific heat and dilatometric measurements have been used frequently to measure T_m. These methods are advantageous in that very slow heating rates may be used. Sharples and Swinton [32] used a rate of 1°C/24 hours to determine T_m for polydecamethylene terephthalate. Many accurately determined values of T_m

have been obtained from optical measurements, using a fairly slow heating rate i.e. 0.1-1.0°C/min[22,23,25]. Differential thermal analysis (DTA) has been used to determine T_m[7,16,17 29-31,33,34]. Normally heating rates are necessarily rather faster, but values are claimed to be in agreement with those obtained by other methods[7,29].

When DTA is used to measure polymer melting temperatures or heats of fusion, difficulties may be encountered due to the appearance of multiple melting peaks[31,35-43]. Presence of these peaks depends on thermal history of the sample and appears to be due to different types of crystallites present. These effects are discussed further in section 5.2.

From the nature of the two phase system measurement of heats of fusion may be used to determine the degree of crystallinity of a polymer[29,43-50]. However, it is necessary to know ΔH^*_f, the heat of fusion for a 100% crystalline polymer. This value can only be obtained by extrapolation methods. Flory[51] proposed methods involving depression of melting temperature due to copolymerisation or added diluent. Various results using the copolymer method have been reported[52-55]. These results are lower than those obtained by other methods [52,56-60]. Dole [58] showed that the effect of surface free energy of crystallites in lowering melting points is significant, and accounts for these low results. The diluent method appears to give more accurate results[3,13,56-59]. Kirshenbaum[60] has made a calculation of entropies of fusion and hence ΔH^*_f. These values are in good agreement with experimental values. An alternative approach is to use measured heats of fusion to calculate ΔH^*_f by using independently determined values of the degree of crystallinity[59]. Yagfarov[49] has suggested a novel method of using thermal data to estimate degree of crystallinity which does not require knowledge of ΔH^*_f. He uses measurement of heat capacities and heat effects of phase transitions for two samples with different degrees of crystallinity.

Wunderlich[43] discusses the accuracy of different thermal methods in measuring heats of fusion. Practically, one of the main sources of error lies in the estimation of peak baseline, and a method has been suggested to reduce this[61]. Theoretical difficulties may also arise. Crystallinities determined by density and heat of fusion measurements[45] are in agreement for samples of polyethylene which are crystallised, then melted. If the samples are cooled to room temperature before melting, crystallinities determined by the thermal method are lower, due to the formation of small crystallites which contribute to the interfacial enthalpy.

Degrees of crystallinity may be obtained in theory from any crystallinity dependent property. Density measurements may be used if unit cell dimensions, and hence the 100% crystalline density, is known. Other methods used for polyesters and polyamides include X-ray diffraction [62-65], specific heats[66], and infra red analysis[67-69]. Richardson[41] has reviewed the topic of crystallinity determination and indicates that there is no reason to expect agreement between different methods, which after all depend on different properties. He stresses that as many techniques as possible should be used for a particular polymer. This point is also discussed by Wakelyn and Young[64] who use differential scanning calorimetry (DSC) and X-ray diffraction. They suggest that serious discrepancies between methods indicate a particular material characteristic (e.g. orientation effects). Howard and Knutton[47] reported 95% crystallinity (DSC determination) and 30% crystallinity (density determination) for the same polyester, but did not account for this enormous difference. The need for independent determinations, together with careful consideration of the factors involved in the method used is indicated.

1.2.3. Structure in crystalline polymers.

Considerable attention has been given to the structure of the crystalline phase in polymers. On a molecular scale X-ray diffractometry has been used to show that linear macromolecules will pack into a lattice, analogous to a monomeric crystalline substance. Polymer chains are normally in a linear, substantially fully extended configuration or a helical configuration. Crystallographic data for polymers is reviewed by Miller and Nielsen[70] by Geil[71], and is also available in the Polymer Handbook[74], Data ~~was~~ have been obtained for various linear polyesters[72-80] polyterephthalates[81-85], and polyethylene isophthalate[18].

Fuller et al[75-80] used X-ray fibre diagrams to show that linear polyesters have a planar zig-zag structure (Fig.1.2). Those with even numbers of methylene groups have layers of dipoles tilted, and the crystal repeat unit is equal to the chemical repeat unit. A monoclinic structure was suggested and has more recently been confirmed for the 26, 28 and 210 polyesters[72,73]. These workers have shown that the unit cell contains two adjacent chains held together by Van der Waal's forces. They have accounted for the small reduction in repeat distance observed experimentally, compared to the theoretical length of a fully extended chain, in terms of distortion in the glycol unit. When odd numbers of methylene groups are present the layers of dipoles are perpendicular to the chain, the crystal repeat unit is twice the chemical repeat unit and the cell is believed to be orthorhombic. This picture applies generally to homologous series of polyesters, although variation occurs in specific cases (e.g. when the $C=O$ group concentration is high).

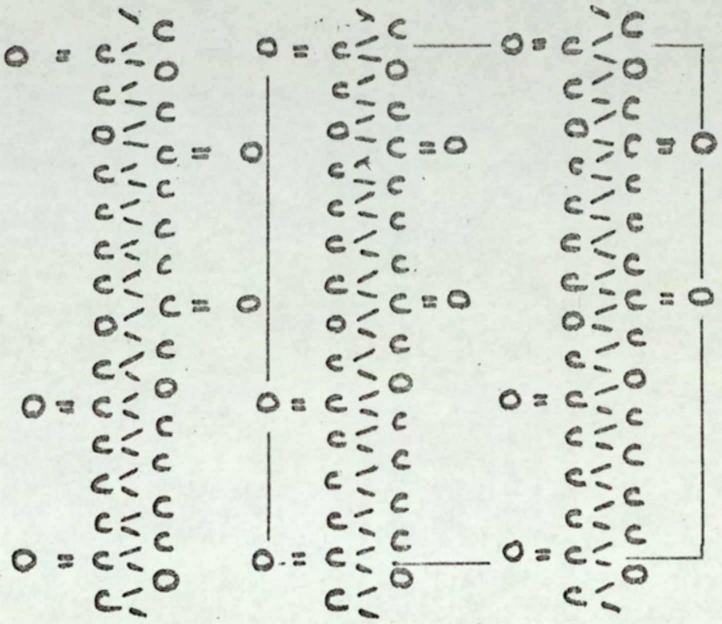
Hill and Walker[1] concluded that the polymer melting point depends on the arrangement of molecules in a crystal lattice. Flory et al[13] suggested that greater heats of fusion for polyesters than polyamides indicated different crystal structures. Heats of fusion of polyesters are similar to one another, allowing for different repeat unit lengths, indicating similar crystal structures. Those of terephthalate polyesters are similar to their aliphatic analogues, again suggesting a similar structure.

The crystal structure of polyethylene terephthalate is

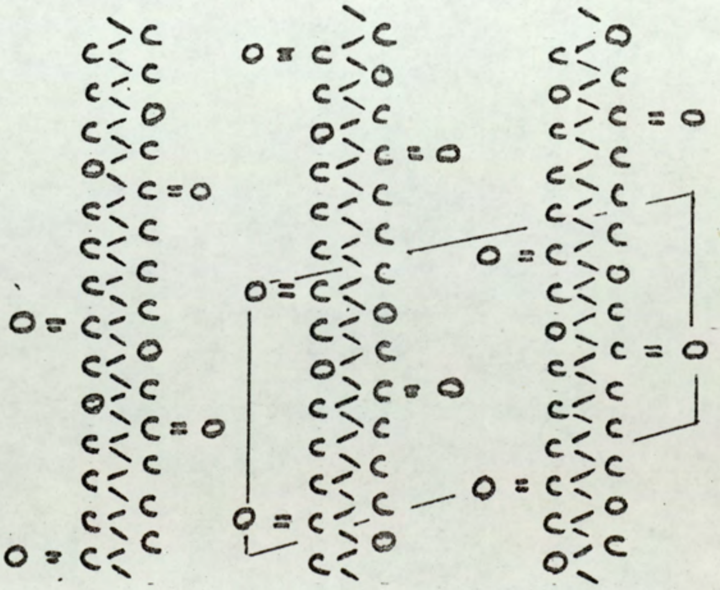
CRYSTAL STRUCTURES IN ALIPHATIC POLYESTERS.

(REFERENCE 75)

FIG. 1.2.



A) POLYETHYLENE AZELATE.



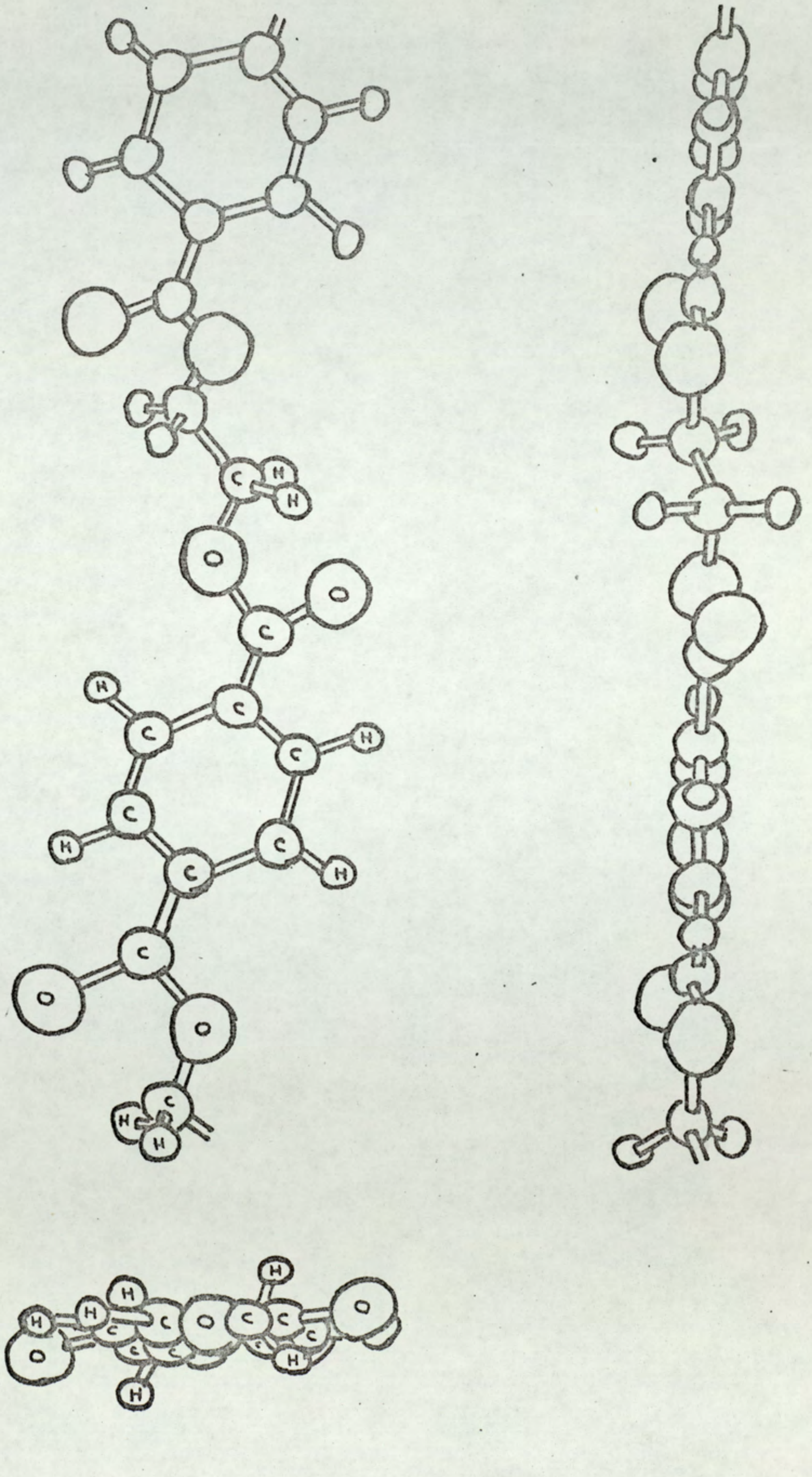
B) POLYETHYLENE SUBERATE.

well established[83]. The unit cell is triclinic and contains one chemical repeat unit. The molecules are nearly planar in configuration. (Fig.1.3.) The X-ray diffraction patterns of 2T, 6T, and 10T polyesters are similar, indicating that 6T and and 10T molecules have a flat extended configuration like 2T.

Conix and Van Kerpel[3] discussed heats of fusion of the isomers 2T (7,600 cal.Mole^{-1}) and 2I (10,100 cal.mole^{-1}). They suggested that the difference may be due to the 2I molecule having a different configuration. Yamadera and Somoda[18] reported two different X-ray diffraction patterns for this polymer. For a stretched sample the repeat distance was 21.0A°, corresponding closely to the theoretical value for a fully extended structure (20.8A°). For a sample crystallised from tetrachloroethane the distance reported to be was 14.8A°, A different configuration was suggested in the two cases, but the pattern obtained in the latter case was typical of 'powder type' photograph with a random arrangement of crystallites, invalidating any calculation of repeat distance.

Theories have been introduced to relate the crystal lattices described to other experimental observations concerning crystalline polymers. X-ray diffraction patterns of polymers were found to consist of relatively broad lines. The thickening was explained by the presence of very small crystallites in polymers, having an average dimension of 100-200 A°. The length of any one polymer chain will be many times greater than this. Experimental densities led to the fringed micelle model [86]. According to this model the molecules ordered themselves

Fig. 1.3. Chain Configuration in Polyethylene Terephthalate.
(Reference 83)



into crystallites along limited portions of their lengths, while the remainder passed through entangled amorphous regions. Thus one molecule may pass through many small crystallites. This model partially accounted for the behaviour of crystalline polymers, but did not account for the appearance of spherulites, which were first reported for macromolecules in 1945[87].

Spherulites are birefringent structures having spherical symmetry, and are detectable in a polymer film on the optical microscope scale, when using crossed polaroids. For certain polymers crystallised under suitable conditions they may be seen to nucleate and grow as circular entities with the frequently described 'Maltese cross' appearance. Optical determinations of the orientation of molecular chains in spherulites shows that the long chain axes are at right angles to the radii. Thus tangential orientation is responsible for the extinction of light in opposite quadrants to give the appearance described. If the refractive index along the radius is greater than the tangential refractive index, the spherulite is termed positive; if the reverse is true the spherulite is negative.

Characteristic features of spherulites have been described in detail by Keller[88]. They have been shown to be aggregates of smaller crystalline units which are in fact the crystallites already described. Spherulites as large as one centimetre in diameter have been recorded but in many crystallisable polymers separate entities are too small to be resolved using an optical microscope, and the polymer appears as a birefringent mass. In many cases this is due to a high nucleation density, resulting in a large number of very small spherulites[21].

Spherulitic structures in polyesters have been reviewed by Geil[71]. Two types of spherulites having different X-ray diffraction patterns were observed for polyethylene terephthalate, the type being dependent on the crystallisation temperature[94]. Subsequently Keller[95-97] investigated the spherulitic structure in this polymer in more detail. He related two types of positive spherulites to differences in molecular configuration, suggesting that this was helical in the larger spherulites formed at higher temperatures. He also produced negative spherulites. Positive, negative, and banded spherulites have been observed for polyethylene adipate[92]. The melting of these phases has been followed by microscopy for this polymer[90].

It is now generally accepted that spherulites are formed by fibrils extending outwards from a central nucleus. Branching occurs as the fibrils grow, till a spherulitic structure, which includes amorphous regions, is formed. It is likely that in the early stages of growth a spherulite nucleus develops from a single crystal.

For many years it was thought that single crystals could not be isolated from polymers. However in 1957 the existence of single crystals of polyethylene was reported from three independent sources[98-100]. Such crystals have normally been obtained by slow crystallisation from very dilute solution, and observed using an electron microscope.[71] The crystals are in the form of very thin lamellae, with a thickness of the order of 100 A°. It was shown by electron diffraction that the molecular chain lies perpendicular to the faces of the lamella, ie. across the width. As a polymer molecule may be as long as 10,000 A°, and the faces of the lamellae are smooth, chain folding is indicated. Lamella thickness is found to depend on crystallisation temperature, indicating that the growth process is temperature dependent. These concepts are important in the study of polymer morphology, although the exact relationship between single crystals and melt crystallised polymers has not been determined. The morphology and structure of bulk crystalline polymers has been discussed in detail by Keith[89]. The overwhelming majority of work on polymer single crystals has concerned polyethylene, but crystals have been reported for for most classes of crystalline polymers, including some polyesters[71,101,103].

1.2.4. Crystallisation kinetics.

The study of isothermal crystallisation rates is informative when an indication of the crystallisation behaviour of a polymer is required. For such studies the molten polymer is cooled quickly to temperatures at which crystallisation will occur. After an induction time crystallisation proceeds at an accelerating rate. The rate passes through a maximum then decreases till an almost constant level of crystallinity is obtained. A small amount of further crystallisation may occur over a long period of time. The crystallisation process is continuous, and the isotherms are sigmoidal in shape. If a series of isotherms are normalised and plotted against log (time), they are found to be superimposable when shifted along the log (time) axis.

The temperature dependence of crystallisation rate is an important factor. If a parameter representing rate, is plotted against temperature, the following behaviour is observed for some polymers. (Examples are given in references 23,93,94,102). Near the polymer melting temperature, T_m, crystallisation is infinitely slow. As the temperature is decreased the rate increases, passes through a maximum, then decreases as the glass transition temperature is approached. A similar temperature dependence is observed for overall crystallisation, nucleation and growth processes, and is due to opposing forces which control rate.

The probability of growth of a small crystal nucleus is governed by two factors. The larger a molecular cluster becomes, the greater is the rate of dispersion of molecules from its surface. On the other hand, a larger nucleus is favoured thermodynamically, as the decrease in internal energy associated with the capture of each new molecule increases with increasing nucleus size. There is a critical size for the growth of a nucleus, which is larger as the crystallisation temperature approaches the melting temperature. As temperature, and therefore thermal agitation decreases, the critical size is decreased and nucleation and growth processes are favoured, so the crystallisation rate increases. As the temperature is further decreased the effect of increasing viscosity becomes apparent. Molecular motion is reduced and the crystallisation rate decreases.

For many polymers the maximum rate is sufficiently fast to prohibit any rate measurements on the lower temperature side of the maximum. In some cases the critical nucleus size is still large when the viscosity factor becomes effective; the solid polymer will then be amorphous.

Various methods have been used to measure isothermal rates. Those relevant to this work are dilatometry, optical microscopy and thermal methods. Dilatometry has been too widely used to warrant detailed discussion here. Dilatometer design is important[104]. Too large polymer samples result in difficulties of heat transfer while attempting to maintain isothermal conditions.

Optical microscopes fitted with crossed polars have frequently been used to measure spherulite growth rates, either directly with a micrometer eyepiece, or photographically. Nucleation rates have also been measured directly and results have been combined to give a measure of overall crystallisation rate[91]. The direct measurement of this value by optical microscopy was first reported by Magill[105] in 1961. This method relies on the detection of depolarised light which is transmitted through a polymer film as crystallisation occurs, and it has subsequently been used by several workers[22,106-108].

Thermal methods for crystallisation rate measurement depend on the evolution of heat that occurs during the process. The total amount of heat which has been given out by any time is proportional to the amount of crystallisation which has occurred. Thermal methods are normally differential, and are of two types.

i) DTA, when the temperature during crystallisation between the sample and an inert reference is recorded, and

ii) DSC, when the energy required to maintain the sample and reference at the same temperature is recorded.

A commercial instrument of type i) is the Du Pont 900 thermal analyzer; that of type ii) is the Perkin-Elmer differential scanning calorimeter.

Martin and Müller [109] constructed a DTA apparatus and were among the first to report a differential thermal technique for measuring crystallisation rates. Chiu[110] used this method for measuring very rapid rates for isotactic polypropylene. He assumed that the first part of the crystallisation curve, which could not be recorded as the the sample had not reached thermal equilibrium, to be a mirror image of the latter half. It will be shown that this is not necessarily true. In 1966 Godovskii et al[111,112] used DTA to study crystallisation kinetics for polyethylene and polypropylene, and compared their results with dilatometry[112,113]. Samples used were relatively large (0.3-0.7g.). Differences in DTA and dilatometry results for isotactic polypropylene were attributed to two types of nuclei in the melt. It was suggested that the nucleation of crystallites was detected by calorimetry, while dilatometry and microscopy followed the growth of spherulites. Results obtained after altering the melting treatment were put forward to support this theory. Fatou and Barrales-Rienda[114] however claimed continuity between dilatometry and DSC results for polyethylene, by using similar plots to those described in section 4.1., which demonstrate the temperature dependence of rate. Hay et al have used DSC to measure crystallisation rates for polyethylene [115] and polyethylene oxide[116]. Their results agreed with dilatometry results, but followed the crystallisation to a lower conversion, and were claimed to be less precise. Miller[117] used DSC in a novel manner to measure crystallisation rates of polyethylene terephthalate, at temperatures below that of the maximum cystallisation rate. The method relied on the rather exceptional thermal behaviour of this polymer. i.e. it may be quenched, and will crystallise on subsequent heating. The crystallisation exotherm will be decreased by annealing at lower temperatures. This decrease is a measure of the crystallisation which has occurred at the annealing temperature.

1.2.5. Factors affecting crystallisation kinetics.

Certain experimental factors affect crystallisation rates. Thermal history is critical in this respect.

Attention should be given both to the melting treatment prior to crystallisation, and to previous treatment of the polymer. A relatively low melting temperature or short melting time result in a shorter induction period and a more rapid crystallisation rate than more stringent conditions. These results led to the concept of incomplete melting where a residue of ordered structures in the melt act as nuclei for subsequent crystallisation[93,94,118,119]. The occurrence of self seeding[21] confirms this observation. If a polymer containing distinct spherulites is heated just above its melting temperature, then recrystallised, the spherulites present previously may act as nuclei, so that crystallisation initially occurs in these regions. Schultz[120] studied thermal history effects in polyethylene by melting the polymer at various temperatures and recording the temperature of maximum crystallisation rate on subsequent cooling. Meltingtime also affects crystallisation. For both sporadic and predetermined nucleation in nylon 6, Magill[121,122] observed an increase in induction time, when using melting times up to 15 minutes and suggested that fusion for half an hour at 270°C was necessary to give complete melting of samples. Normally it is more convenient to use increased melting temperatures rather than long melting times, providing that degradation is avoided. Sharples and Swinton[32], studying polydecamethylene terephthalate, suggested that nuclei were produced by degradation during melting, resulting in variations in nucleation density in different samples.

Melting conditions may alter the type of nucleation occurring. Magill[122] reported that the transition temperature observed in the crystallisation of nylon 6, from heterogeneous to homogeneous nucleation, was lowered as the fusion temperature was increased. An increased melting temperature was also reported to result in a change from a heterogeneous process to a homogeneous process for polypropylene, studied by dilatometry[113]. McLaren[22] claimed that although the total number of spherulites present at a given time was lower if higher melting temperatures were used, the actual nucleation rate was not very dependent on melting temperature.

Some controversy arises over the effect of melting conditions on the spherulite growth rate, G. Some workers have reported[25,123] that G is independent of fusion conditions. Burnett and McDevitt[25] claimed that for nylon 66, G did not vary with melting temperature, but were using melting times of only 30 seconds. For the same polymer McLaren[22] found that G was greater using lower melting temperatures, and was also inversely proportional to melting time, up to a time of 30 minutes. From these results he inferred that units larger than single chain segments may add on to spherulites, and that ordering of these units may affect G. Order in polymer melts has been reported elsewhere[124].

It is particularly difficult to summarise the effect of molecular weight on crystallisation rate, as this appears to depend on the class of polymer. Results for the polyesters will be reviewed briefly. Ueberreiter et al[102] used rather low molecular weight samples of polyethylene succinate (M_n 820-4415) and found that crystallisation rate decreased with increasing molecular weight. The rate of decrease appeared less at higher molecular weights. The same effect was observed for polyethylene terephthalate[94] although these samples were in the range M_v 11,200-40,000. Jackson and Longman[106] used polyethylene terephthalate samples ofmolecular weight M_v 20,000-40,000 and again reported a decreasing rate, and also a narrowing crystallisation temperature range with increasing molecular weight.

For nylon samples moisture is found to accelerate crystallisation, probably due to a plasticising action[22,121]. The present work showed that drying of the polyester samples did not alter crystallisation rate. This was probably because the equilibrium moisture content in nylons is as much as ten times as great as that in polyethylene terephthalate, for example.

In Figs 1.4 and 1.5 overall crystallisation rate constants K and spherulite growth rates G reported for linear polyesters are collected together. They are plotted against ΔT °C where $T = T_m^1 - T$; T_m^1 is the reported polymer melting temperature and T is the crystallisation temperature. Although the experimental factors discussed above do alter crystallisation rates, effects are small compared with those due to major structural changes. Differences due to such changes include different degrees,

Fig. 1.4. Crystallisation rates of Linear Polyesters.

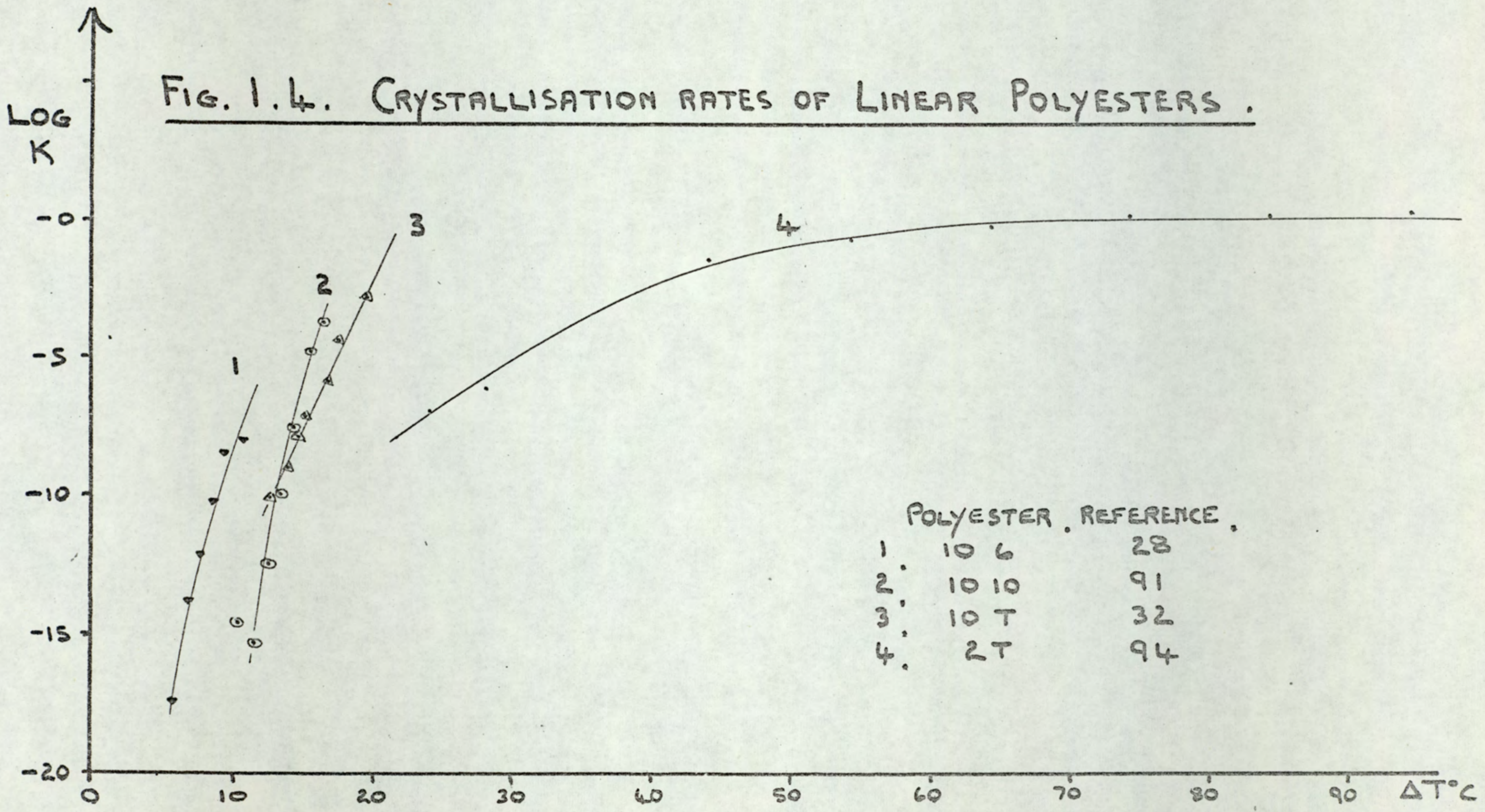
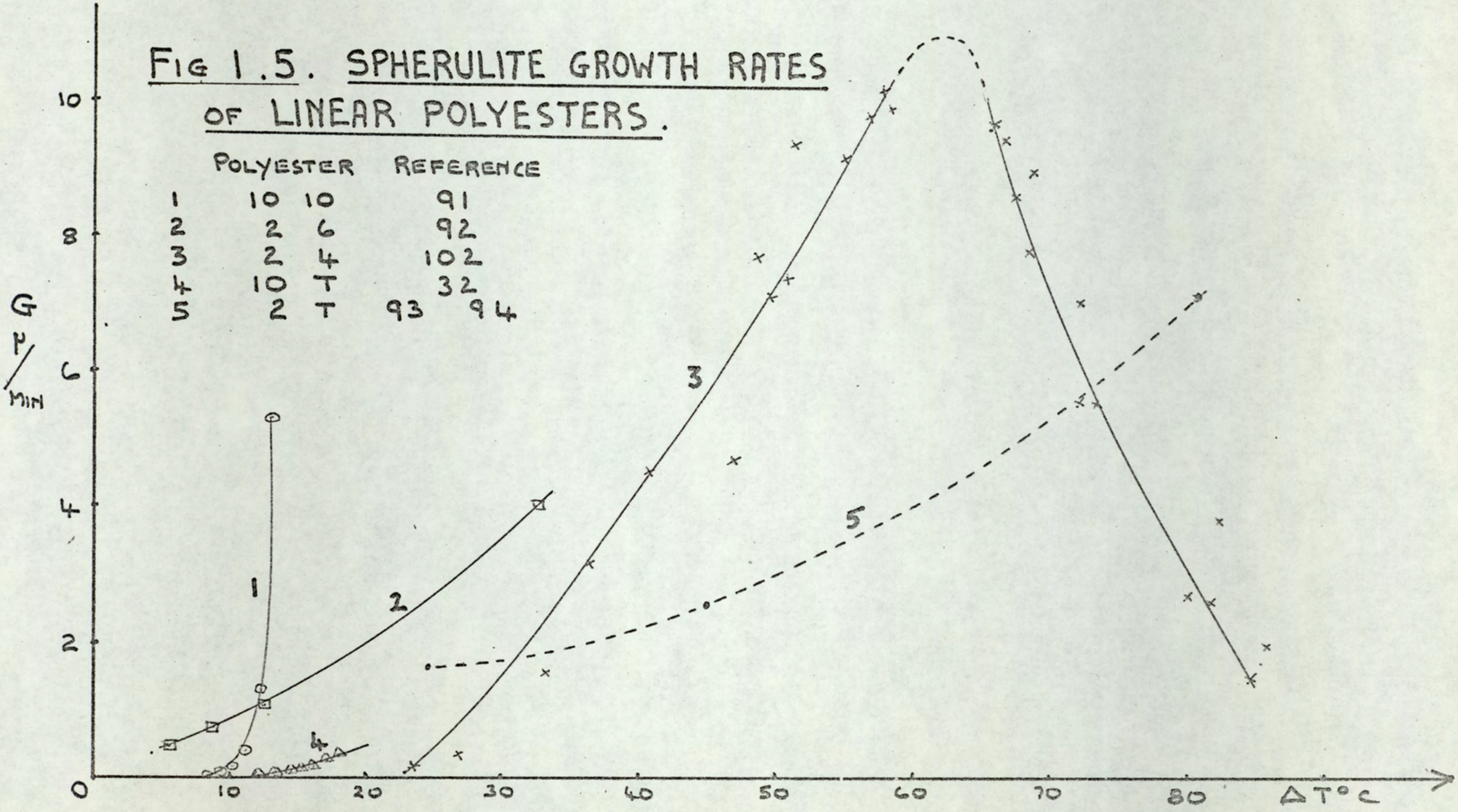


FIG 1.5. SPHERULITE GROWTH RATES OF LINEAR POLYESTERS.



of supercooling necessary for different polymers, different temperature coefficients of crystallisation, and different temperature ranges within which crystallisation is measurable. These effects are illustrated in Figs.1.4 and 1.5. and will be discussed in detail later. (Chapter 6)

1.2.6. Theories of crystallisation.

Theories have been put forward concerning both the time dependence and temperature dependence of crystallisation, in order to explain experimental results in terms of crystallisation mechanisms.

One of the basic equations was originally developed by Avrami[127] for the crystallisation of metals. The equationhas been adapted to describe the isothermal crystallisation of polymeric materials, assuming that nucleation occurs at randomly spaced points in the crystallising mass, and that the subsequent growth develops in one, two or three dimensions to form rods, discs or spheres.

It can be written

$$\theta = \exp(-Kt^n) \qquad (2)$$

where θ is the volume fraction of unchanged amorphous phase at time t,

K is the overall rate constant,

n is an integer, the value of which depends on the nature of growth and nucleation. (Table 1.3)[9].

Table 1.3. Values of n for various types of nucleation and growth.

Growth habit	Homogeneous nucleation	Heterogeneous nucleation.
Three dimensional	4	3
Two dimensional	3	2
One dimensional	2	1

If nucleation is heterogeneous, or predetermined, all growing centres are initiated at the start of the process when t=0; if nucleation is homogeneous or sporadic nuclei are activated at a constant rate throughout the crystallisation. For intermediate situations, when the rate of nucleation decreases during the process, intermediate n values may be obtained, which are not allowable on the simple Avrami theory.

For analysis of results by the Avrami equation θ is expressed in terms of experimental values. For example, for dilatometry,

$$\theta = \frac{h_t - h_\theta}{h_o - h_\theta} \qquad (3)$$

where h_t is the height of the mercury column at time t, h_o and h_θ are the initial and final heights respectively.

Equation (2) may be written

$$\log(\log_e 1/\theta) = \log K + n\log t \qquad (4)$$

Thus K and n can be evaluated from a plot of $\log(\log_e 1/\theta)$

against log t, which should be linear. In practice, deviations from linearity occur and the log(log) plot is rather insensitive, so other methods for evaluating K and n have been suggested.

By differentiation and rearrangement of equation (2)n may be calculated for each point measured,[104,115,116,128]. (Chapter 4). This method is very effective in demonstrating deviations from the theory.

Godovskii and Slonimiskii[112] used a thermal method for measuring crystallisation rate, and calculated n from the time at which the heat evolution was at a maximum, which corresponded to the inflection point in the crystallisation isotherm. These workers claimed that this method was no more accurate than a log(log) plot. This seems likely as they were relying on a single point determination.

Recently attempts have been made to use computing techniques to fit experimental results to theoretical equations[107,126,129-132], with some sucess.

The half-time of crystallisation $t_{\frac{1}{2}}$ has been frequently used as it may be obtained directly from experimental results and is useful, for example, to investigate the temperature dependence of crystallisation in a polymer. Substituting for t and θ in the Avrami equation gives,

$$K = 2.3 \log 2 \, (t_{\frac{1}{2}})^{-n} \qquad (5)$$

Relationships between the overall rate constant K and the microscopically measured quantities were first reported by Morgan[133]. These are ;

For homogeneous nucleation

$$K = \frac{1}{3}\pi G^3 \dot{N} \qquad (6)$$

and for heterogeneous nucleation

$$K = \frac{4}{3}\pi G^3 N \qquad (7)$$

Where G is the radial rate of spherulite growth in μ/minute

$\dot{N}$ is the rate of increase of nuclei in no./cm^3/minute

N is the number of nuclei/cm^3.

Subsequently it was shown [28] that a density correction should be included in these equations.

Then $$K = \frac{1\rho_c}{3\rho_L} G^3 \dot{N} \qquad (6a)$$

and $$K = \frac{4}{3}\frac{\rho_c}{\rho_L} G^3 N \qquad (7a)$$

where ρ_L is the density of the liquid polymer

ρ_c is the density of the totally crystalline polymer

Godovskii and Slonimiskii[113] have postulated the growth of plate crystals, detectable by calorimetry, in polypropylene, in addition to the spherulite growth to which equations (6a) and (7a) apply. They use an additional equation,

for plate growth, $K = G^3Ml$ (8)

where M is the number of nuclei for plate growth/ cm^3

l is the plate crystal thickness.

Boon et al[119] combined equations (6a) and (7a) with the Avrami equation (2) in order to analyse their experimental results for isotactic polystyrene. For such equations, n values were 3 and 4 respectively. These workers introduced the concept of a third type of nucleation having an intermediate n value. They suggested that induced nuclei may be created if a sample of polystyrene was severely supercooled, then crystallised from the glassy state, and further that, at the start of crystallisation, a fixed number of these nuclei were present each having the probability ν of growing into effective nuclei. A term νt was introduced into the equation governing crystallisation; if νt was large the equation reduced to the case $n = 3$; if νt was small the case where $n = 4$ was observed. Experimental results obtained by dilatometry and spherulite growth were successfully fitted to these equations using a computer.

It has been mentioned that in practice deviations from the Avrami equation are normally observed. These have been attributed both to experimental factors, and to assumptions inherent in the theory[107]. The existence of some type of secondary crystallisation is well known. It is believed that a primary process occurs which approximates to the Avrami equation, but that analysis of results is complicated by the secondary process, which is thought to be due to an increase in the amount of crystallinity, either by crystallisation of material initially excluded from the crystallising entities, or by perfection of existing crystallites.

Different workers have claimed that primary processes are consecutive, overlapping only to a small degree[21], or concurrent. Banks et al[128] measured isothermal crystallisation rates of polyethylene by dilatometry. Using this technique, following the initial rapid process, a slow volume decrease is observed over extremely long time periods. It is therefore difficult to estimate a final value for substitution in equation (3). n values throughout the crystallisation ~~was~~ were calculated from a differentiated Avrami equation. h_∞ was selected which gave a constant value of n over the longest period of time. It was found that for different samples crystallised for times before this value of h_∞ was reached, similar melting temperatures were recorded. On melting samples crystallised for different times beyond this contraction, an increase in melting temperature was found with increasing time. These results indicated that the two processes did not overlap significantly, and that the secondary process was due to increasing perfection in existing crystallites. Hay et al[104] have used a similar method to analyse dilatometry results for polyethylene oxide, and have indicated errors introduced in n values resulting from estimation of h_0,

h_∞ and dh/dt, which are required for substitution in the differentiated Avrami equation.

Gordon and Hillier[129,130] approached the problem differently. For polyethylene they were able to isolate the primary process under certain conditions. They showed that this process fitted the Avrami equation, and was explained by a model incorporating the growth of single crystals by chain folding. When the additional secondary process occurred, they postulated that in a given crystallising entity this followed the primary process immediately, with a corresponding increase in density, interpreted as an increase in lamella thickness. This theory was developed[131] to account for the fractional n values which had frequently been reported, using a model in which constant radial growth of spherulites was followed by an increase of crystallinity within the spherulites according to a first order rate equation. A decreasing fractional n value was attributed to the two processes having corresponding half lives. In this case the isotherms resemble those obtained in the absence of secondary crystallisation. A number of Avrami processes with different but integral values of n were claimed to give an apparently increasing n value. When the theory was applied to polypropylene [132] a better fit was obtained to experimental results if the secondary process was assumed to be second order.

Price[134] also claimed that the secondary process was due to transformation of material within spherulites, but suggested that this normally started when the specimen was completely filled with spherulites. Schultz and Scott[135] were able to isolate the secondary process for polyethylene and study this at different temperatures. Their results indicated that a large amount of the secondary crystallisation was due to the nucleation and growth of new crystallites in regions which had not crystallised during the primary process.

Many theories have been developed concerning the temperature dependence of crystallisation.
Mandelkern et al[28] have deduced an equation for the overall rate of crystallisation, assuming spherical nucleus formation, followed by spherical growth (referred to as K_s^s).

$$\text{Log } K_s^s = A - 7.28\sigma_s^3 \; T_m^2 / \; (\Delta H_u)^2(\Delta T)^2 kT \qquad (9)$$

where T_m °C is the polymer melting temperature

T °C is the crystallisation temperature

$\Delta T = T_m - T$

σ_s is the interfacial free energy/ unit area between crystal nucleus and liquid

ΔH_u is the heat of fusion/unit volume of repeat unit

k is Boltzmann's constant

$$A = \log \left[\frac{\rho_c}{\rho_L} \, \frac{\pi}{3} \, N_o G_o^3 \qquad \frac{-4E_D}{2.3kT} \right] \qquad (10)$$

where N_o is a constant which is related to nucleation, and is only slightly temperature dependent

G_o is related to spherulite growth

E_D, the apparent activation energy of viscous flow, serves as an approximation for the energy of activation for transport across the liquid crystal interface. (E_D changes over an extended temperature range, but both E_D and G_o can be assumed constant over ranges of about 10^oC.)

Equations of type (9) can also be derived for rate constants assuming disc nucleation followed by disc type growth K_d^d, or disc nucleation followed by spherulite growth K_s^d. In all these derivations the temperature dependence of the crystallisation rate constant is found to be the same. Thus, assuming A is constant which is normally a good approximation, a plot of log K or log $(1/t_{\frac{1}{2}})^9$ against $T_m{}^2/ T(\Delta T)^2$ should be linear, dependent on the value used for T_m. Results obtained from such plots will be discussed (section 4.1.).

When crystallisations are measured at large supercoolings, the variable term in equation (9) becomes smaller, so the value of $4E_D/ 2.3kT$ will be relatively more important and E_D can nolonger be considered constant. This term will eventually dominate as T is increased, so the rate of crystallisation will decrease with decreasing temperature because of the decreased mobility. Thus these equations explain the experimentally observed maximum in a plot of crystallisation rate against temperature.

At low supercoolings the temperature dependence of the rate constant has been summarised by equations of the type,

$$\log K = A - \frac{B}{\Delta T} \qquad (11)$$[128]

$$\log K = A - \frac{B}{\Delta T^2} \qquad (12)$$[9,128]

This equation assumes an integral value for n, independent of temperature. However, in some cases n varies with temperature, and it has been proposed that the equations should be modified to,

$$\log K = A - \frac{nB}{\Delta T} \qquad (11a)$$

$$\log K = A - \frac{nB}{\Delta T^2} \qquad (12a)$$

Banks et al[128] reported that their results for polyethylene best fitted equation (12a).

Equation (9) is developed from contributions due to nucleation and growth[9,28]. It is concluded that the primary nucleation act involves the formation of an unrestricted three dimensional nucleus and is described by the equation,

$$\dot{N} = N_0 \exp\left[\frac{-E_D}{kT} - \frac{CT_m^2}{T\Delta T^2}\right] \qquad (13)$$

where C is a constant, and other terms are defined as before.

Mandelkern et al[26] have listed equations which have been used to describe the temperature dependence of spherulite growth. These are

$$G = G_o \exp(-E_D/kT - \Delta F_2^* / RT) \qquad (14)^{91,102}$$

$$G = G_oT \exp(-E_D/kT - \Delta F_2^* /RT) \qquad (15)^{28}$$

$$G = G_o \exp(-E_D/kT - \Delta F_3^* / RT) \qquad (16)^{102}$$

$$G = G_oT \exp(-E_D/kT - \Delta F_3^* / RT) \qquad (17)$$

ΔF_2^* and ΔF_3^* are the critical free energies for nucleation for two and three dimensional processes respectively. The first term in the brackets is the transport term; the second term represents the work required to form a crystal nucleus. On substituting for ΔF_2^* and ΔF_3^* in the above equations, and taking logs,

$$\ln G = \ln G_o - (E_D/kT) - (A_2T_m/ kT\Delta T) \qquad (14a)$$

$$\ln (G/T) = \ln G_o - (E_D/kT) - (A_2T_m/ kT\Delta T) \qquad (15a)$$

$$\ln G = \ln G_o - (E_D/kT) - (A_3T_m^2 /kT\Delta T^2) \qquad (16a)$$

$$\ln (G/T) = \ln G_o - (E_D/kT) - (A_3T_m^2/ kT\Delta T^2) \qquad (17a)$$

A_2 and A_3 are constants related to the heat of fusion and to surface free energies between the crystal nucleus and liquid.

It is assumed that the linear growth rate of nuclei is controlled by monomolecular nucleation on an already existing crystal face. As for the overall crystallisation rate, the experimentally observed maximum in the temperature dependence of growth rate is predicted by these equations. It is found in practice that on substituting experimental results in these four equations, no distinction can be made between them, i.e. it is not possible to use experimental results to determine growth mechanisms by this method[26].

Hoffman's theory[136] has frequently been used [123,125,126] to calculate the transport term in equations (14) - (17) This method is based on the Williams, Landel and Ferry equation[137].

Then $E_D = C_1/(C_2 + T - T_g)$ (18)

Where T_g is the glass transition temperature of the polymer

C_1 and C_2 are believed to be universal constants although some controversy has arisen in the values given to these[126].

By making certain assumptions the theory described has been used to obtain surface free energies between the liquid and crystal interface, values of G_o, and other molecular parameters governing the temperature dependence of crystallisation[9,25,28,112,126]. Magill[24] has also suggested an alternative, general expression for the transport term and fitted experimental results to his equation by curve fitting analysis, using a computer. Hoffman et al[138] have reviewed the most recent theories of nucleation and growth.

CHAPTER 2.

MATERIALS.

2.1. Polymer preparations.

2.1.1. Introduction.

Table 2.1. Reagents used.

Chemical	Supplier	Purification.
acetic anhydride	Fisons.	-
adipic acid	Hopkin & Williams (GPR)	-
antimony trioxide	Hopkin & Williams	-
butyl titanate in butanol (solution)	Laporte Industries Ltd.	-
chloroform	I.C.I.	-
o-chlorophenol	Fisons	-
dimethyl adipate	BDH	redistilled.
dimethyl isophthalate	Eastman Organic Chemicals	recrystallised from methanol/water
dimethyl terephthalate	BDH	recrystallised from ethanol
ethylene glycol	Fisons	redistilled
hexamethylene glycol	BDH	recrystallised twice from ethyl acetate
pentamethylene glycol	BDH	redistilled
tetrachloroethylene	BDH	-
tetramethylene glycol	BDH	redistilled
zinc acetate dihydrate	Hopkin & Williams (Analar)	
nitrogen	British Oxygen Corporation	white spot grade

polyethylene terephthalate   I.C.I. (P&P division)
$Mn(OAc)_2$/ GeO_2 catalysed

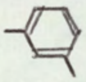
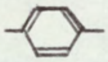
Polyesters were prepared by condensation polymerisation, reacting the appropriate glycol with a dicarboxylic acid or the corresponding dimethyl ester, normally in the presence of a catalyst[17,139,140].

2.1.2. General method.

In all cases except one (sample 66/1) an ester exchange reaction was used, excess glycol being reacted with a dimethyl ester in presence of 0.1% catalyst. The reaction proceeded in two stages.

1. Elimination of methanol to form 'monomer'.

$$CH_3OOCXCOOCH_3 + 2HOYOH \rightarrow 2CH_3OH + HOYOOCXCOOYOH$$

where X = $(CH_2)_4$,  or 

Y = $(CH_2)_2$, $(CH_2)_4$, $(CH_2)_5$ or $(CH_2)_6$.

11. Elimination of glycol to form polymer.

$$HOYOOCXCOOYOH \rightarrow \left[-OYOOCXCO-\right]_n + HOYOH$$

The reaction was carried out in the apparatus shown in Fig. 2.1. The reactants were mixed in tube A and melted in a sand bath under a stream of nitrogen. The nitrogen flow was observed in the oil trap as shown. The temperature was increased and maintained in the region of 140-200°C while methanol collected in the trap. Sufficient time was allowed for stage I to go to completion. A high molecular weight sample cannot be prepared unless all the methanol is removed. The temperature was then increased

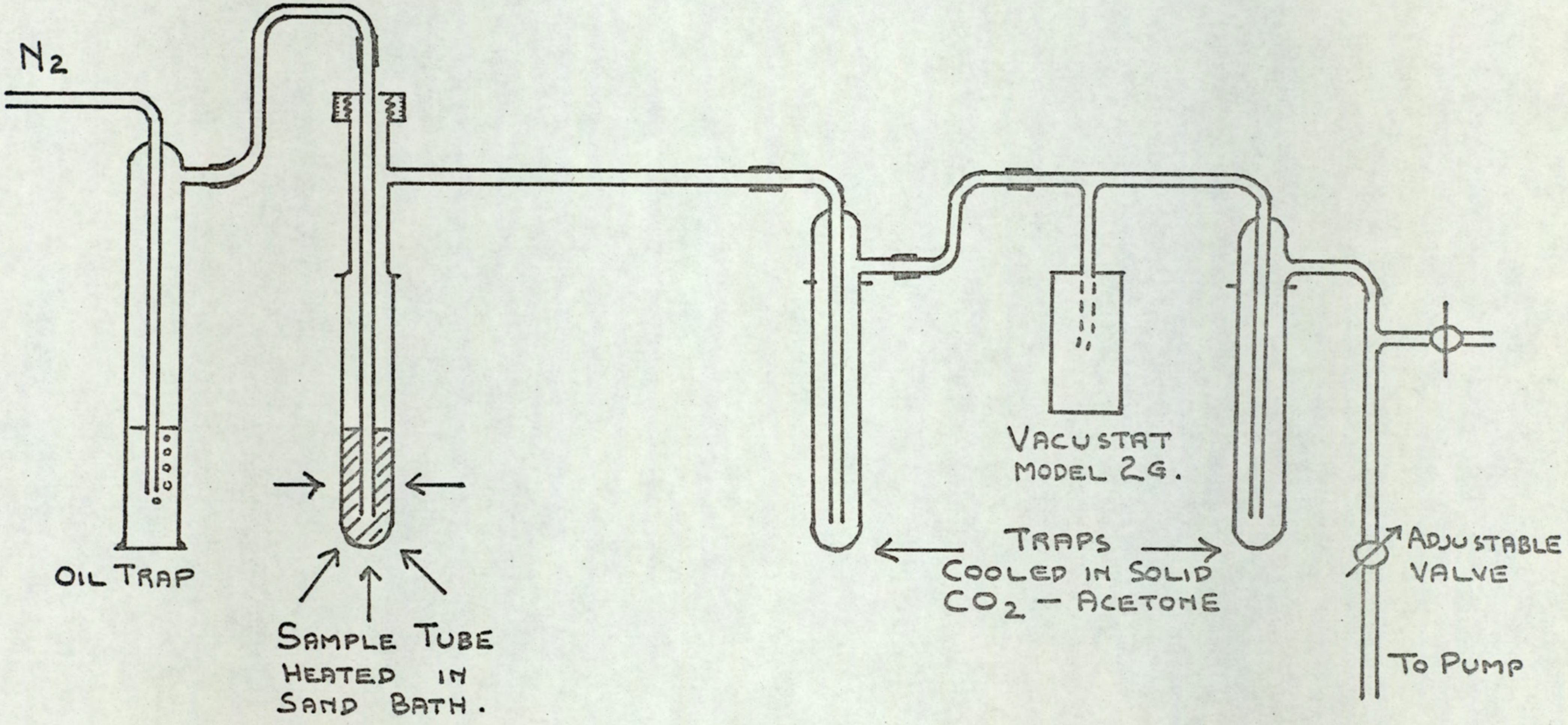


Fig 2.1. Vacuum Line used for sample preparation.

and the pressure reduced very carefully using clips to control the vacuum, and maintain a very slow flow of nitrogen. The reaction was continued under reduced pressure until an increased viscosity was observed. Then Tube A was removed from the sand bath and allowed to cool slowly, wrapped in a cloth. (Rapid cooling would cause rapid crystallisation which results in the glass shattering). The polymer produced (10-15g) was cooled in liquid nitrogen and broken into small chips by hammering.

2.1.3. Specific conditions used.

Note. Sample 66/1 is polyhexamethylene adipate, sample number 1. This notation is used throughout the work.

Sample 66/1

This sample was prepared by the condensation of hexamethylene glycol (2% excess) with adipic acid without a catalyst. (Excess glycol was used to allow for volatility). Reactants were heated at 160-170°C for 25 hours, then the pressure was reduced to 0.2-0.4 mm.Hg, and the sample heated for a further 25 hours. The temperature was gradually increased to 225°C during this time. A white polymer was produced.

Sample 66/2.

A 10% excess of hexamethylene glycol was heated with dimethyl adipate and 0.1% butyl titanate solution as catalyst for 2 hours at 150-180°C. Pressure was reduced to 0.2mm. Hg over a period of 3½ hours, the temperature being gradually increased to 225°C. The polymer produced was yellow in colour, and was subsequently reprecipitated.

Sample 46/1

A 10% excess of tetramethylene glycol was heated with dimethyl adipate and 0.1% butyl titanate solution for 2 hours at 150°C. The pressure was reduced to 0.2mm. Hg over a period of 1 hour. The temperature was then increased to 200°C, and the sample heated for a further 18 hours. This polymer was yellow in colour and was reprecipitated, according to the method described in section 2.1.5.

Sample 4T/1

Tetramethylene glycol (50% excess) and dimethyl terephthalate were heated with 0.1% butyl titanate solution for 3 hours at 150-180°C The temperature was increased to 200°C for another hour, then further increased to 250°C. The pressure was reduced to 0.5mm. Hg, and the sample maintained at this pressure for 3 hours at 250°C. The sample produced was white in colour.

Sample 4T/2

Preparation was as for 4T/1, but the final temperature was 255°C, and the pressure 1.3mm. Hg.

Sample 4T/3.

Preparation was as for 4T/1, but the sample was finally heated for 5 hours at 265°C and 0.5mm Hg pressure. The increased temperature resulted in a lower molecular weight[17].

Sample 5T/1

Pentamethylene glycol (50% excess) was heated with dimethyl terephthalate and 0.1% butyl titanate solution for half an hour at 160°C. The temperature was increased to 200°C for 1½ hours, then to 280°C for 2 hours. This temperature was maintained for a further hour, while the pressure was reduced to 0.1mm. Hg. A glassy amorphous polymer was initially produced. This crystallised after several days.

Sample 6T/1.

Hexamethylene glycol (50% excess) was heated with dimethyl terephthalate and 0.1% butyl titanate at 200°C for 2 hours. The temperature was increased to 280°C for 1 hour, then the sample heated at this temperature and a pressure of 0.05mm. Hg for another hour. A white polymer was produced.

Sample 41/1

Tetramethylene glycol (50% excess) and dimethyl isophthalate were heated with 0.1% butyl titanate for 1 hour at 160°C. The temperature was increased to 180°C for 2 hours, then to 240°C. The pressure was reduced to 0.02mm. Hg, and the reactants heated for another 2 hours. A glassy, amorphous polymer was initially produced. This crystallised after several days.

Sample 2T/1

The butyl titanate catalyst could not be used to prepare this polymer as it causes discolouration[17,139], so an alternative catalyst was used[141].

Ethylene glycol and dimethyl terephthalate in the molar ratio 2.2:1 were heated together, then 0.01% of zinc acetate and 0.02% of antimony acetate in ethylene glycol solution were added, at 150°C. During the next 3 hours the temperature was gradually increased to 215°C. It was further increased to 275°C, the pressure being reduced to 0.3mm. Hg. Polymerisation was continued under these conditions for 2 hours. The polymer produced was white in colour.

2.1.4. Catalysts.

Without a catalyst only low molecular weight samples could be produced, and a long reaction time was necessary (Sample 66/1). Butyl titanate was used where possible as this is soluble, and its presence is not considered to alter crystallisation behaviour[139].

Antimony acetate was selected as another suitable soluble catalyst, for the preparation of polyethylene terephthalate. This was prepared as follows[141]. Equimolecular quantities of antimony trioxide and acetic anhydride were heated in ethylene glycol till a clear solution was produced. It was unnecessary to isolate the antimony acetate, which was added direct to the reaction tube in ethylene glycol solution.

2.1.5. Polymer precipitation.

Samples 66/2 and 46/1 were yellow in colour, as obtained. These samples were purified by precipitation. An approximately 20% solution of polymer in chloroform was prepared. This solution was added dropwise to about five times the volume of methanol. The methanol was cooled with solid carbon dioxide, and stirred continuously using a magnetic stirrer. The precipitated polymer was filtered off, dried and the process repeated. Finally the polymer was dried overnight in a vacuum oven at about 30°C. 80% of the polymer was recovered. It was whiter in colour, and of higher molecular weight.

The remaining polymers were used as prepared.

2.2. Methods of characterisation.

2.2.1. Membrane osmometry

Polymer molecular weights were measured using the Mechrolab Model 502 high speed membrane osmometer. Detailed description of this instrument and its operation is given in the instruction manual[142], and will only be summarised here. Solution in the upper part of the instrument is separated by the membrane from the solvent below. Normal flow of solvent up into the solution compartment is prevented, as the movement is detected by an optical system and pressure automatically adjusted by an electro-mechanical servo system to prevent any net flow. The osmotic head is measured by the position of the solvent reservoir in the elevator unit, which is recorded directly on a dial. This head is measured for each solution, and also for the situation when solvent is present on each side of the membrane. The latter value is known as the solvent reference level.

Aromatic polyesters were dissolved in a filtered 60:40 mixture of o-chlorophenol/tetrachloroethylene; aliphatic polyesters were dissolved in filtered chloroform. All measurements were made at 25°C. Membranes were cut from

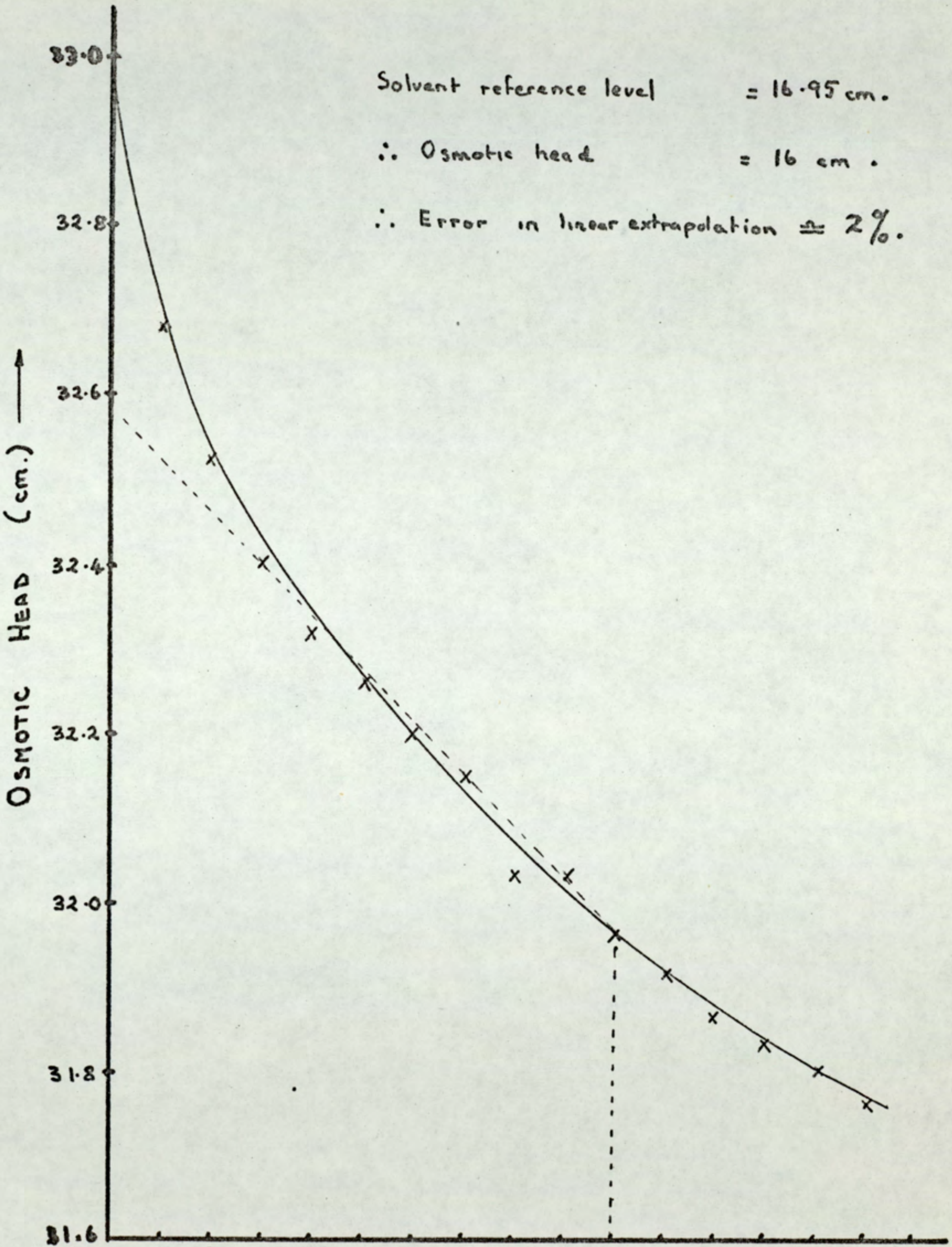
Sylvania regenerated cellophane, washed in distilled water and conditioned to methanol by soaking for four hours in each of the following solutions.

1. 1:3 methanol/water
2. 2:2 methanol/water
3. 3:1 methanol/water
4. methanol

Membranes were stored in methanol and similarly conditioned to the appropriate polymer solvent when required, using methanol/solvent mixtures.

Stock solutions containing approximately 8 $g.l^{-1}$. polymer were prepared, and successively diluted to give a total of four concentrations for each polymer. The method described[142] was used in molecular weight measurement. However as the polyesters had relatively low molecular weights diffusion of the polymer molecules occurred. This resulted in a lowered osmotic head and therefore a too high molecular weight. To correct the osmotic head to the value which would be obtained in the absence of diffusion, readings were taken at one minute intervals for ten minutes. The almost linear plot obtained was extrapolated to zero time. If such a graph is plotted on an expanded scale (Fig.2.2) the error in such an extrapolation is shown to be of the order of only 2%. The solvent reference level was not absolutely stable until ten minutes after the solvent had been levelled in the solution compartment, but errors due to these fluctuations were small compared with diffusion effects.

FIG.2.2. DRIFT IN OSMOTIC HEAD — DUE TO DIFFUSION



Solvent reference level = 16.95 cm.

∴ Osmotic head = 16 cm.

∴ Error in linear extrapolation ≏ 2%.

The difference between the solution reading and the solvent reference level corresponded to the osmotic pressure Π for each solution of concentration c. For each polymer a linear plot of Π/c was obtained, and the value of the intercept $(\Pi/c)_{c=0}$ was used to calculate the number average molecular weight M_n, from the equation,

$$M_n = \frac{RT}{(\Pi/c)_{c=0}} \qquad (19)$$

The gas constant R is 0.08208 litre-atmosphere/degree. mole. Because the osmotic pressure is expressed in terms of a particular solvent, it is convenient to convert R to the corresponding units. Calculated 'RT factors' at 25^oC (298^oK), and the density values for the solvents used are listed in Table 2.1. (T is the solution temperature in ^oK).

Table 2.2 RT factors for polmer solvents at 25^oC

Solvent	Density $g.cm.^{-3}$	RT $cm.g.mole^{-1}$
chloroform	1.480[143]	$1.80x10^4$
o-chlorophenol	1.258[144]	
tetrachloroethylene	1.614[145]	
60:40 o-chlorophenol/ tetrachloroethylene	1.401*	1.66×10^4

*weighted average density.

From the slope of the Π/c against c graph, A'_2, the second virial coefficient for a polymer/solvent system may be obtained. It is defined by the equation,

$$A'_2 = \frac{1}{RT}\frac{\Delta(\Pi/c)}{\Delta c} \qquad cm.^3g.^{-2}mole \qquad (20)$$

of the membrane, but if it was clamped in position with care the membrane lifetime was found to be over a month at 25°C.

The aromatic polyesters were dissolved in the mixed solvent by refluxing for ten minutes at 140°C. This treatment did not appear to cause serious hydrolytic degradation of the polymers, as no molecular weight change could be detected after increasing the reflux time to one hour.

Aliphatic polyesters dissolved readily in chloroform without heating. With chloroform as solvent difficulties were due to solvent volatility, which resulted in leaks developing in the solvent system, and an unstable solvent reference level. Careful membrane conditioning was necessary according to the method described, to avoid hardening and distortion of the membranes.

For the low molecular weight sample 66/1, M_n was measured using a Mechrolab vapour pressure osmometer (Model 301A). The polymer was dissolved in tetrahydrofuran.

2.2.2. Viscometry.

Intrinsic viscosities were measured on some of the polymer samples for comparison with M_n values. The Mark-Houwink equation relates intrinsic viscosity $[\eta]$ to M_v, the viscosity average molecular weight.

$$[\eta] = K'M_v^{\,a} \qquad (22)$$

Since values of the constants K' and a were only available for 46, 66, and 2T polyesters,[74,147], this method could not be used to measure molecular weights for the whole series of polyesters.

For viscosity measurements, o-chlorophenol was used as solvent for aromatic polyesters; chloroform was used for aliphatic polyesters. Solvents were filtered prior to use. The solvent flow time was measured, using a clean, dry Ubbelohde viscometer. A 1% solution was prepared and its flow time measured. By successive dilutions flow times were obtained at six additional concentrations. Flow time measurements were repeated until they agreed to within ± 0.1 second. All measurements were made at 25°C.

Intrinsic viscosities were obtained as follows

$$\eta_r = \frac{f_2}{f_1} \qquad (23)$$

where η_r is the relative viscosity of the solution

f_1, f_2 are the flow times of the solvent and solution.

$$\eta_{sp} = \eta_r - 1 \qquad (24)$$

where η_{sp} is the specific viscosity of the solution

At low concentrations η_{sp}/c is approximately proportional to c, and the intercept of this plot, $(\eta_{sp}/c)_{c=0} = [\eta]$. In addition a similar intercept should be obtained if $(\log_e \eta_r)/c$ is plotted against c. If both plots are made on the same graph, $[\eta]$ may be obtained from a double

Table 2.3. Molecular weight data for linear polyesters.

Sample description	M_n g.mole^{-1}	A'_2 cm.$^{-3}$g.$^{-2}$mole	χ	Amorphous density g.cm^{-3}	$[\eta]$
66/1	5,000	-	-	-	-
66/2 (before precipitation)	-	-	-	-	0.615
66/2* (after precipitation)	16,500	5.3×10^{-3}	-	-	0.658
46/1*	14,700	4.0×10^{-3}	-	-	0.620
2T/1*	12,200	1.9×10^{-3}	0.15	1.335[83]	-
2T (I.C.I sample)	23,400	2.0×10^{-3}	0.15	1.335	-
4T/1*	13,400	1.7×10^{-3}	-	-	0.590
4T/2	11,100	1.9×10^{-3}	-	-	0.450
4T/3	9,300	1.9×10^{-3}	-	-	0.392
5T/1*	10,600	4.7×10^{-3}	-	-	-
6T/1*	11,800	3.5×10^{-3}	-	-	-
4I/1*	12,800	2.7×10^{-3}	0.06	1.268[3]	-

*Samples used for isothermal crystallisation rate measurement. χ Values were calculated in the cases where amorphous densities were available for the polymer.

extrapolation.

2.2.3. Melting temperature determination.

Polymer melting temperatures were measured using a polarising microscope, fitted with a hot stage. The amount of light transmitted through a film of polymer was recorded using a photocell. The microscope is described further in section 3.3.2.

Samples were first crystallised slowly (over a period of 16-72 hours), then heated at $\frac{1}{2}^{\circ}$C/minute. Each measurement was repeated twice. Melting temperatures observed were dependent on the heating rate, but the melting temperature of a pure sample of benzoic acid was in agreement with the reported value (122°C) if heating rates $\leq 1^{\circ}$C/minute were used.

The melting temperature was defined as the temperature at which the last trace of birefringence disappeared. This was observed on an X-Y recorder. The temperature axis was calibrated using a Pye potentiometer.

2.3. Results.

2.3.1. Molecular weight determinations.

Molecular weight data are collected in Table 2.3.

In order to eliminate serious differences in crystallisation rate due to molecular weight, attempts were made to prepare the different polymers with similar molecular weights. In practice the molecular weight range was 10,600-16,500. For a given polymer this variation is sufficient to change $t_{\frac{1}{2}}$ by several orders[94]. However it is less significant when the entire crystallisation behaviour of different polymers is studied. (For example, the degree of supercooling required for crystallisation, and the temperature range over which crystallisation is measurable).

Intrinsic viscosity measurements for polyhexamethylene adipate demonstrate the increase in average molecular weight which occurs when the polymer is precipitated. The lower molecular weight fraction is not precipitated by the amount of methanol used.

For polytetramethylene adipate, constants for the Mark-Houwink equation have been reported[147].

$$K' = 6.6 \times 10^{-4} \qquad a = 0.68$$

Using these values M_v for sample 46/1 is equal to 23,500.

$$M_v/M_n = 1.6$$

This is a reasonable value for this ratio for a condensation polymer, indicating that the M_n value obtained by the extrapolation method described is of the correct order.

For polytetramethylene terephthalate samples $[\eta]$ and M_n values appeared to correspond, but K' and a were not available.

Typical osmometry results are shown in Fig.2.3, for polyhexamethylene terphthalate. Fig.2.3A indicates the extrapolation procedure used. The slope of the line shown in Fig.2.3^{B} was used to calculate the A'_2 values listed.

FIG. 2.3A. DRIFT IN OSMOTIC HEAD WITH TIME.

SAMPLE 6T/1

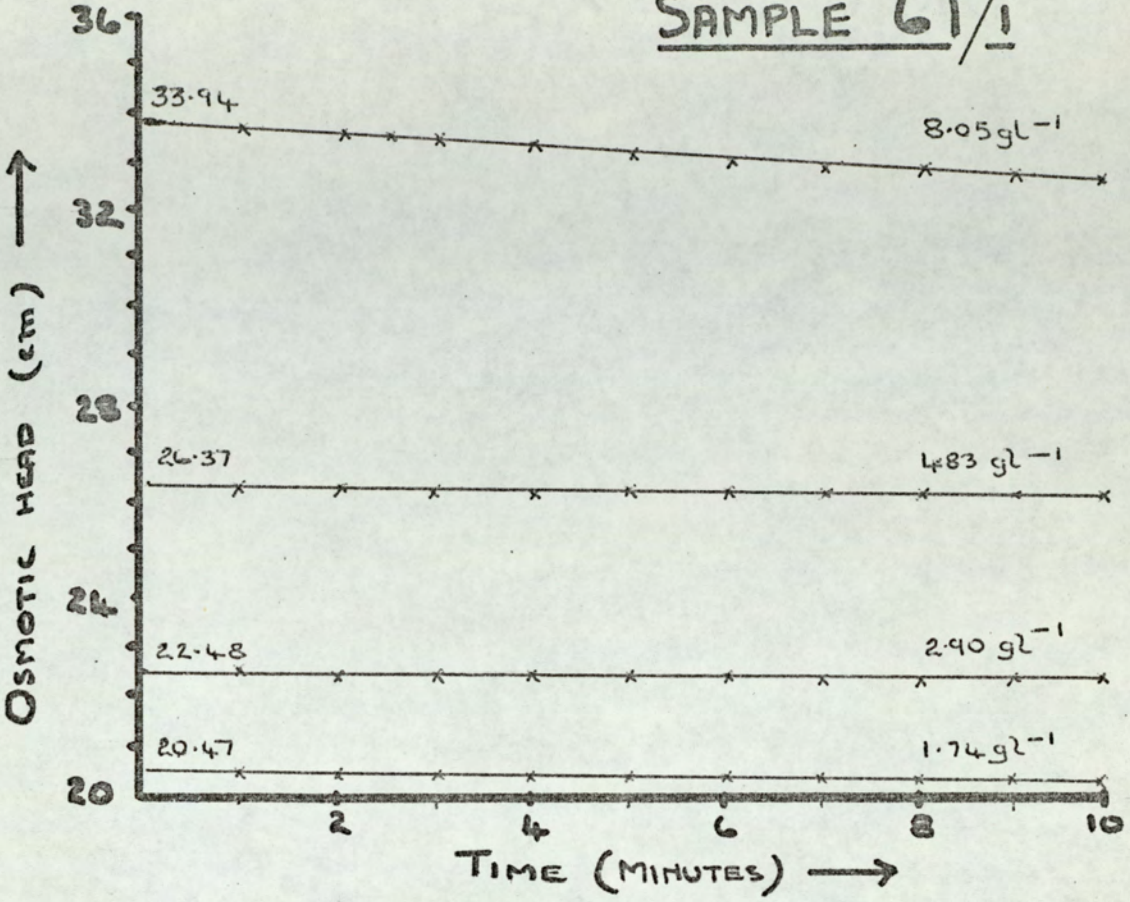


FIG. 2.3.B. GRAPH OF π/c AGAINST C.

SAMPLE 6T/1

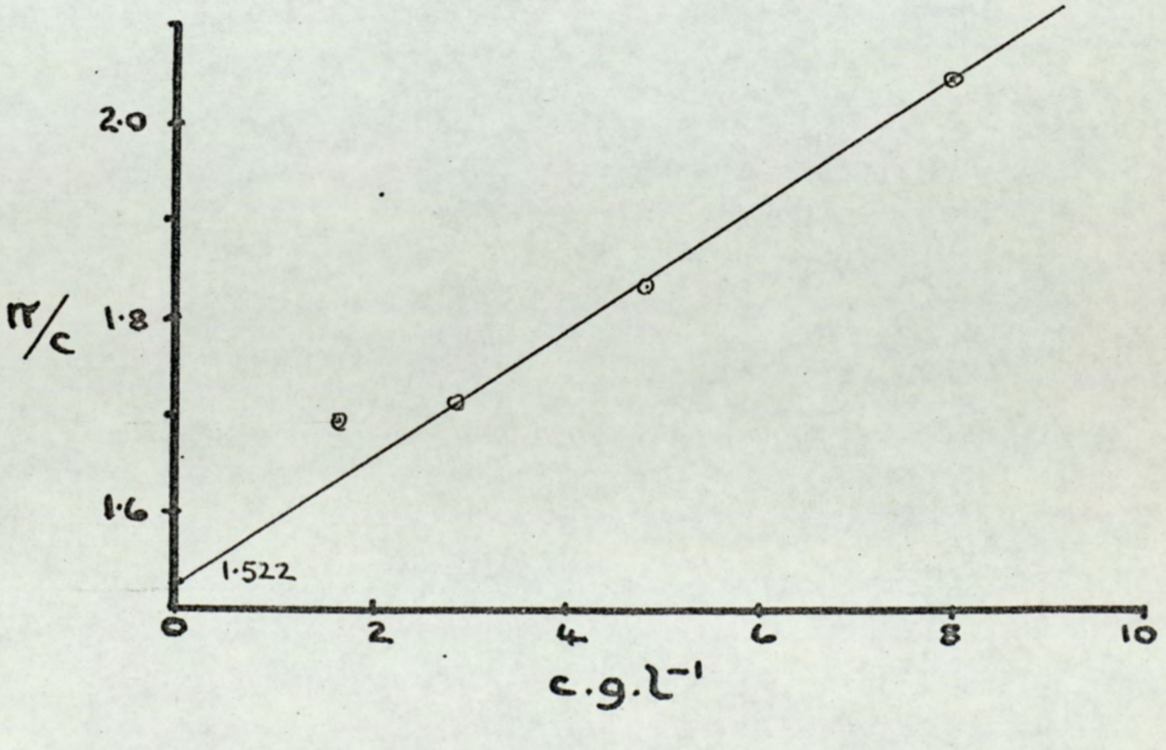


Table 2.4. Polymer melting temperatures.

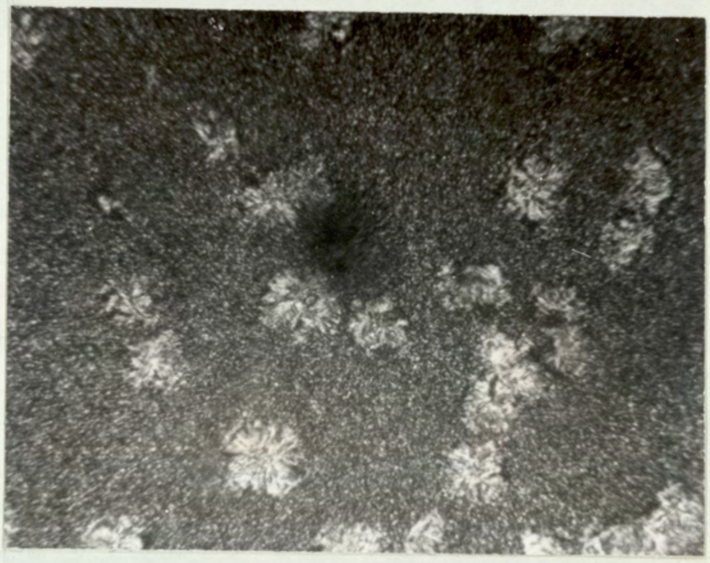
Sample description	Crystallisation temp. °C	Crystallisation time (hrs)	T_m °C	T_m^{*} °C	$(T_m^{*}-T_m)$ °C
66/1	54 - 55	72	60	64	4
66/2	54 - 55	72	61	65	4
46/1	51 - 52	16	60	70	10
2T/1	241 -244	16	276	283	7
4T/1	215	24	234	242	8
5T/1	115	16	142	150	8
6T/1	140	17	156	162	6
4I/1	105	72	150	160	10

2.3.2. Polymer melting temperatures.

Table 2.4. shows the crystallisation treatment used prior to melting temperature (T_m) measurement. T_m^* is the thermodynamic melting temperature estimated from crystallisation results by the method described in Chapter 4. It appeared that ($T_m^* - T_m$) was larger in cases where large spherulites could be grown. Such spherulites would be produced using the slow crystallisation conditions indicated. For sample 46/1 it was observed that such large spherulites melted 1°-2° C lower than the small spherulites produced by quenching the partially crystallised samples to room temperature. The two types of spherulites are shown in Fig.2.4. Thus the recorded melting temperature for this polymer was probably too low; this could also be true of samples 4I, 4T and 5T.

A typical melting trace obtained for the polyester samples is shown in Fig. 2.5 for polyethylene terephthalate. The apparent increase in depolarised light intensity just before melting is due to the coloured appearance of the polyester samples when observed using crossed polars. This is due to the high order of birefringence in such samples. Melting actually starts far below the final melting temperature (e.g. at approximately 200°C for the sample shown). As the sample starts to melt, the amount of birefringence decreases, so the coloured appearance of the sample decreases, and the light actually detected by the photocell increases. At the point where the depolarised light

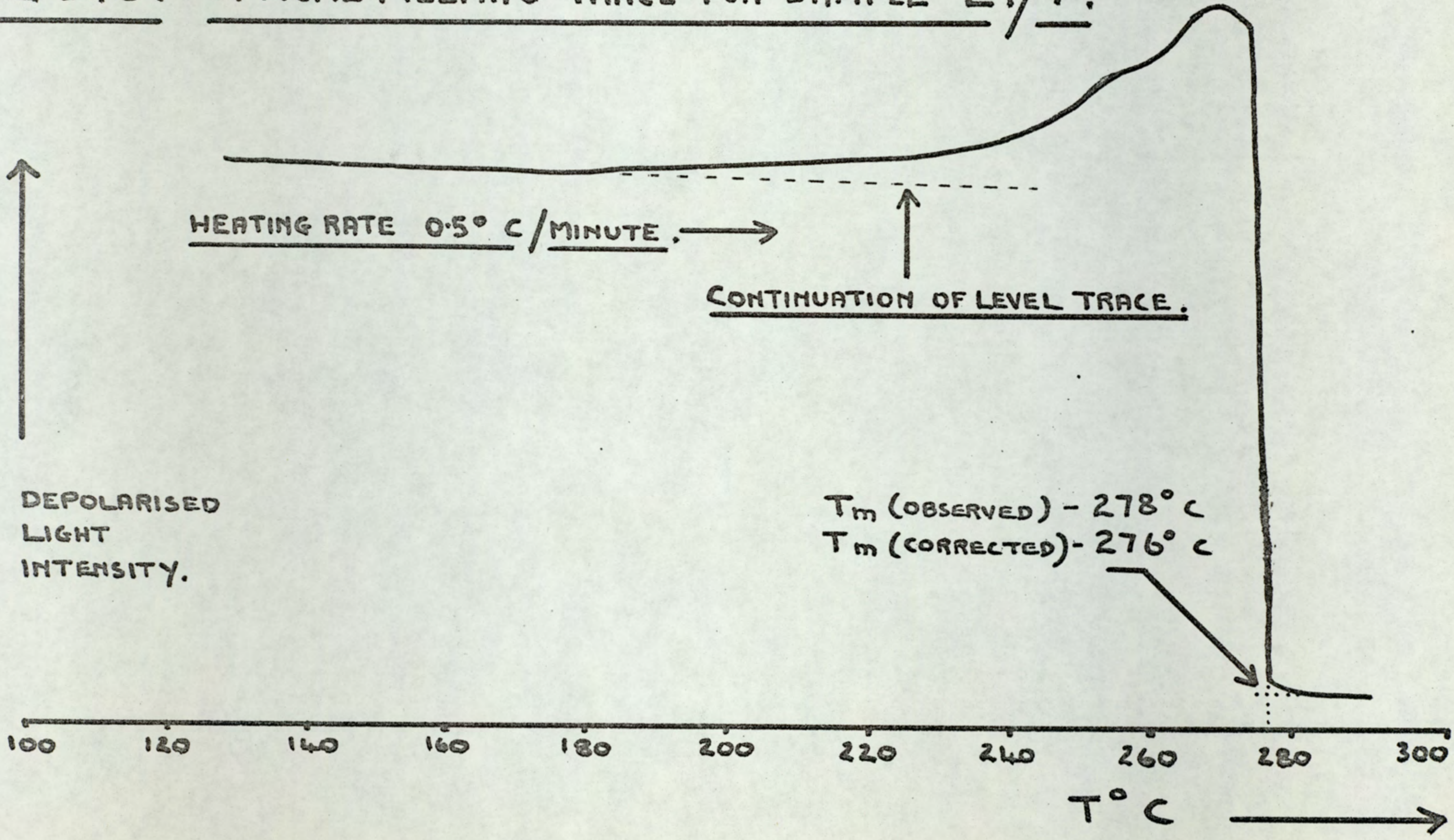
FIG. 2.4. SPHERULITES IN 46/1 POLYESTER.



Sample crystallised isothermally, then quenched.

intensity begins to decrease, the sample appears black and white. Due to this effect optical microscopy is not a suitable technique for measuring isothermal crystallisation rates of polyester samples (Section 3.3).

Fig 2.5. Optical Melting Trace for Sample 2T/1.



CHAPTER 3.

INSTRUMENTAL TECHNIQUES.

3.1. Dilatometry.

Dilatometry was used to measure isothermal crystallisation rates. The microdilatometers used were a modification of those which have been described previously[148]. (Fig. 3.1B.) The polymer sample (0.15-0.20g.) was placed in tube A, which was then sealed at X. The main stem of the dilatometer consisted of 0.4mm. bore Veridia tubing. Tube B was used as a mercury reservoir.

The vacuum line shown in Fig. 3.1A was used for filling the dilatometers. A Genivac single stage rotary pump (Type GRS2) was used as a backing pump for a mercury distillation pump. Traps were placed in liquid nitrogen. Bulbs E and F were used to provide doubly distilled mercury. The air condenser was used to prevent mercury distilling back into contact with the greased joints. Pressure in the system was measured using a Genivac Penning gauge head (Type PNH1) connected to D via a copper glass joint.

Clean mercury was poured into bulb E through socket D using a long stemmed funnel to avoid contaminating the mercury with grease. The gauge head was replaced. The dilatometer was connected to the vacuum line at C. A small amount of Apiezon T grease was used at the top of this quickfit joint, as it was important to prevent any grease from entering the dilatometer. Tubes A and B were in planes

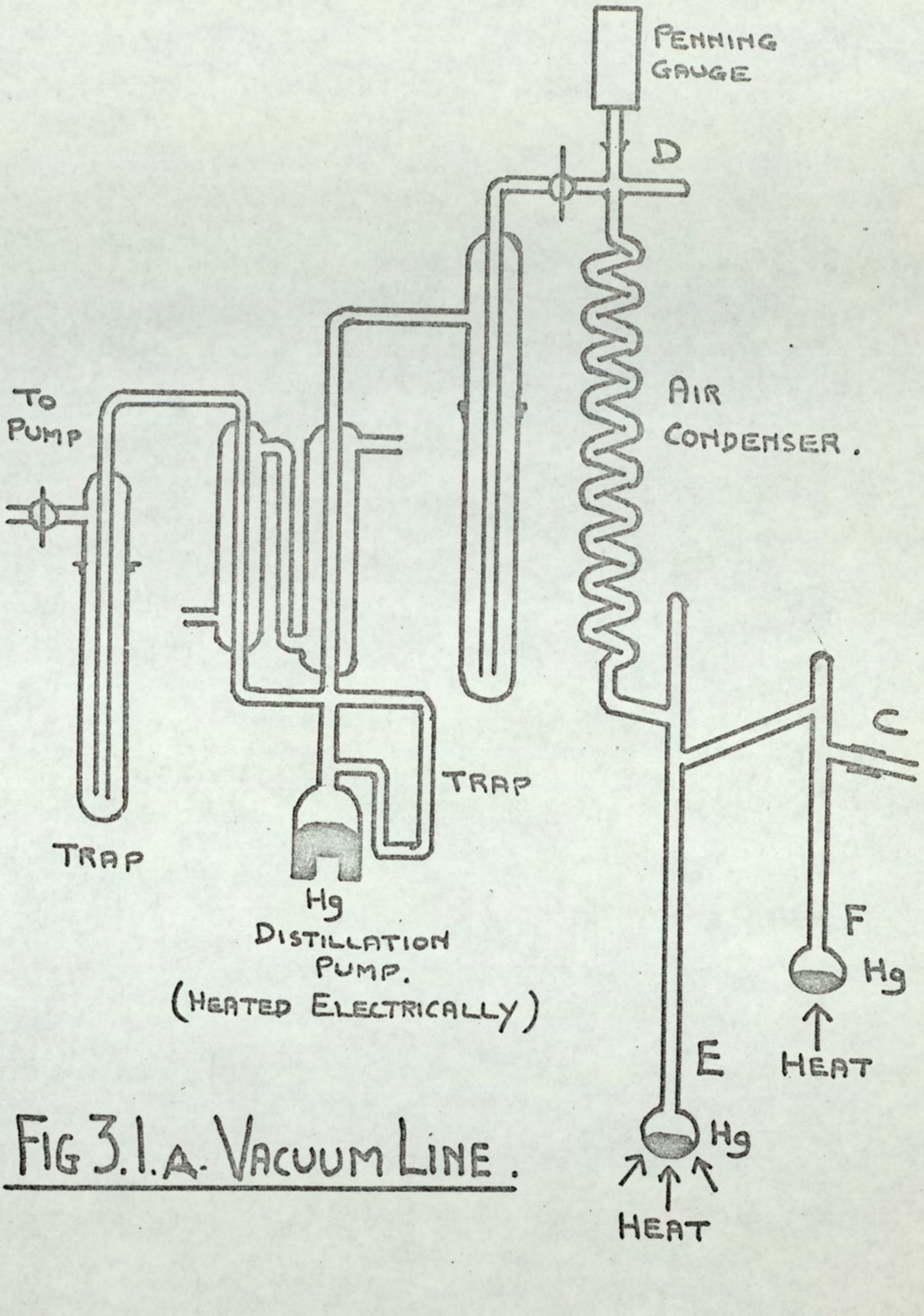
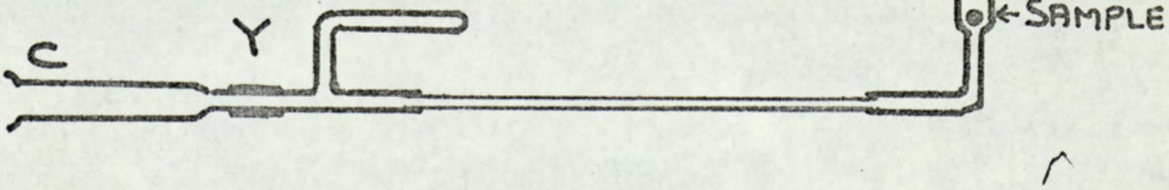


FIG 3.1.A. VACUUM LINE.

FIG 3.1.B. DILATOMETER.
(ENLARGED SCALE)



at right angles to one another. Initially the dilatometer was rotated so that tube A pointed downwards, and the polymer could be heated using a small oil bath. Normally the polymer was held just above its melting temperature at a pressure of 2 x 10^{-4}mm. Hg for 3-4 hours, to remove air and any volatile material. The dilatometer was then rotated so that tube B was directed downwards. Bulb E was heated to distil mercury into bulb F. When sufficient mercury had distilled bulb F was heated to distil mercury into tube B. The dilatometer was sealed off at Y, using a hand torch, then mercury was poured through the capillary into A. The dilatometer was opened to atmospheric pressure, and the amount of mercury was adjusted so that the meniscus was at the top of the capillary when the dilatometer was at the crystallisation temperature.

Oil baths were used for melting and crystallising the polymer in the dilatometer. The baths were fitted with a stirrer, a boost heater and a control heater. For the melting bath this heater was controlled to ± 0.6°C by an AEI Sunvic regulator in conjunction with a Gallenkamp contact thermometer. For the crystallisation bath the AEI regulator was replaced by a Tetcol mercury switch type regulator, and the temperature control was further improved by fitting the 500 watt control heater with a variable rotary transformer. Temperature control was ± 0.02°C at temperatures of about 50°C, and ± 0.3°C at higher temperatures.

A polymer sample was melted under selected conditions, then the dilatometer was transferred rapidly to the crystallisation bath, the capillary being adjusted to a vertical position. The height of the mercury column was measured using a cathetometer. A stop watch was started as the dilatometer was placed in the crystallisation bath, and measurements were initially made every minute to estimate the time taken for the dilatometer to reach the temperature of the oil bath. (i.e. the time for the mercury level to become constant). This time, which varied from 2-5 minutes according to the amount of supercooling required, was deducted from the recorded time. A plot of height h_t against time t represented the crystallisation isotherm.

3.2...Differential scanning calorimetry.

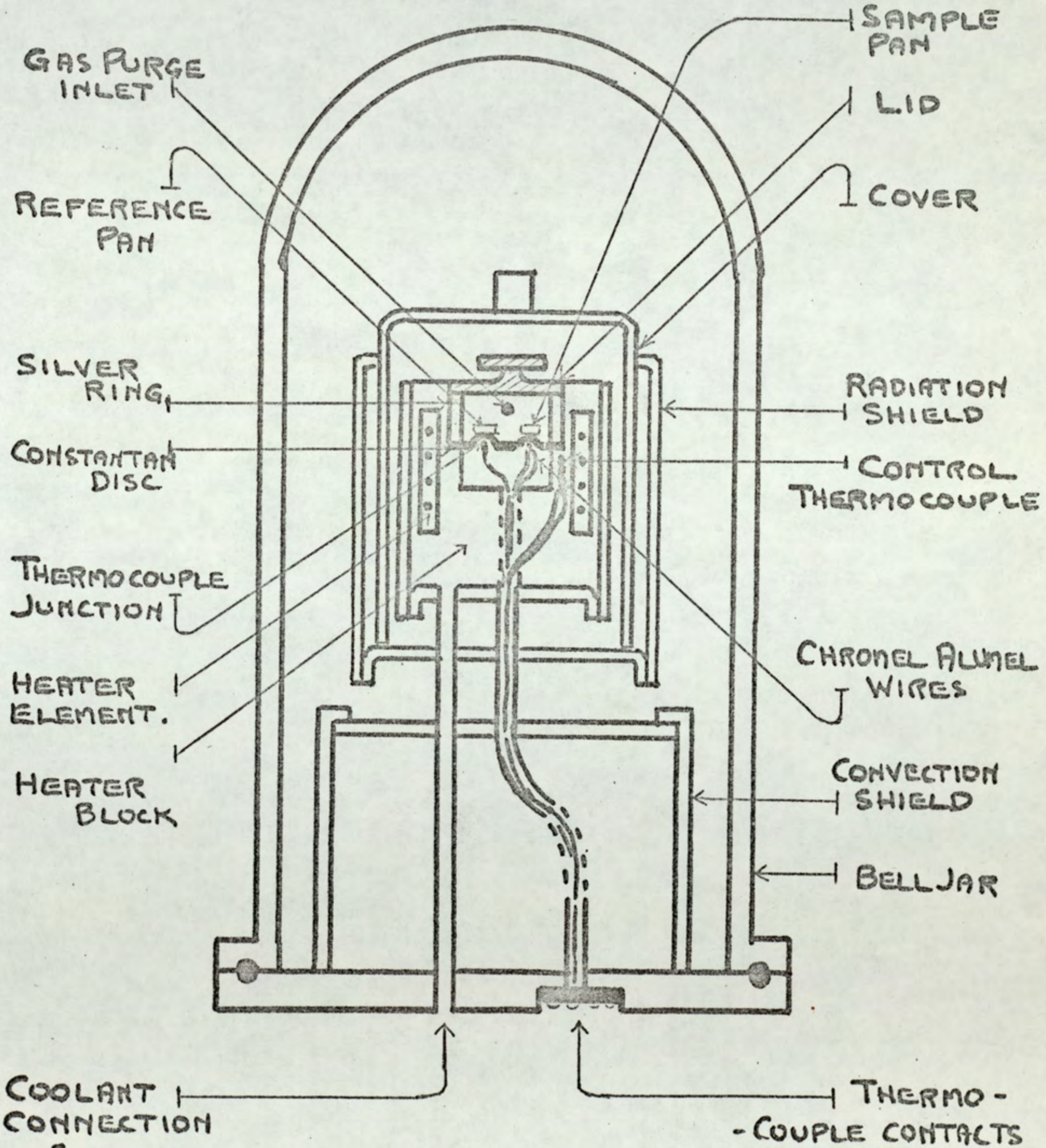
(NOTE. For this work the Du Pont DSC cell is used with the Du Pont 900 thermal analyzer. The temperature difference between sample and reference is recorded. Thus the method, as defined conventionally (section 1.2.4.) is DTA rather than DSC. It is referred to as DSC merely according to the Du Pont nomenclature).

3.2.1. Isothermal crystallisation rates.

The Du Pont instrument has been used with modifications to measure isothermal crystallisation rates. The method depends on the heat evolved during crystallisation, which results in a temperature difference T_d between sample and reference. Hay[115] has suggested that conventional thermal analysis techniques cannot be used to measure isothermal crystallisation rates as the sample temperature changes during crystallisation. However using the present equipment with improved sensitivity and temperature control these measurements were possible. Although the sample temperature changed due to crystallisation, the change was not sufficient to significantly alter the crystallisation rate. T_d values measured were in the region of 0.02-0.2°C. The larger values of T_d were obtained for the most rapid crystallisation rates, when the temperature dependence of crystallisation rate was at its lowest, so errors due to the sample temperature change T_d were no more serious than those due to experimental temperature fluctuation.

Operation and construction of the Du Pont thermal analyzer are described in the handbook[149]. The instrument is equipped with an X-Y recorder. Temperature programming or isothermal control is effected with two silicon controlled rectifiers (SCRs) in the heater circuit. A cross section of the cell is shown in Fig.3.2. Sample and reference pans, made of aluminium, are placed on the raised platforms of a thermoelectric disc, which is made of constantan. Chromel wire is welded at the centre of the base of each platform. Thermocouple junctions thus formed are used for measuring the temperature difference between sample and reference. The signal between these two junctions is fed to the 900 T_d amplifier and observed on the Y-axis of the recorder. An alumel wire is also welded to the centre of

FIG 3.2. DSC CELL.



[GAS PURGE AND VACUUM CONNECTIONS ARE NOT SHOWN.]

the front raised platform, forming a chromel-alumel thermocouple which is used to measure the temperature of that platform. The corresponding cold junction of the thermocouple is placed in crushed ice at $0^{\circ}C$, and the output observed on the X axis of the recorder.

The constantan disc also serves to transfer heat radially inwards from the heating block to the sample and reference which are otherwise thermally isolated. A chromel-alumel thermocouple situated close to the heater windings is used to operate the temperature programmer-controller via a feed back mechanism. The sample chamber is protected from external temperature changes by a series of shields and lids as shown. The entire cell is covered with a glass bell jar.

Purge gas enters the 900 through a purge connection, passes through a rotameter, and is preheated to enter the sample chamber at the block temperature. Vacuum and cooling connections to the cell are also available.

To obtain the required sensitivity in T_d measurement, an external time base recorder was required. A 1mV Honeywell Electronik 19 recorder, fitted with a Disc integrator (Model 352-B) was used for this purpose. This was connected to Y axis access points on the 900, through a resistance box and a coarse zeroer. The circuit diagram is shown in Fig. 3.3A. The resistance box served as a span control to provide a wide range of sensitivities, shown in Table 3.1. The coarse zeroer was necessary to bring the external recorder on scale.

FIG 3.3. A. CIRCUIT DIAGRAM FOR ZEROER AND SPAN CONTROL.

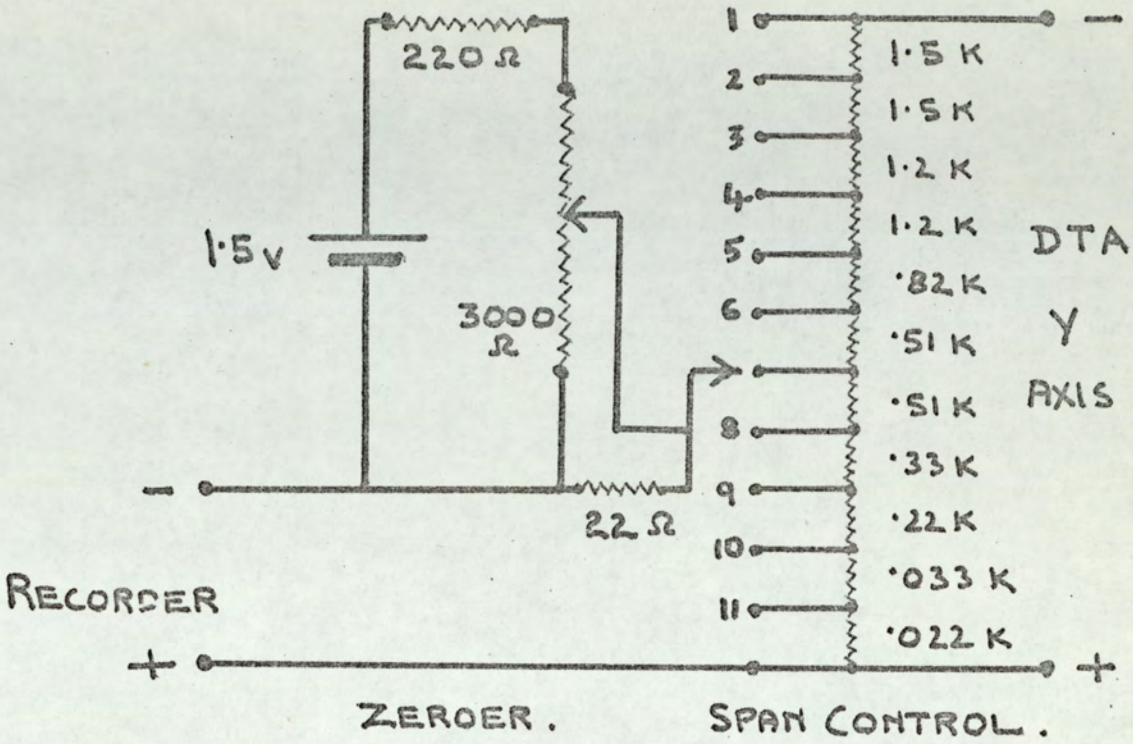
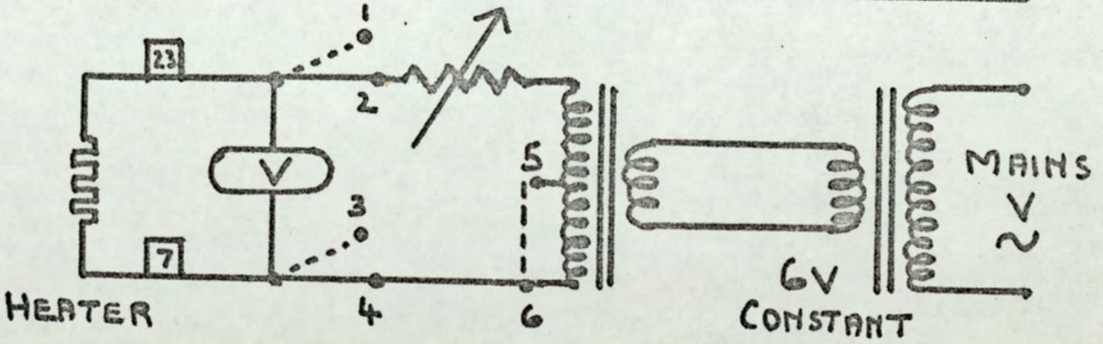


FIG 3.3. B. CIRCUIT DIAGRAM FOR EXTERNAL HEATING SUPPLY.



7 . 23 . – PIN NUMBERS ON ACCESSORY PLUG.
1 . 3 . – CONNECTIONS FOR DSC HEATER SUPPLY.
2 . 4 . – CONNECTIONS FOR EXTERNAL HEATER SUPPLY.
5. – SWITCH POSITION FOR 120 V OUTPUT.
6. – SWITCH POSITION FOR 60 V OUTPUT.

Table 3.1. Span control settings for T_d measurement.

Span control setting	T_d mV/inch	T_d °C/inch
1	0.00013	0.0032
2	0.00016	0.0039
3	0.00021	0.0051
4	0.00027	0.0068
5	0.00041	0.0102
6	0.00061	0.0153
7	0.00089	0.0223
8	0.00165	0.0362
9	0.00362	0.0905
10	0.01816	0.4540
11	0.04534	1.1335

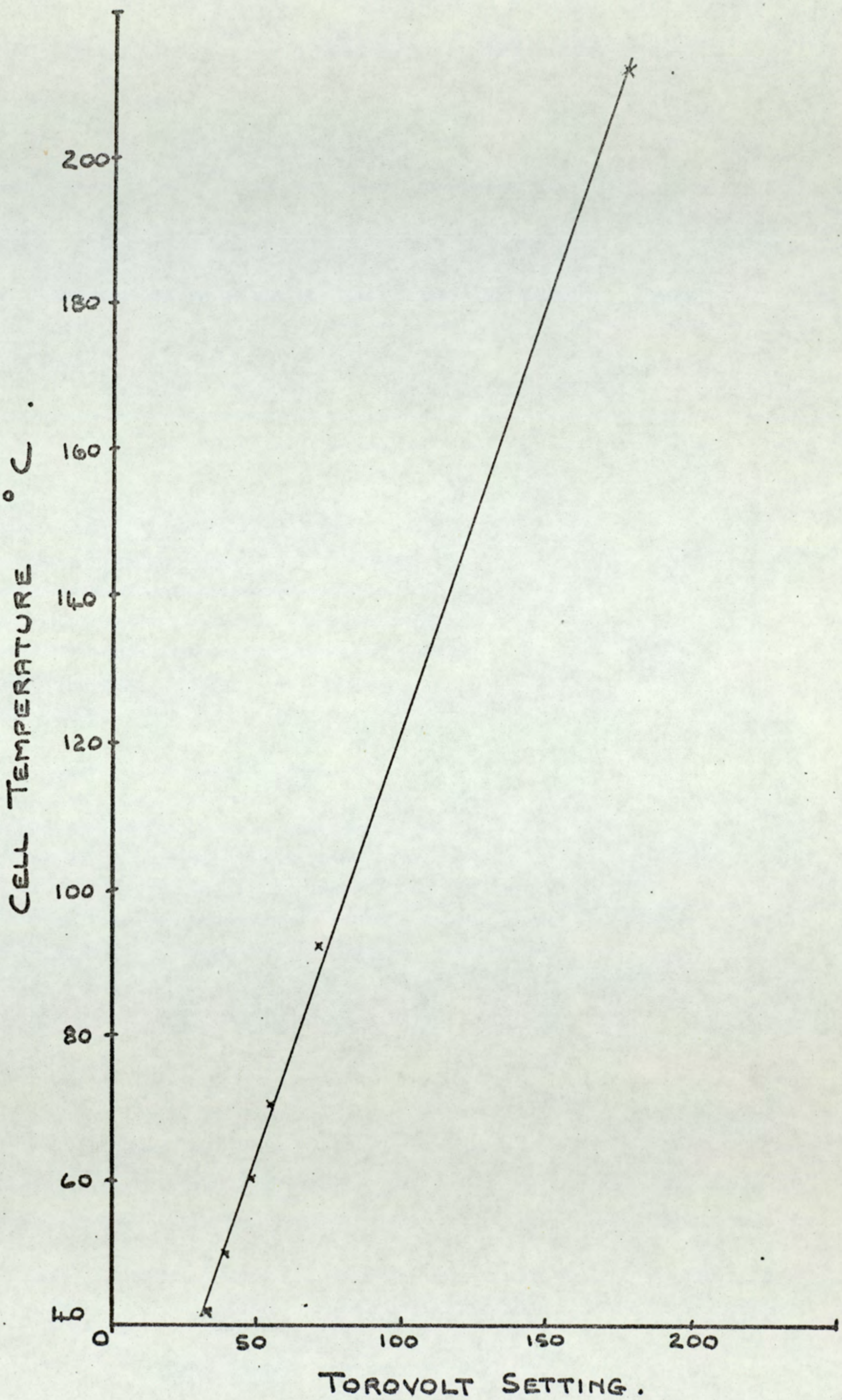
The temperature control requirements were not fulfilled by the standard programmer. To measure isothermal rates it was necessary to hold the sample at the melting temperature, then cool as rapidly as possible, but without overshooting to the crystallisation temperature. This control could not be achieved with the Du Pont programmer, as fluctuations before a steady temperature was reached were considerable due to a tendency of the programmer to 'over-correct', making it impossible to record the onset of crystallisation. Due to the very efficient insulation of the DSC cell it was found that isothermal temperature control could be improved considerably by using a constant stable voltage supply to the heater. Modules for the 900, such as the DSC cell were equipped with accessory plugs making connections at the back of the instrument. One such plug was adapted so that an alternative heat supply could be used. This additional heater circuit is shown in Fig. 3.3B. Mains voltage was transformed using an Advance Volstat to give a 6 volt constant voltage supply. A Lovolt isolating transformer converted this to a stabilised voltage which could be varied from 0-60 volts or 0-120 volts using a Cressall Torovolt transformer to control the cell at the required temperature. The calibration graph is shown in Fig. 3.4. An additional voltmeter indicated the heater voltage, supplied from either source.

Temperature variation during an experiment was followed on a Bristol's 1mV recorder connected to X-axis access points on the 900. This was considerably more sensitive than the X-Y recorder. A Pye potentiometer connected at the same points was used at intervals to check the X axis temperature calibration, and correct the observed temperatures.

At temperatures $<100^\circ$C the temperature could be controlled to $\pm 0.1^\circ$C Control becomes progressively poorer at higher temperatures, but was acceptable up to about 220°C. At higher temperatures control was difficult, and fluctuations resulted in irreproducible results.

To perform a crystallisation experiment, 10-25mg. of polymer were placed in an aluminium sample pan (6.6mm. internal diameter). The polymer was melted, and a lid placed in contact with the molten polymer so that the sample

Fig. 3.4. DSC cell.
Temperature Calibration.
(0 – 60 Volt Supply to Heater)



was in the form of a thin disc. For polyethylene terephthalate, which is prone to oxidation, the edges of the pan were crimped. Glass beads (a similar weight to the sample) were used as reference. The sample was placed on the rear raised platform; the reference on the front platform, which has its temperature recorded on the X-axis. The cell was closed and heated to the required melting temperature for a given time. The cell heater was switched off, and the cell was cooled using a cooling attachment. This was made from brass rod. The lower half was machined to fit over the cell when the bell jar and cover had been removed; the upper part could be filled with a cooling medium (water, ice, solid carbon dioxide, or liquid nitrogen, according to the temperatures concerned, and the degree of supercooling required). The cooling was followed on the external temperature recorder. As the crystallisation temperature was approached the cooling attachment was removed, the cell cover replaced, then the external heater supply was switched on. Initially the voltage used was about 10% higher than that given by the calibration graph (Fig.3.4.) The voltage was reduced slowly to the required value to bring the temperature into control. Exact cooling conditions required were determined experimentally for each polymer. Crystallisation rates were measured over the largest possible temperature range in each case. $t_{\frac{1}{2}}$ values measured were between 5 and 150 minutes. At faster rates temperature equilibrium could not be achieved quickly enough; at slower rates T_d was too small for accurate measurement.

The Disc integrator is a mechanical device which measures peak areas. A ball positioned on a flat disc rotates at a speed proportional to its distance from the centre of the disc. The ball is moved across the disc whenever the recorder pen moves from its baseline. Movement of the ball is used in turn to drive the integrator pen. Honeywell chart paper (680000 2) is used in conjunction with the integrator. The integrator pen is adjusted so that it travels backwards and forwards across a one inch channel at the edge of the chart paper. (Fig.3.5A). The number of times the pen crosses this channel increases as the recorder pen moves away from the baseline. Thus the number of squares crossed represents the peak area at a given time. Distances travelled by the integrator pen are represented as follows.

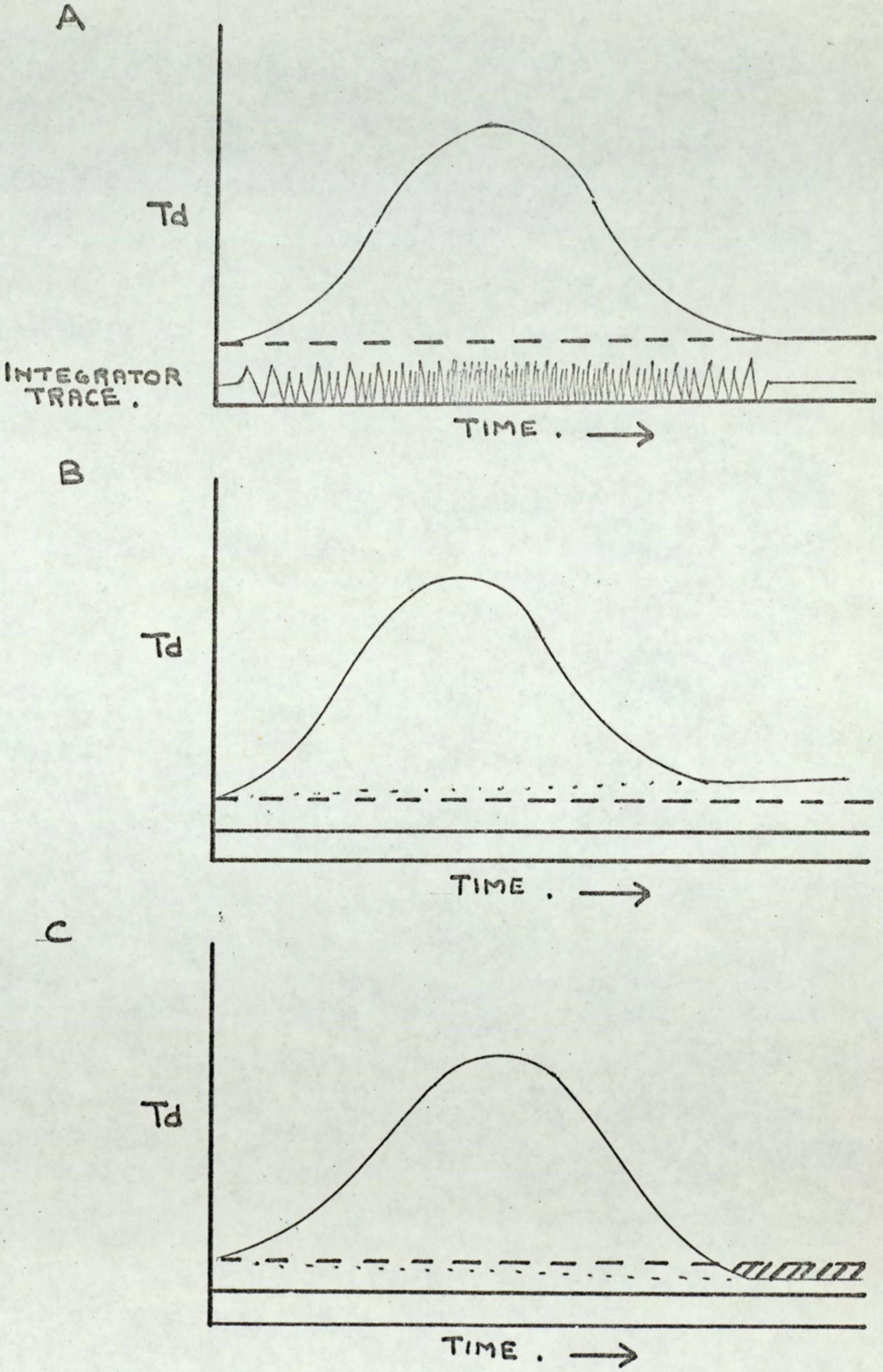
1 inch $\equiv$ 100 area units
1/10 inch $\equiv$ 10 area units

distance between peaks $\equiv$ 600 area units.

(A peak is produced when the pen has crossed the channel six times as shown in Fig. 3.5.A)
Using this system, areas may be estimated with an accuracy of ± 1 unit. A chart speed giving a suitable number of units is selected. The total number of area units from zero time to time t represents the area of the curve up to that time. Such areas are measured at suitable intervals, and used to plot the crystallisation isotherm. (Fig.5.2.)

Ideally the curve obtained is as shown in Fig.3.5A. In practice curves shown in Fig.3.5B or 3.5C may be observed. This baseline drift appears to be related to sample geometry or to the ratio of sample: reference weight, but

FIG 3.5. TYPICAL DSC CRYSTALLISATION TRACES.



cannot always be eliminated. In such cases a correction is made assuming the true curve to have a baseline as shown by the dotted lines. A steady baseline is obtained before and after crystallisation.

Then for Fig. 3.5B.

Baseline drift x = no. counts/inch after crystallisation-
no. counts/inch before crystallisation

Assume the total area A_n up to each inch is to be measured. The baseline drift occurs over a total of D inches.

Then baseline drift/inch = x/D

Let A_1', A_2' A_3' ......A_n' be total areas counted at
1, 2, 3, ...n inches, and
A_1, $A_2 A_3$............A_n be corrected areas counted at
1, 2, 3............n inches.

Then

$A_1 = A_1' - x/D$

$A_2 = A_2' - 2x/D - x/D$ where first term is correction/2inches and second term is is correction necessary as error is cumulative.

$$A_3 = A_3' - 3x/D - (x/D + 2x/D)$$

$$A_n = A_n' - nx/D - \sum_{m=0}^{m=n-1} mx/D \qquad (25)$$

Similar corrections may be made for the case shown in Fig. 3.5.C, when

$$A_n = A_n' + nx/D + \sum_{m=0}^{m=n-1} mx/D \qquad (26)$$

In this case there is an additional difficulty as the integrator counts the area of the shaded region shown, and the peak correction has to be calculated by difference.

Each area measurement is corrected as shown. This is not too tedious if the first correction terms are listed, then added to give the cumulative correction.

DSC has been used to measure crystallisation rates of all the polyesters except 4I which crystallised too slowly.

3.2.2. DSC melting and crystallisation temperatures.

For these measurements the sample was placed on the front raised platform in the DSC cell so that its temperature was recorded directly. An empty aluminium sample pan with lid was used as reference. Samples were melted for 5 minutes at temperatures 20-30°C above the melting temperature, then cooled at 5°C/minute. The crystallisation temperature was recorded, then the sample was heated at 5°C/minute to record the DSC melting temperature. This information was useful in selecting melting and crystallisation conditions for the isothermal measurements, in estimating the degree of supercooling required for crystallisation, and in finding the highest temperature at which crystallisation occurred at the cooling rate used. The latter temperature was important when crystallisation conditions prior to heat of fusion measurements were selected.

5.2.3. Heats of fusion.

The Du Pont DSC cell was used to measure heats of fusion for the polymer samples. Samples of 5-15mg. were weighed accurately on an Oertling six figure balance. The sample was placed on the rear raised platform. An empty aluminium sample pan with lid was used as reference. The adjustment on the DSC accessory plug was used to give a steady baseline.

All polymers were treated in a similar manner. Each sample was crystallised overnight at a temperature for which $t_{\frac{1}{2}}$ was greater than 100 minutes. It was assumed that a high degree of crystallinity would be developed after this treatment. In order to give a steady baseline before melting, the sample was then cooled, if necessary, to the temperature at which the crystallisation rate was observed (section 5.2.2.) to be at a maximum. Any further crystallisation was noted, then the sample was heated at 5°C/minute. The temperature difference due to fusion was recorded on the external T_d recorder. Several inches of baseline were recorded on either side of the transition. The sample was then allowed to cool in the DSC cell through the temperature of maximum crystallisation rate, then the fusion process was repeated.

Pure samples of gallium, indium, tin and lead were used to calibrate the cell so that heats of fusion could be calculated from peak areas. Areas were measured as before using the Disc integrator, and corrected by the difference in area units counted one inch before, and one inch after the transition. This method was subjective in that it relied on selection of the points at which the transition started, and was completed. These points depend on the sensitivity of the recorder used. For this reason the same sensitivity setting ('10') was used for all measurements made. Use of the same sensitivity, and the same correction method throughout should produce results which are at least comparable. For metal samples it was found important to use a single chip of metal; several small samples distributed over the sample pan produced a peak with several shoulders, and an area that was irreproducible.

Variables affecting ΔH, the measured heat of fusion have been related[149] by the equation,

$$\Delta H = \frac{EAS}{MC} \qquad (27)$$

where E is the calibration coefficient

A is the peak area

S is the Y axis sensitivity

M is the sample mass

C is the chart speed of the external recorder.

For this work S and C were kept constant throughout (C was equal to 1 inch/minute) so,

$$E \doteq \frac{M\Delta H}{A} \text{ mcal/area unit} \qquad (27a)$$

where ΔH is the heat of fusion in mcal.mg^{-1}

M is the sample mass in mg.

A calibration plot of E against the observed transition temperature was drawn (Fig.5.20.).

3.3. Microscopy.

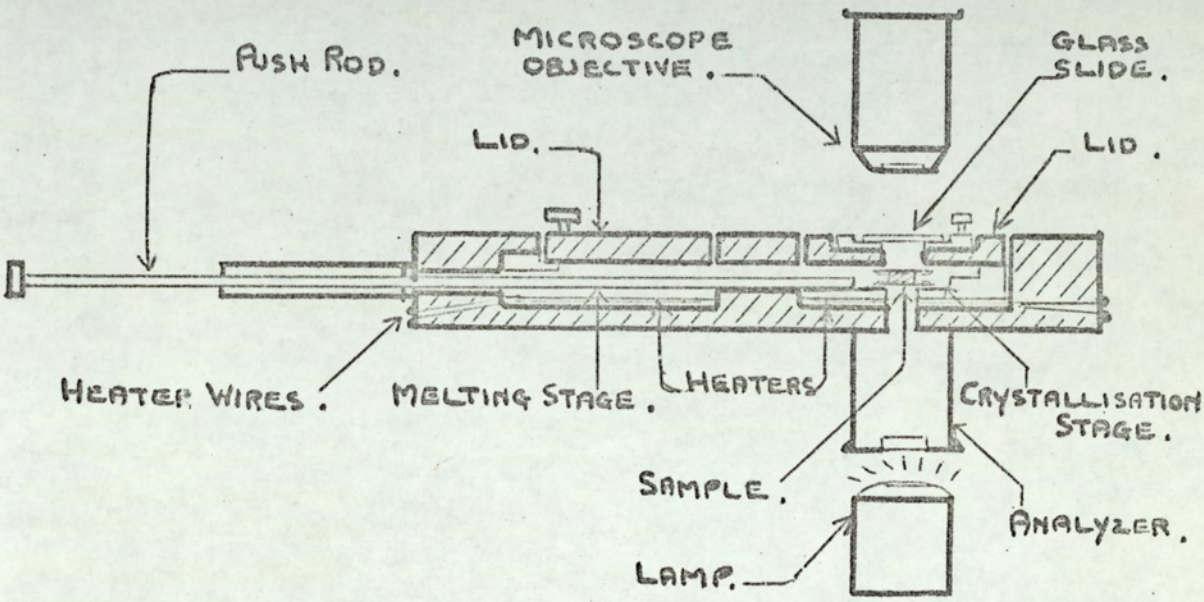
3.3.1. Isothermal microscopy.

Attempts were made to measure isothermal crystallisation rates by optical microscopy. It was found that this technique was not suitable for the polyester samples, but the hot stage microscope was used for spherulite growth measurements.

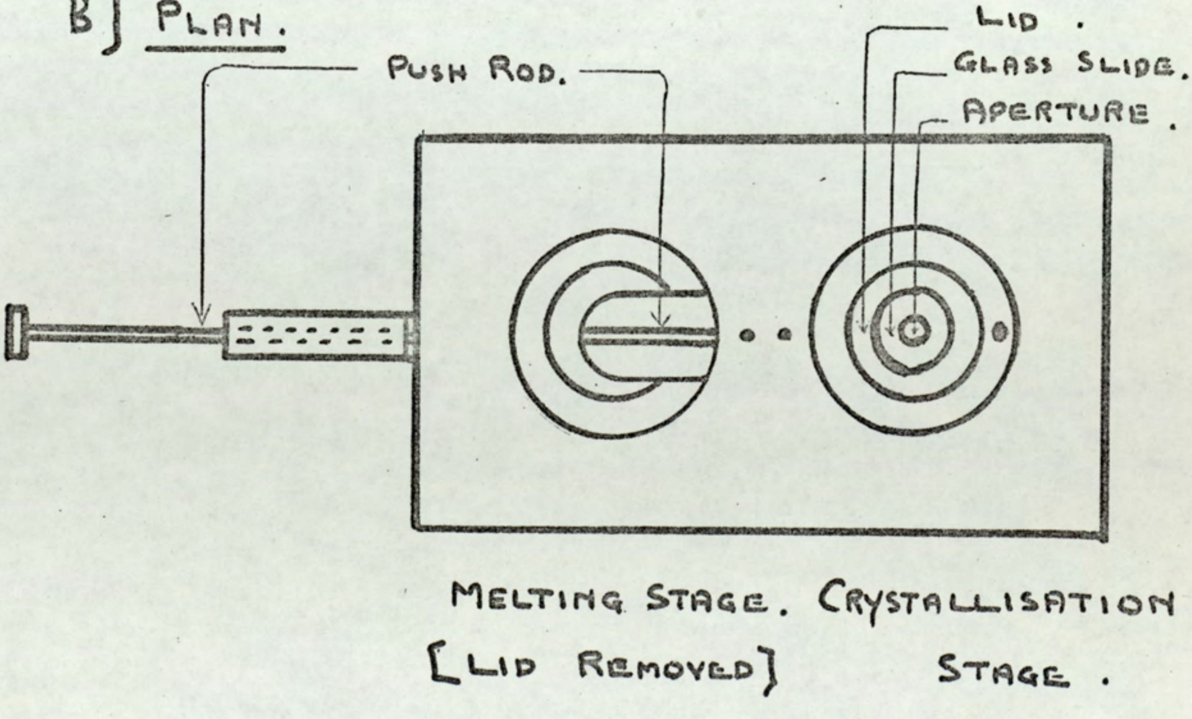
Construction of the hot stage microscope has been described elsewhere[150]. A Swift polarising microscope was fitted with a double hot stage, situated in an asbestos block. The first stage was used for melting the sample, which could then be transferred by means of a push rod to the second stage which was viewed by the microscope. (Fig. 3.6). This stage was viewed from below with a 6 volt lamp which was supplied with a stabilised voltage. The two stages were heated independently by heaters wound on mica discs. The temperature of the melting stage was adjusted using a rotary Regavolt. It was measured using a chromel-alumel thermocouple, and recorded directly by a meter. The temperature of the crystallisation stage was measured using a similar thermocouple and a Pye potentiometer. It was controlled to within $\pm$ 0.2°C by a platinum resistance thermometer which was one arm of a Wheatstone bridge network. The signal from this circuit controlled the operation of a silicon controlled rectifier, which in turn controlled the heater.

FIG 3.6. DOUBLE HOT STAGE MICROSCOPE.

A] CROSS SECTION.



B] PLAN.



For crystallisation studies different accessories could be fitted on to the microscope described. The polymer sample was viewed through crossed polars. A Beck micrometer eyepiece was used to measure spherulite growth rates. This was calibrated by measuring the known spacing of lines on a standard slide in terms of divisions on the micrometer scale. Averaging about a dozen determinations resulted in the relationship,

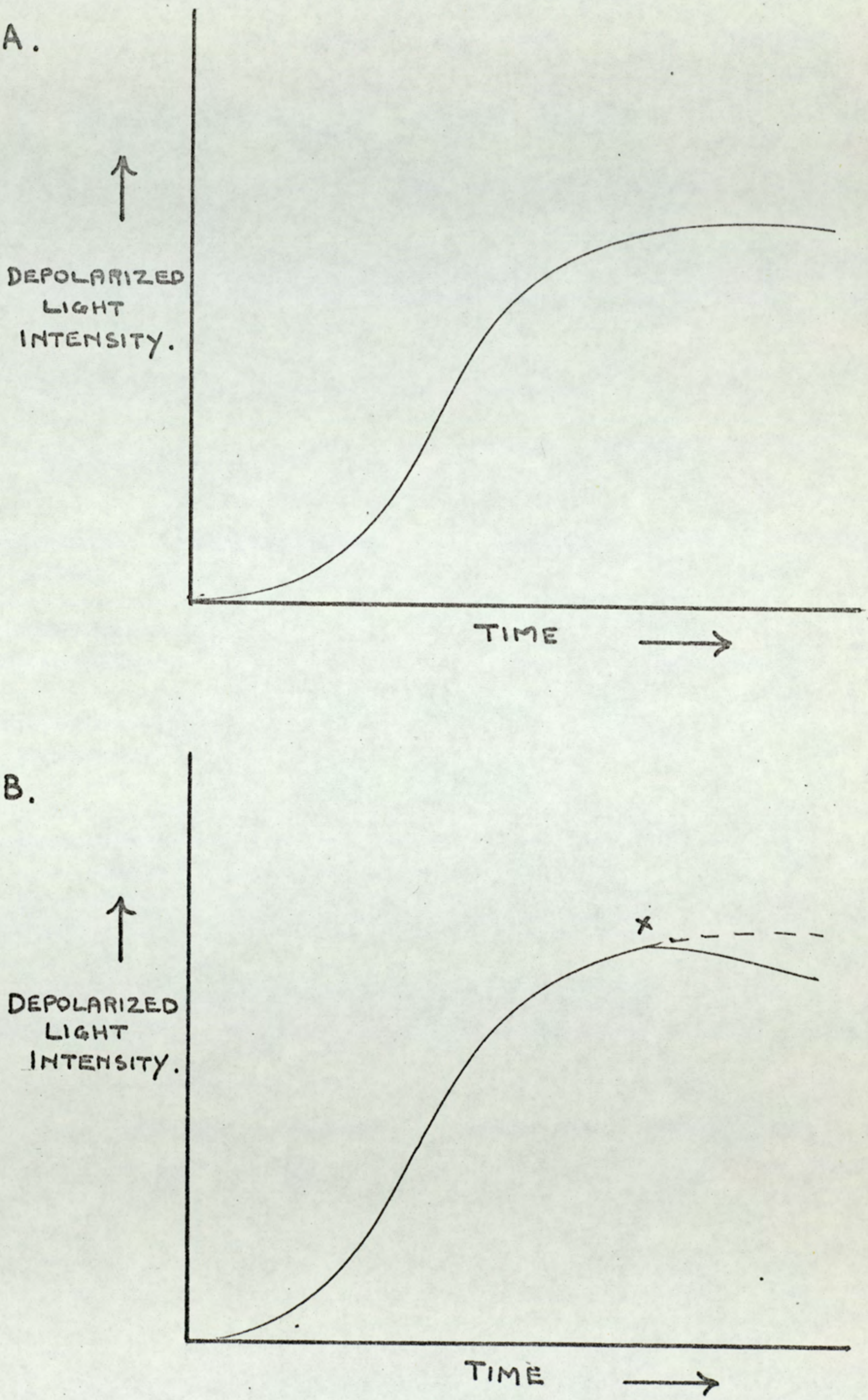
$$1 \text{ division} \equiv 0.1\ \mu$$

Alternatively the measuring eyepiece was replaced by a Beck reflex attachment camera. Kodak Plus-X black and white panchromatic film was used.

For overall crystallisation rate measurement a photocell attachment was used as discussed in section 2.3.2. The voltage corresponding to the depolarised light intensity was recorded on a Bristol's 10mV recorder. A typical crystallisation isotherm obtained by this method is shown in Fig. 3.7A. However for the polyester samples curves were of the form shown in Fig.3.7B, for the reasons explained in section 2.3.2. The inversion of the trace at X, which was more severe in thick samples, or rapidly crystallised samples, made analysis of isotherms impossible beyond the initial stages, Overall crystallisation rates were therefore measured by alternative methods.

To measure spherulite growth rates a small chip of polymer was melted on the melting stage, between two clean, dust free cover slips. (16mm. diameter). Melting conditions

FIG 3.7. TYPICAL CRYSTALLISATION TRACES OBTAINED BY OPTICAL MICROSCOPY.



were determined experimentally for each polymer, but had to be sufficiently stringent to reduce the number of nuclei so that measurable spherulites were obtained instead of a vast number of small spherulites. After melting the sample was transferred by the push rod to the crystallisation stage which was at a suitable temperature. A stop watch was started, and the size of selected spherulites was measured at suitable intervals. Growth rates, obtained from plots of spherulite size against time were measured over the widest possible temperature range for each polymer.

Growth rates were measured for 46, 4T, 5T, and 4I polyesters. In other cases all melting conditions used still resulted in a vast number of tiny birefringent structures.

3.3.2. Programmed microscopy.

A second single hot stage microscope, also described elsewhere[150] was used as an accessory for the Du Pont 900 thermal analyzer through a modified accessory plug. Design of the hot stage was similar, but its temperature was programmed or controlled by the Du Pont 900, and recorded on the X axis of the X-Y recorder. The Y axis recorded the depolarised light intensity of the sample, via a photocell detector similar to that used for the double hot stage microscope. This programmed microscope was used to record optical melting traces for the polymer samples, and to measure their melting temperatures (section 2.2.3).

3.4. X-ray diffraction.

In order to find whether the polymer crystal structure affected crystallisation rate, X-ray diffraction powder type photographs and fibre diagrams were obtained.

3.4.1. Powder photographs.

Precipitated polymer samples were required. Samples 46/1 and 66/2 were already available in this form. The remaining samples were precipitated as follows. A 5% solution was prepared by heating the polymer in nitrobenzene, On cooling slowly to room temperature most of the polymer was precipitated. The precipitate was filtered off under reduced pressure using a number 3 glass sinter, then washed three times with cooled methanol. It was dried overnight in a vacuum oven at about 40°C.

The sample was placed in a thin walled glass capillary which was fixed at the centre of a Phillips pattern 11.46cm. diameter powder camera. Ni filtered Cu K_{α} radiation was provided using a Solus-Schall X-ray generator, with an accelerating voltage of 40KV, and a cathode current of 20mA. Film used was Ilford X-ray film (Industrial G). Exposure times were between $\frac{3}{4}$ hour and 3 hours.

Line spacings on the photographs were measured using a precision micrometer. As the lines were broad, their positions were obtained by taking the average of measurements made at the outer edges.

The line spacing L between each pair of arcs is used to calculate the corresponding interplanar spacing in the sample, as follows.

The Bragg equation is written, for powder type photographs as

$$\lambda = 2d \sin\theta \qquad (28)$$

where λ is the wavelength of the radiation used (1.542 A^{o} for Cu K_{α} radiation)

d is the interplanar spacing

θ is the angle of reflection.

From the geometry of the system, and the radius of camera,

$$\theta = L/4 \qquad (29)$$

where θ is expressed in degrees, and L in mm.

Values of θ are calculated from equation (29) and substituted in equation (28) to obtain d values.

3.4.2. Fibre diagrams.

Sample preparation depended on the melting and crystallisation behaviour of each polymer.

Samples 46/1 and 66/2.

Samples used had not previously been precipitated. Each sample was melted in a groove 5cm. x 1mm. x 1mm. which had been cut in a stainless steel block. The heated block was then cooled rapidly by placing in liquid nitrogen, to avoid the development of a high degree of crystallinity at this stage. The sample was brought to room temperature, then removed from the block as a rod having approximately the above dimensions. The rod was clamped in a Hounsfield tensometer, and drawn at room temperature, at 5% full speed to form a fibre.

Sample 4T/1.

A fibre was drawn out from the molten polymer using a glass rod. It crystallised during drawing, but attempts to obtain a highly drawn fibre were not very successful, due to the rapid crystallisation of the polymer on cooling.

Sample 5T/1.

A sample of polymer was heated in an oven in a 10ml. glass syringe at about 140°C and the melt extruded through the nozzle. The rod of polymer produced was crystallised under tension at about 80°C for several hours. It was heated using a hot air blower.

Sample 6T/1.

Again the polymer was extruded through a syringe, after heating just above the melting temperature. The rod produced was drawn using the tensometer. During the drawing process it was heated to about 80°C.

Sample 4I/1.

On extrusion through the syringe this polymer produced an amorphous rod. This was crystallised under tension by heating at about 80°C for several hours. A highly orientated sample was formed.

The rigid fibres produced were photographed in a Unicam goniometer using an oscillation angle of 15°C. Each fibre was mounted centrally in the camera. Cu K_α radiation was again used, operating conditions being similar to those used for the powder photographs.

Using drawn samples, the z axes of crystallites in the polymer are vertical, so the photographs may be used to obtain the c axis of the unit cell, which is known as the identity period. Reflections from different planes in the crystal are observed in the photograph. These are known as layer lines, and represent cones of reflected rays. With the z axis vertical, reflections are all in phase, and layer lines are produced when,

$$c \sin \phi = m \lambda \qquad (30)$$

where $\phi = (90 - \omega)^{\circ}$

ω is the semi-vertical opening angle of the cone

m is an integer equal to 0, 1, 2, for zero, first, second layer lines.

From the geometry of the camera,

$$\tan \omega = R/S \qquad (31)$$

where R is the radius of the camera (3.00 cm.)

S is the measured distance between two layer lines.

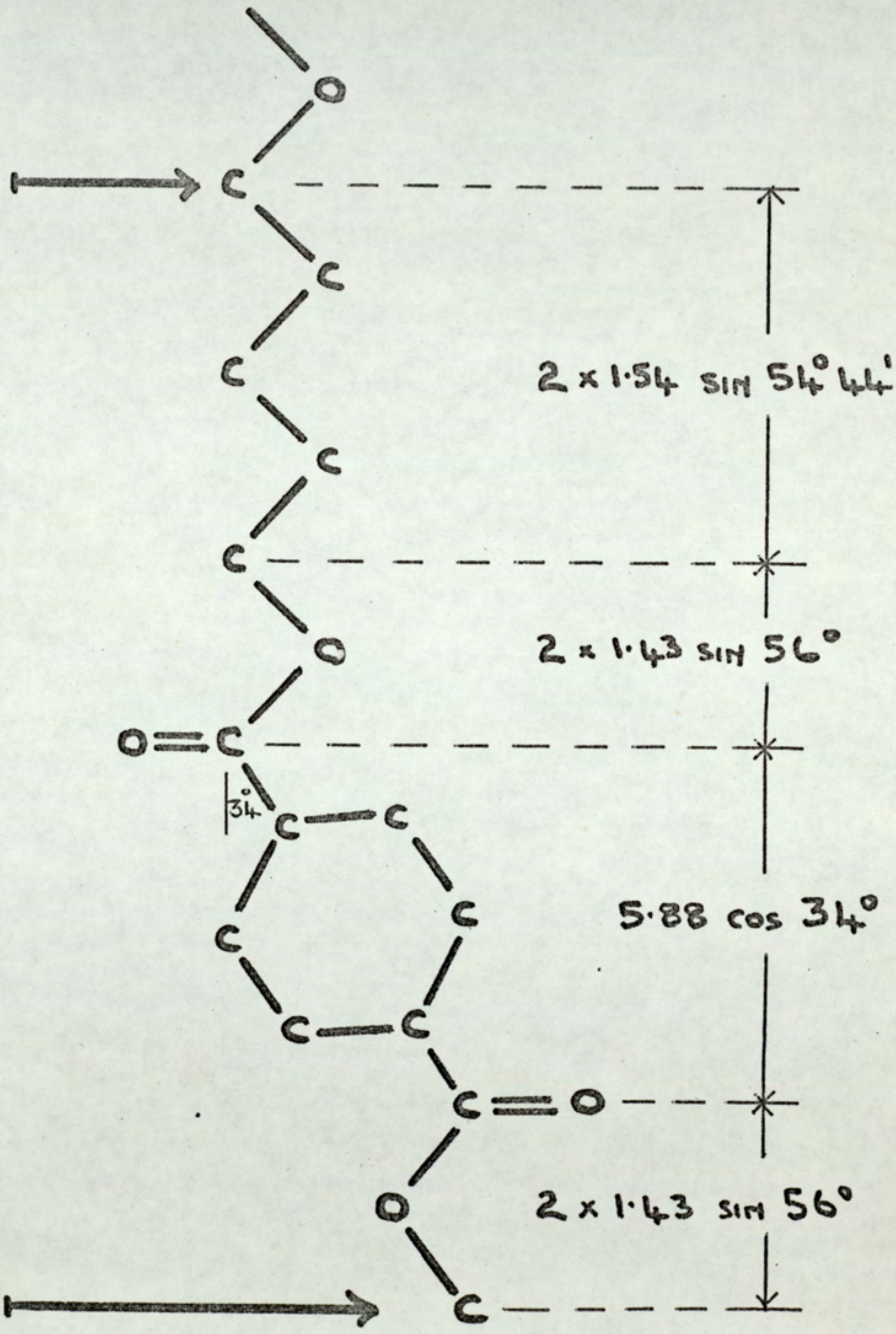
Using equations (30) and (31) the identity period c may be obtained.

c values were compared with the length of a fully extended planar zig zag for each polymer. This length was calculated as shown in Fig. 3.8. Bond lengths and bond angles used are shown in Table 3.2.

Table 3.2. Bond lengths and angles[151].

aliphatic C-C	1.54 A$^{\circ}$
aromatic C-C	1.40 A$^{\circ}$
C-O	1.43 A$^{\circ}$
tetrahedral C<	109°28'
>C=O	112°
O<	112°

FIG 3.8. CALCULATION OF REPEAT UNIT FOR POLYPENTAMETHYLENE - TEREPHTHALATE.



CHAPTER 4.

PROCESSING OF RESULTS.

4.1. Introduction.

Crystallisation half times, $t_{\frac{1}{2}}$, were readily obtained from dilatometry and DSC results. Using dilatometry, crystallisation was observed to continue at a slow rate over a long time period, so it was necessary to estimate h_{∞}, the final height of the mercury column. A plot of h_t against $1/t$ was used for this purpose. The method is demonstrated using some actual results in Fig. 5.7. $t_{\frac{1}{2}}$ was the time at which h_t was equal to $\frac{1}{2}(h_o - h_{\infty})$. h_o, the initial height of the mercury column was obtained directly from the trace of h_t against t.

When DSC was used a time was reached beyond which no further thermal change was recorded. $t_{\frac{1}{2}}$ was the time at which the area under the curve of T_d against t was half the total area on completion of the crystallisation.

$t_{\frac{1}{2}}$ values are useful in comparing rates of crystallisation, particularly as $t_{\frac{1}{2}}$ is not very dependent on the value used for h_{∞}. Also $1/t_{\frac{1}{2}}$ may be substituted in equations of type (9). According to theory a plot of $\log(1/t_{\frac{1}{2}})$ against $T_m{}^2/T(\Delta T)^2$ should be linear. Such plots were drawn for each polymer, initially using the measured melting temperature for T_m. These plots were curved, but if the value used for T_m was increased, straight line graphs were obtained (e.g. Fig. 5.11).

Using spherulite growth rates, instead of $(1/t_{\frac{1}{2}})$, it has been suggested[26] that the melting temperature which yields a straight line when this type of graph is plotted is a reasonable estimate of the thermodynamic melting temperature of the polymer. Spherulite growth rates were obtained for some of the polyesters studied. For sample 4T/1 the same melting temperature gave straight lines when the two types of results were used, indicating that this method may also be suitable for estimating the thermodynamic melting temperature.

To obtain further information concerning crystallisation kinetics, the Avrami equation was used. For dilatometry this is written,

$$\frac{h_t - h_\infty}{h_o - h_\infty} = e^{-kt^n} \qquad (32)$$

A computer program was used to adjust h_∞ between given limits in an attempt to obtain a constant value of n over the greatest proportion of the crystallisation process, according to the technique described by Banks et al[128]. However this method was unsuccessful for the 66 and 4T polyesters which were investigated by dilatometry. Results for these polymers could not be treated in this manner; changing h_∞ did not result in a more consistent value for n.

Subsequently, a different approach was used. On differentiating and rearranging, equation (32) becomes,

$$n = t\frac{dh_t}{dt} \Bigg/ (h_\infty - h_t) \log_e \left[\frac{h_\infty - h_o}{h_\infty - h_t}\right] \qquad (32a)$$

For DSC results, the Avrami equation is written,

$$\frac{A_\infty - A_t}{A_\infty} = e^{-kt^n} \qquad (33)$$

where

$$A_\infty = \int_0^\infty T_d \, dt$$

and

$$A_t = \int_0^t T_d \, dt$$

then

$$n = t \frac{dA_t}{dt} \Big/ (A_\infty - A_t) \log_e \left[\frac{A_\infty}{A_\infty - A_t} \right]$$

or

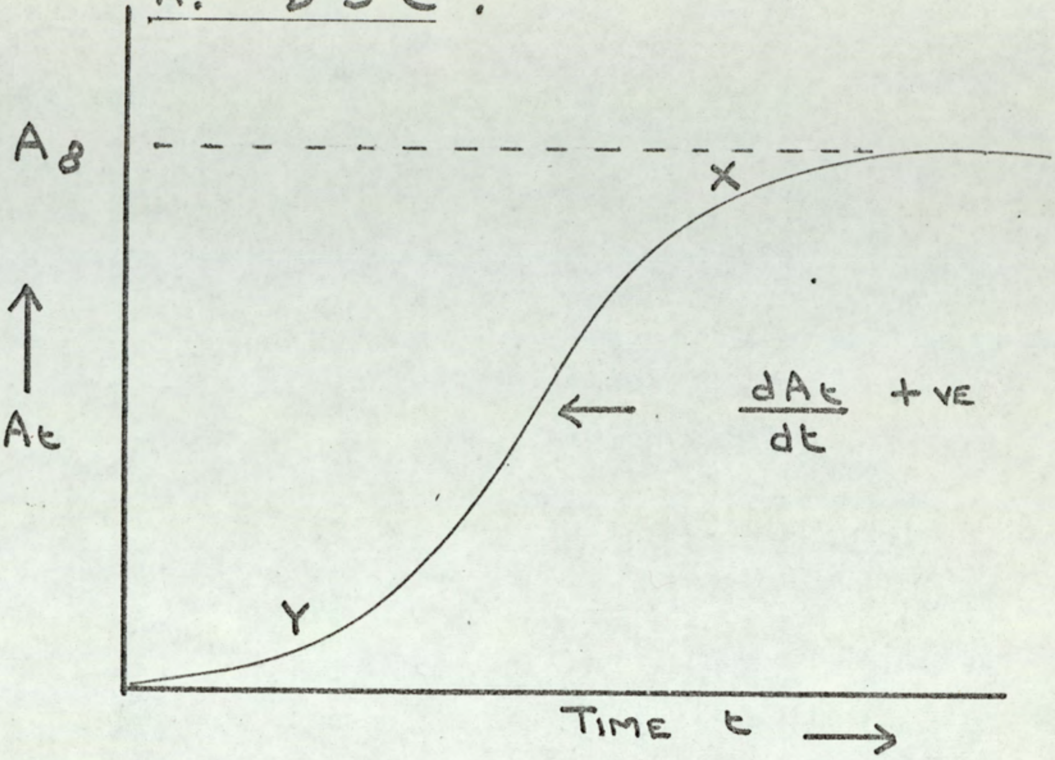
$$n = t \frac{dA_t}{dt} \Big/ (A_\infty - A_t) \log_e \left[\frac{A_\infty - A_0}{A_\infty - A_t} \right] \qquad (33a)$$

The term A_0 is included so that the equations used to analyse results, (32a) and (33a) are similar. In practice, A_0 is always equal to zero. Although the crystallisation isotherms obtained by DSC and dilatometry are similar in shape, they are actually mirror images of one another, through a horizontal plane (Fig. 4.1). The equations compensate for this. In equation (32a), $(h_\infty - h_0)$ and $(h_\infty - h_t)$ are both negative. The first term is larger so the log term is positive. dh_t/dt is negative resulting in a positive value for n. In equation (33a) A_∞, $(A_\infty - A_t)$ and dA_t/dt are all positive, so again n will have a positive sign. Thus the same equation can be used to analyse both types of crystallisation isotherm.

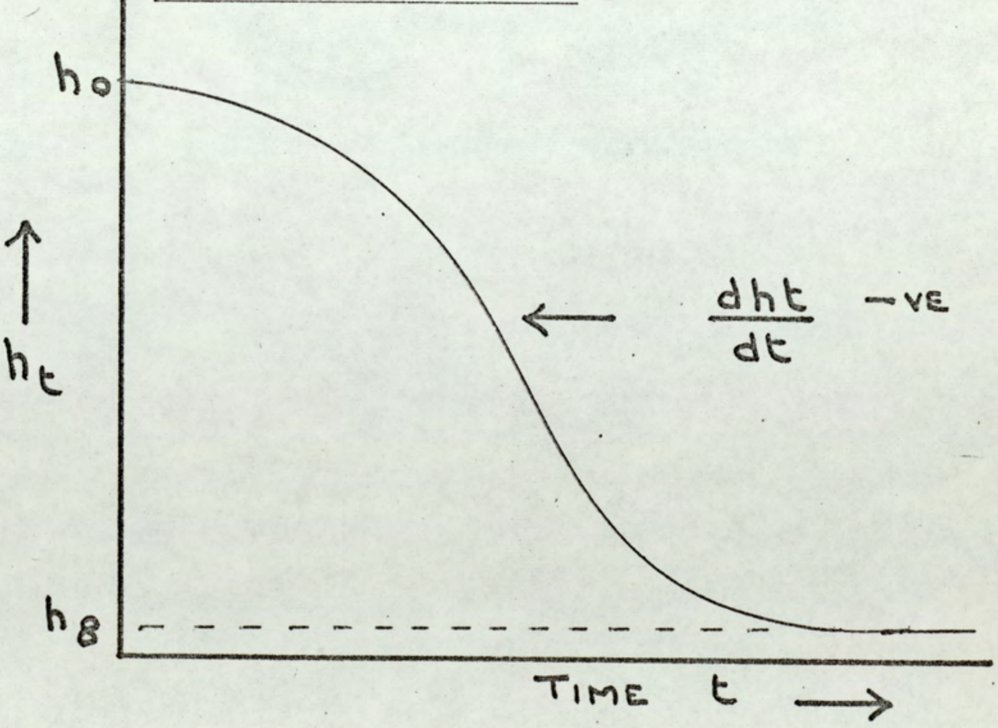
n values were calculated, using a computer program for each value of h_t or A_t. Different h_∞ values could be put

FIG 4.1. CRYSTALLISATION ISOTHERMS.

A. DSC.



B. DILATOMETRY.



into the program, so that the effect of changing h_∞ could be observed. The program is written in terms of 'A' values, but applies equally to dilatometry results throughout. dA_t/dt was obtained at time t_2 from $(A_{t_3} - A_{t_1})/(t_3 - t_1)$ where A_{t_1}, A_{t_2}, A_{t_3} were adjacent measurements made at times t_1, t_2, and t_3. Therefore the larger the number of measurements made, the greater the accuracy in this term, particularly where the slope of the curve is changing rapidly. (i.e. at X and Y in Fig. 4.1.).

The computed n values were listed. The constancy of n was assessed as follows. An arbitrary error limit in n of ± 0.2 was allowed. If x n values had been computed, the (x/2) th value was used as standard. Working outwards from this standard in both directions, each n was compared with its value, and listed as a selected n value if it was within the fixed limits. The process was repeated in each direction, until two adjacent n values were outside the limit. The average of the selected n values was calculated, and used to obtain the crystallisation rate constant K from equation (5). A value of $t_{\frac{1}{2}}$ was put into the program for substituting in this equation. From the last selected n, the % crystallisation which fitted to an Avrami equation with a constant n was calculated. This figure was only approximate, depending on the frequency of values calculated in this region. (A value was always obtained for K and the % crystallisation, but was only meaningful if n was constant for the major part of the crystallisation. This was determined by inspection). If isolated n values were obtained, which were outside the limits, these were printed as zero in the list of selected n values, and were not included in the average n.

The print out of the program included details such as melt temperature and time, and crystallisation temperature. The program was useful in finding the effect of variables such as h_∞. It demonstrated where crystallisation kinetics were governed by an Avrami type equation with a constant n. It also calculated $\log_e (1/\theta)$ and $\log_{10} t$ for standard Avrami plots. Such plots were far less sensitive in assessing the constancy of n, but were useful in showing graphically where deviations occurred.

The program shown below was written in Fortran and run on an ICL 1900 computer. It is followed by a typical set of results obtained for polyethylene terephthalate using DSC. (Q represents θ. The remaining symbols have already been defined, or are explained in the program.)

4.2. COMPUTER PROGRAM.

```
          MASTER
C         POLYMER CRYSTALLISATION KINETICS AVRAMI ANALYSIS
C         SOLVE FOR EITHER A OR H
C         PROGRAM A
C         ISNO IS SAMPLE NUMBER
C         N IS THE NUMBER OF DATA POINTS
C         NI IS THE NUMBER OF A INFINITY VALUES TO BE USED
C         M TEMP IS THE MELTING TEMPERATURE IN DEGREES C
C         M TIME IS THE MELTING TIME IN MINUTES
C         ACR IS THE CRYSTALLISATION TEMPERATURE IN DEGREES C
C         T HALF IS HALF LIFE TIME
C         ATO IS THE VALUE OF A OR H AT ZERO TIME
C         ATI IS THE VALUE OF A OR H AT TIME INFINITY
C         III IS ONE FOR A AND TWO FOR H
          DIMENSION AT (100), T(100), ATI(10),AN(100)
C         O IS THE A OR H VALUE AT ZERO TIME
          COMMON MO, KK,S,Q,R,TT,B,L,K,IK,SN,RS,M,CR,BN,KJ,
          LL,NN
     999  READ(1,900)III,ISNO,N,NI,M TEMP, MTIME,ACR,T HALF,
          ATO
          READ(1,910) (T(J),AT(J),J=1,N)
          READ(1,920) (ATI(JJ),JJ=1,NI)
          DO 360 JJ=1,NI
          WRITE(2,800)
          WRITE(2,810)ISNO,M TEMP, M TIME, ACR,N,NI,ATI(JJ),
          ATO
          WRITE(2,850)
          IF(III-2)15,16,16
      15  WRITE(2,860)
          GO TO 875
      16  WRITE(2,865)
```

```
875    MA=N-1
       DO  10,J=2,MA
       B=ATI(JJ)-AT(J)
       IF(ABS(B)-,001)202,917,917
917    K=J+1
       KK=J-1
       S=(AT(K)-AT(KK))/(T(K)-T(KK))
       IF(ABS(S)-,001)202,834,834
834    Q=B/(ATI(JJ)-ATO)
       R=ALOG(1.0/Q)
       IF(ABS(R)-,001)202,868,868
868    AN(J)=(T(J)*S)/(B*R)
       TT=A LOG(T(J))/A LOG(10.0)
       GO TO 404
202    B=0.0
       TT=0.0
       R=0.0
       AN(J)=0.0
       Q=0.0
404    WRITE (2,870)T(J),AT(J),B,Q,TT,R,AN(J)
 10    CONTINUE
       J=N/2
       MO=0
555    IF(AN(J)-4,0)115,115,200
200    MO=MO+1
       J=J+1
       IF(MO-1)555,555,500
 500   J=N/2
       MO=0
 510   J=J-1
```

```
      IF(AN(J)-4,0)115,115,520
520   MO=MO+1
      IF(MO-1)510,510,~~510~~,550
550   WRITE(2,880)ATI(JJ)
      GO TO 360
115   IK=J-1
      NN=IK
      LL=J
      L=0
      SN=AN(J)
      RS=1.0
      DO 250,M=1,IK
      K=J-N
      IF(L-2)33,22,22
33    IF(ABS(AN(J)-AN(K))-.2)40,40,30
40    L=0
      NN=K
      RS=RS+1.0
      SN=SN+AN(K)
      GO TO 250
30    L=L+1
22    AN(K)=0.0
250   CONTINUE
      L=0
      II=J
      DO 350,M=1,II
      K=J+M
      IF(L-2)44,66,66
44    IF(ABS(AN(J)-AN(K))-.20)400,400,300
400   L=0
```

```
      LL = K
      RS=RS+1.0
      SN=SN+AN(K)
      GO TO 350
300   L=L+1
 66   AN(K)=0.0
350   CONTINUE
      WRITE (2,890)
      IF(III-2)25,26,26
 25   WRITE (2,700)
      GO TO 707
 26   WRITE (2,747)
707   WRITE(2,710) (T(K),AT(K),AN(K),K=NN,LL)
      RN=SN/RS
      AK =(A LOG(2.0))/(T HALF**BN)
      CR=((ATO-AT(LL))*100.0)/ATO-ATI(JJ))
      WRITE (2,750)BN,CR,AK
360   CONTINUE
      GO TO 999
800   FORMAT(1H1,////,36X,50H POLYMER CRYSTALLISATION
      KINETICS, AVRAMI ANALYSIS)
810   FORMAT(//,10X,11H SAMPLE NO I6,//,10X,11H MELT TEMP
      I6,//,10X,11H MELT TIME I6,//,10X,12H CRYST TEMP
      F10.3,//,10X,3H N I6,//,10X,16H INFINITY VALUES I6,
      //,LOX,16H INFINITY VALUE F10.3,//.10X, 6H ATO F10.3)
850  FORMAT (////,42X,17H COMPUTED RESULTS)
860  FORMAT(//,18X,2H T,10X, 2H A,8X,6H ATI-A,10X,2H
     Q,7X,6H LOG T,8X,10HN LOG(1/Q),10X,2H N)
865   FORMAT(//,18X,2H T,10X,2H H,8X,6H ATI-H,10X,2H
      Q,7X,6H LOG T,8X,10 H N LOG(1/Q),10X,2H N)
870   FORMAT(/,13X,F10,3,2(1X,F10.3),4X,F10.3,1X,F10.5,6X,
      F10.5, 5X,F10.3)
880   FORMAT(////////,10X,33H N VALUES GREATER THAN 4
```

```
     FOR ATI F10.3)
890  FORMAT(////,40X,38H  SELECTED RESULTS FOR LIMITING
     N VALUE)
700  FORMAT(////,40X,2H T,20X,2H A,20X,2H N)
747  FORMAT(////,40X,2H T,20X, 2H H,20X,2H N)
710  FORMAT(/,34X,F10.3,10X,F12.3,11X,F10.3)
750  FORMAT(////,10X,11H AVERAGE N F10.3,//,10X,32H
     AVRAMI CRYSTALLISATION PERCENT F10.3,//,10X,12H
     RATE CONST F10.7)
900  FORMAT(610,3F0,0)
910  FORMAT(2F0.0)
920  FORMAT(F0.0)
     STOP
     END
```

4.3. PRINT OUT OF RESULTS (OBTAINED FOR POLYETHYLENE TEREPTHALATE CRYSTALLISED AT 230.2°C)

POLYMER CRYSTALLISATION KINETICS, AVRAMI ANALYSIS

```
SAMPLE NO 3062

MELT TEMP  295

MELT TIME   20

CRYST TEMP 230.200

 N     19

INFINITY VALUES  1

INFINITY VALUE   31650.000

ATO   0.000
```

COMPUTED RESULTS.

T	A	ATI-A	Q	LOG T	NLOG(1/Q)	N
2.900	1550.000	30100.000	0.951	0.46240	0.05021	2.067
4.900	4330.000	27320.000	0.863	0.69020	0.14712	1.869
5.900	6150.000	25500.000	0.806	0.77085	0.21606	1.804
6.900	7700.000	23950.000	0.757	0.83885	0.27877	1.834
7.900	9700.000	21950.000	0.694	0.89763	0.36597	1.844
8.900	11450.000	20200.000	0.638	0.94939	0.44906	1.848
10.900	15350.000	16300.000	0.515	1.03743	0.66357	1.978
12.900	19300.000	12350.000	0.390	1.11059	0.94108	2.039
14.900	22700.000	8950.000	0.283	1.17319	1.26308	2.030
16.900	25460.000	6190.000	0.196	1.22789	1.63180	2.020
18.900	27530.000	4120.000	0.130	1.27646	2.03888	1.980
20.900	28980.000	2670.000	0.084	1.32015	2.47266	1.955
22.900	30000.000	1650.000	0.052	1.35984	2.95396	1.985

COMPUTOR RESULTS (CONT.)

T	A	ATI-A	Q	LOG T	NLOG(1/Q)	N
24.900	30670.000	980.000	0.031	1.39620	3.47494	1.865
26.900	31020.000	630.000	0.020	1.42975	3.91677	1.635
28.900	31270.000	380.000	0.012	1.46090	4.42232	1.490
32.900	31540.000	110.000	0.003	1.51720	5.66201	2.509

SELECTED RESULTS FOR LIMITING N VALUE.

T	A	N
7.900	9700.000	1.844
8.900	11450.000	1.848
10.900	15350.000	1.978
12.900	19300.000	2.039
14.900	22700.000	2.030
16.900	25460.000	2.020
18.900	27530.000	1.980
20.900	28980.000	1.955
22.900	30000.000	1.985
24.900	30670.000	1.865

AVERAGE N 1.954

AVRAMI CRYSTALLISATION PERCENT 96.904

RATE CONST 0.0063913

4.4. Discussion of results. (obtained for polyethylene terephthalate)

An average n of 1.9, constant within the specified limits for 97% of the crystallisation was reported. To consider the validity of this result computed and selected n values were compared. The standard n was 2.039, so n values between 1.839 and 2.239 were allowed. From the operation of the program, the first selected n was that calculated at 7.9 minutes from the start of crystallisation. The two previous values were outside the limit, so the program stopped. However since errors are magnified at the start of crystallisation, and the first two n values listed were actually within the limits, it was reasonable to assume that the n value of 1.9 does apply for 97% of the crystallisation. In such a case it is meaningful to quote the crystallisation rate constant calculated, and consider that the crystallisation is governed by an Avrami equation with n close to 2.

CHAPTER 5.

RESULTS.

5.1. Rates of crystallisation and spherulite growth.

5.1.1. Polytetramethylene adipate.

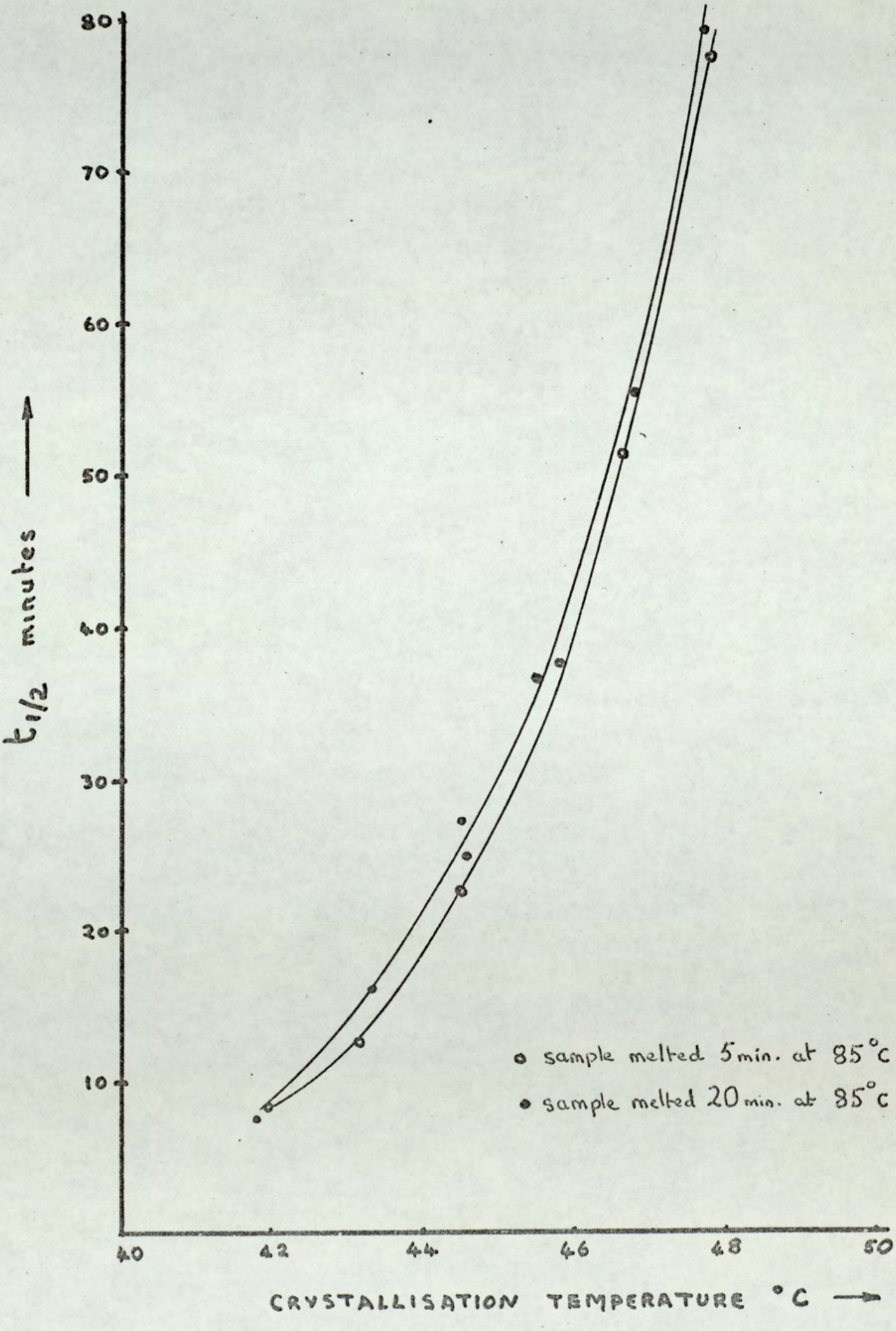
For this polymer overall crystallisation rates, measured using the Du Pont DSC cell are shown in Fig.5.1. Rates were measured after melting samples for 5 minutes and also for 20 minutes at 85°C. (i.e. about 25°C above the observed melting temperature). Increased melting time only produced a small decrease in rate, scarcely distinguishable from experimental scatter. It was assumed that further increase in melting time would not significantly change the rate, so crystallisation isotherms after melting samples for 20 minutes will be used in the subsequent discussion. The rate was not changed very significantly if the melt temperature was increased to 95°C, although in thin films a reduction in the nucleation density was observed under these conditions.

At the crystallisation temperatures used (41-48°C) temperature control of the DSC cell was ± 0.1°C, producing good crystallisation traces of the type shown in Fig. 5.2. For this polymer, t_{max}, the time at which T_d was at a maximum was approximately equal to $t_{\frac{1}{2}}$.

Sample weights used were 10-15 mg. The peak height decreased with decreasing crystallisation rate (increasing temperature), as the heat of crystallisation was extended over a longer time base. The recorder sensitivity was increased. A corresponding increase in noise level occurred,

FIG. 5.1. CRYSTALLISATION HALF TIMES FOR POLYESTER 46/1.

-measured using DSC.



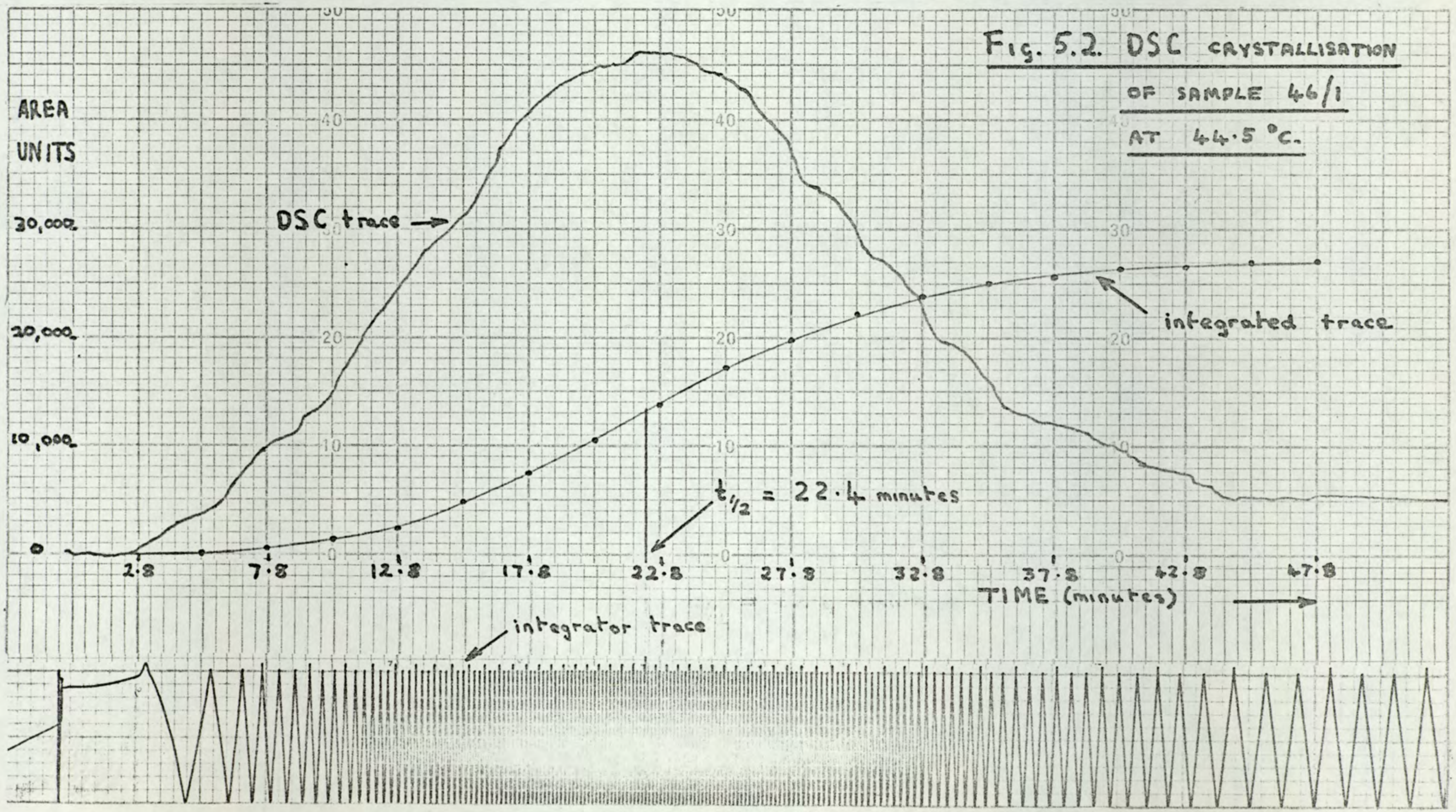


Fig. 5.2. DSC CRYSTALLISATION OF SAMPLE 46/1 AT 44·5 °C.

but was not very serious for samples which crystallised below 200°C.

Providing that the melt temperature was increased spherulite growth rates could be measured at crystallisation temperatures of 46-51°C. Using a melt time of 20 minutes spherulite growth rates were independent of melt temperature within the range 95-105°C. Lower melt temperatures resulted in a high nucleation density, making growth measurements impossible. This situation was also observed if lower crystallisation temperatures were used. Plots of spherulite growth rate against time were linear, and spherulites appeared to be initiated at zero time. Spherulites formed were fibrous in appearance. Like all the polyesters studied, they appeared coloured through a polarising microscope.

Crystallisation data for polytetramethylene adipate are collected in Table 5.1.

For this polymer crystallisation results approximated closely to an Avrami type equation with a constant but fractional value of n applying to a large % of the process (Fig. 5.3.). Average n values at each temperature, together with the % crystallisation for which they apply, and the overall rate constants are shown in Table 5.2. This information was calculated using the computer program described in Chapter 4. The variation in n results in some scatter in K. Since no systematic change in n was observed, the average of those obtained at different temperatures (3.0) was used to calculate the corrected K values shown in the fourth column.

Table 5.1. Crystallisation data for sample 46/1.

$T_m = 60^oC$ $T_m^* = 70^oC$

T^oC	ΔT^oC	$\Delta T^{*o}C$	$t_{\frac{1}{2}}$ min.	$1/t_{\frac{1}{2}}$ min.$^{-1}$	G μ/min.	melt time min.	melt temp. ^{o}C.
41.8	18.2	28.2	7.4	0.135	-	20	82
43.3	16.7	26.7	15.9	0.063	-	20	82
44.5	15.5	25.5	26.9	0.037	-	20	82
44.6	15.4	25.4	24.5	0.041	-	20	82
45.5	14.5	24.5	36.6	0.027	-	20	82
46.8	13.2	23.2	55.2	0.018	-	20	82
47.7	12.3	22.3	78.9	0.013	-	20	82
46.8	13.2	23.2	-	-	1.00	20	95
47.2	12.8	22.8	-	-	0.80	20	95
48.2	11.8	21.8	-	-	0.62	20	95
48.7	11.3	21.3	-	-	0.51	20	95
49.7	10.3	20.3	-	-	0.30	20	95
51.0	9.0	19.0	-	-	0.18	20	95

Table 5.1. Cont.

Note $\Delta T = T_m - T$ $\Delta T^* = T_m^* - T$

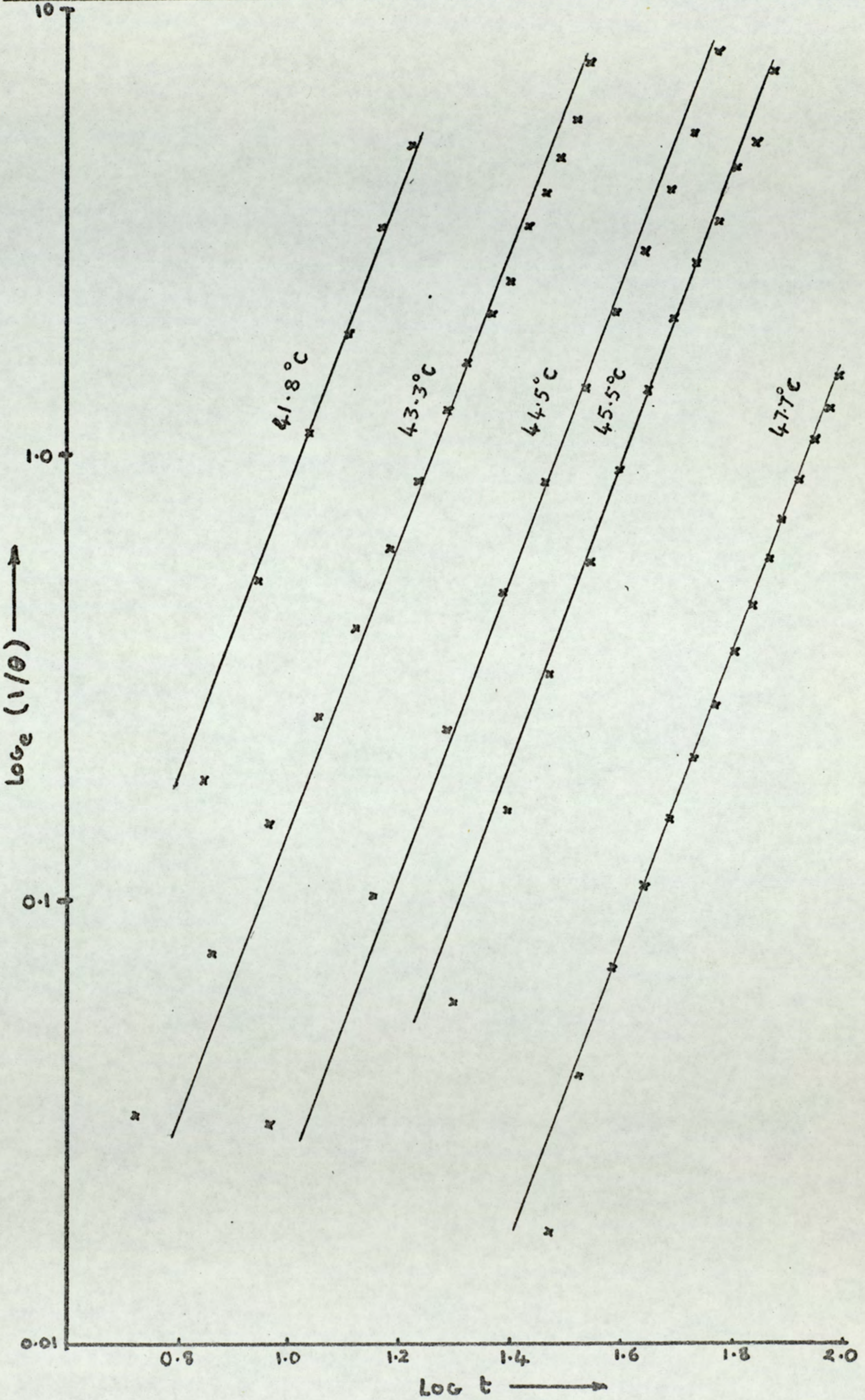
where T_m is the measured melting temperature.

T_m^* is the estimated melting temperature (section 4.1).

Table 5.2. Kinetic analysis for sample 46/1.

T^oC	K	n	K(corrected)	%cryst^n with const. n.
41.8	1.19×10^{-3}	3.2	1.71×10^{-3}	85
43.3	2.59×10^{-4}	2.8	1.73×10^{-4}	81
44.5	4.61×10^{-5}	2.9	3.56×10^{-5}	95
44.6	1.22×10^{-4}	2.7	4.72×10^{-5}	70
45.5	2.70×10^{-6}	3.5	1.35×10^{-5}	87
46.8	1.57×10^{-5}	2.6	4.12×10^{-6}	77
47.7	4×10^{-7}	3.3	1.41×10^{-6}	94

FIG. 5.3. AVRAMI PLOTS FOR POLYESTER 4.6/1



5.1.2. Polyhexamethylene adipate.

Sample 66/1 was studied by DSC and dilatometry in order to compare the two methods; sample 66/2 was studied by DSC. The crystallisation behaviour of the latter sample will be considered first. $t_{\frac{1}{2}}$ values are shown in Figure 5.4. An increased melting time at 82°C resulted in a decreased crystallisation rate. Standard melting times used were 20 minutes at 82°C. An increase in the melting temperature up to 142°C did not significantly change the crystallisation rate. Rates measured within a small temperature range (51.3-51.7°C) on samples melted for 5 minutes increase with decreasing crystallisation temperature. (Fig.5.4.). This indicates the accuracy of the temperature control at temperatures of about 50°C.

Crystallisation rates were measurable over a temperature range of only 4°C indicating a high temperature coefficient of crystallisation for this polymer. From the DSC traces obtained it was found that $t_{\frac{1}{2}} > t_{max}$.

For the samples of polyhexamethylene adipate prepared it was not possible to measure spherulite growth rates, even when melt temperatures up to 200°C and melt times up to 16 hours were used in conjunction with high crystallisation temperatures (51-52°C). In all cases the nucleation density was very high, producing a very large number of very small birefringent structures, resulting in an overall granular appearance. DSC results for samples initially melted at 82°C for 20 minutes are shown in Table 5.3.

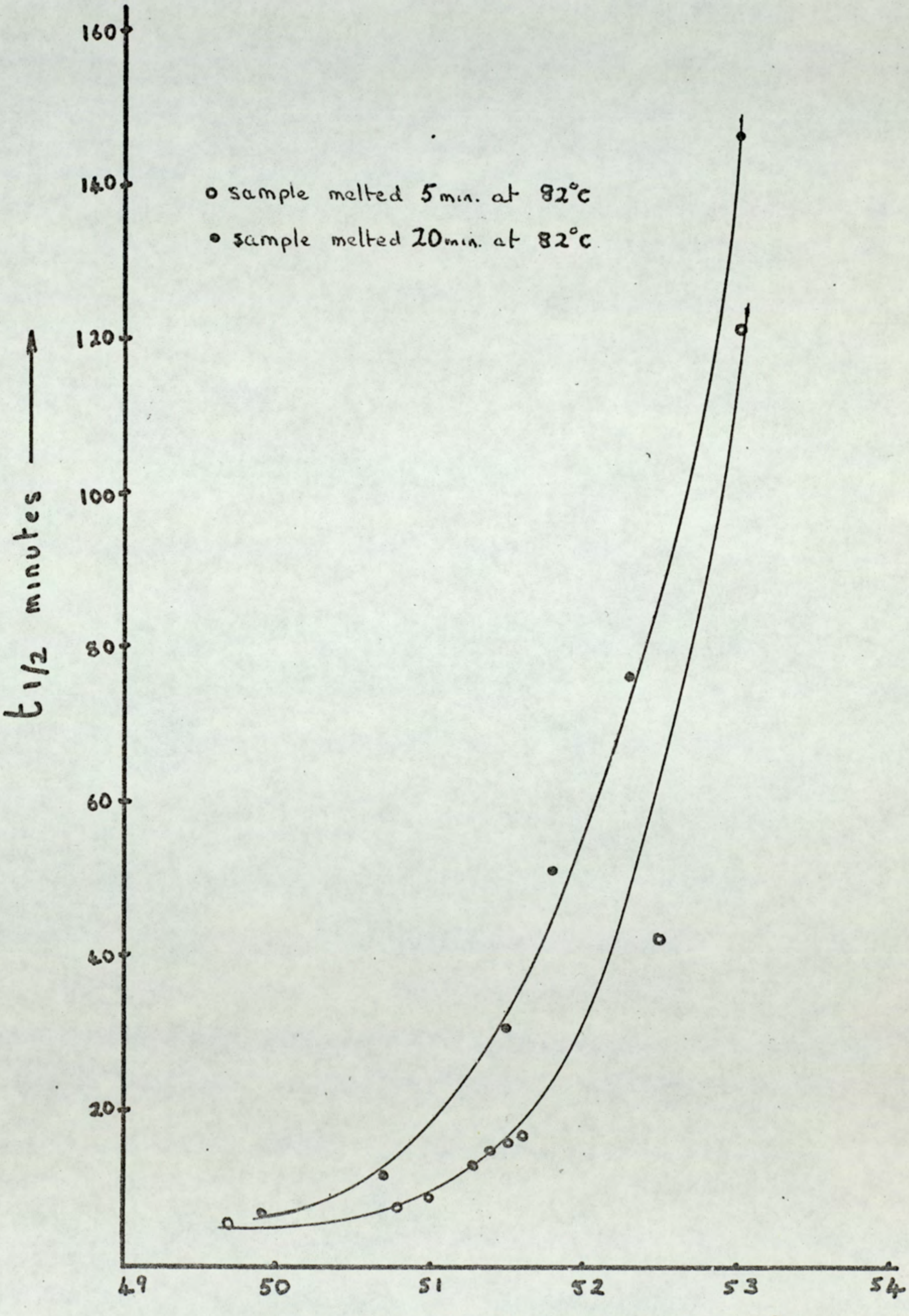
Table 5.3. Crystallisation data for sample 66/2.

$T_m = 61^{\circ}C$ $T_m^{*} = 65^{\circ}C$.

$T^{\circ}C$	$\Delta T^{\circ}C$	$\Delta T^{*\circ}C$	$t_{\frac{1}{2}}$min.	$1/t_{\frac{1}{2}}\text{min}^{-1}$.
49.9	11.1	15.1	6.4	0.156
50.7	10.3	14.3	11.8	0.085
51.5	9.5	13.5	30.9	0.032
51.8	9.2	13.2	50.6	0.020
52.3	8.7	12.7	68.2	0.015
53.0	8.0	12.0	147.0	0.007

FIG. 5.4. CRYSTALLISATION HALF TIMES FOR POLYESTER 66/2.

-measured using DSC.



Except for the fastest rate, when the entire process corresponds to an Avrami equation with n = 2, sample 66/2 does not behave according to this theory. Although standard log-log Avrami plots may appear linear for part of the process, study of individual values obtained from the computer program indicate that n actually decreases continuously. During later stages of the crystallisation the slope of the plots approaches 2. (Fig.5.5.). The slope of the Avrami plots increases as the crystallisation temperature is increased.

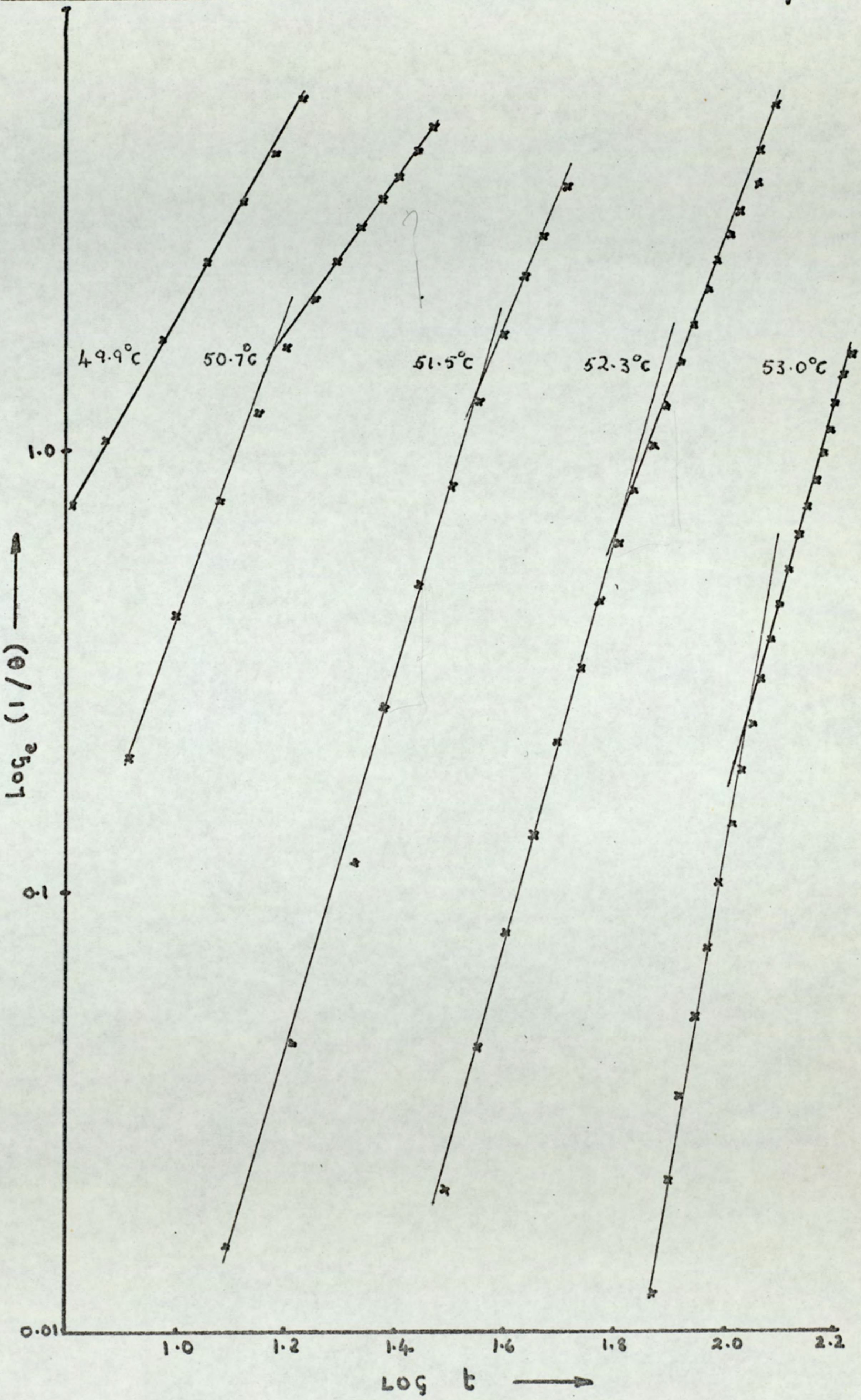
$t_{\frac{1}{2}}$ values obtained by DSC and dilatometry for sample 66/1 are shown in Table 5.4 and Figure 5.6. For these experiments samples were melted for 20 minutes at 75°C.

Each dilatometry experiment was repeated twice. The sample used (approximately 0.17g) was dried for 3 hours at 70°C and 0.005mm.Hg before distilling mercury into the dilatometer. The sample was estimated to be at the crystallisation temperature 2 minutes after the dilatometer was placed in the crystallisation bath.

Table 5.4. Crystallisation data for sample 66/1.

Dilatometry.		DSC	
T°C	$t_{\frac{1}{2}}$min.	T°C	$t_{\frac{1}{2}}$ min.
49.0	2.8	50.0	16.6
50.0	7.2	50.7	31.0
51.0	21.8	51.2	45.4
52.0	63.4	51.5	87.3

FIG. 5.5. AVRAMI PLOTS FOR POLYESTER 66/2.

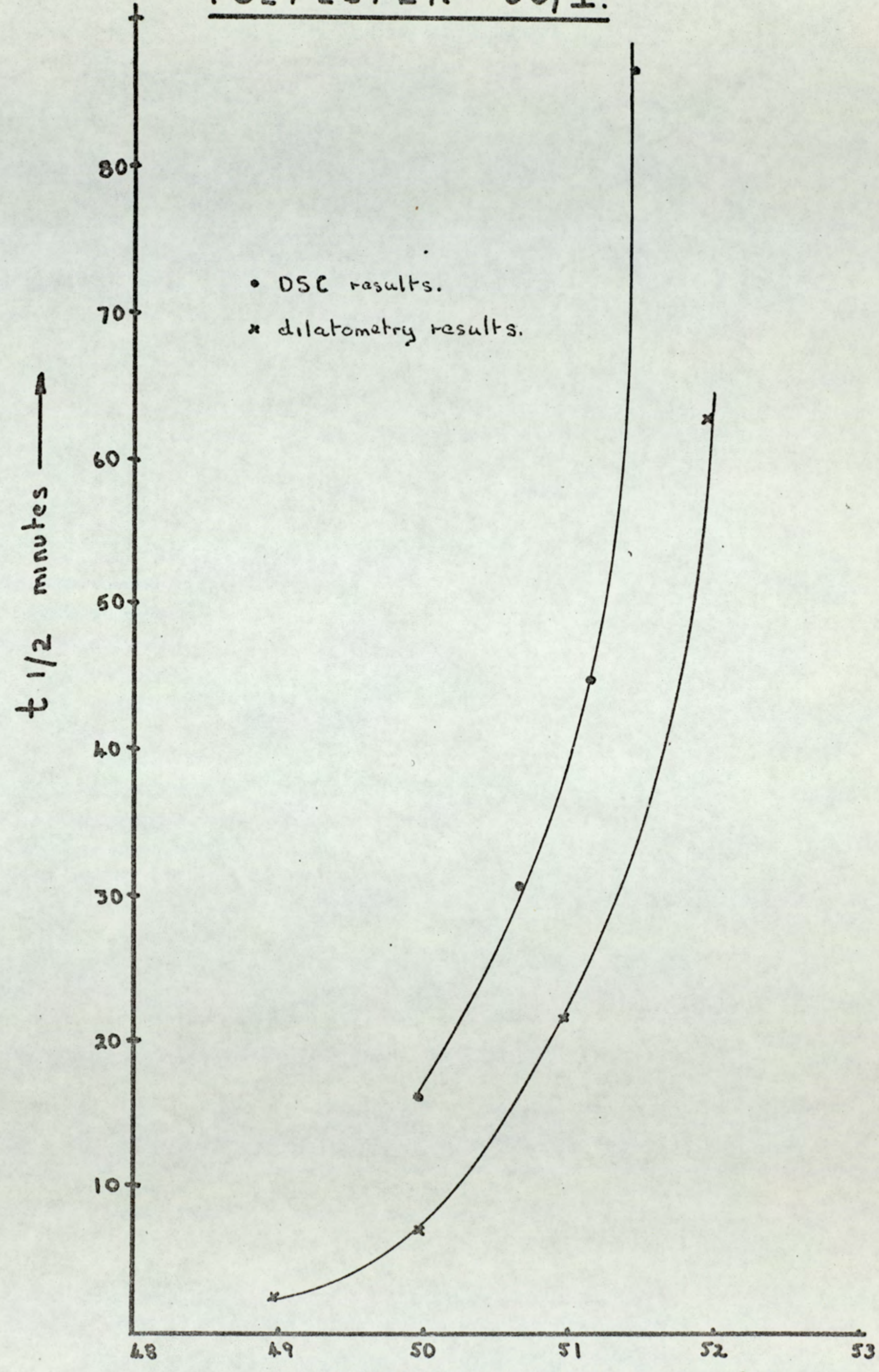


The lower molecular weight sample of 66 polyester (66/1) crystallises more slowly than the higher molecular weight sample (66/2). From Figure 5.6 $t_{\frac{1}{2}}$ values obtained by the two techniques, can be considered comparable as the difference could be due to a difference of 0.7°C in the actual polymer temperature in the two cases. This amount of error is possible as an oil bath temperature measured by a mercury in glass thermometer is being compared with that of a constantan disc using a chromel-alumel thermocouple. The latter measurement is likely to be more accurate as the sensing device is closer to the polymer. The high temperature coefficient of crystallisation observed for polyhexamethylene adipate makes direct comparison of $t_{\frac{1}{2}}$ values difficult. The removal of moisture from the sample used for dilatometry might be expected to reduce the crystallisation rate. However this was not observed.

Kinetic data obtained by the two methods was found to be different. Considering DSC measurements, only the lowest temperature crystallisations ($<51^\circ C$) fitted to an Avrami equation, with $n = 2$ for 96% of the process. At higher temperatures deviations occurred as for sample 66/2, the n value decreasing.

Dilatometry results did not approximate to an Avrami equation in any way, 'n' values being initially greater than 4, and decreasing throughout the process. This was not merely due to selection of the correct value of h_{∞}, different possible values being used in the calculations

FIG. 5.6. CRYSTALLISATION HALF TIMES FOR POLYESTER 66/1.



without significantly changing the results, as shown in Fig. 5.7. A 7% change in h_∞ does not improve the fit to the Avrami equation. h_∞ values selected for estimation of $t_{\frac{1}{2}}$, and to calculate volume contractions were obtained by the method shown in Fig. 5.8. A discontinuity was normally observed in the plot of h_t against $1/t$, at which $h_t = h_{\infty 1}$, the final column height for the more rapid crystallisation. The final value at $1/t = 0$, or $t = \infty$ was assumed to be given by $h_{\infty 2}$, corresponding to the completion ofthe very slow secondary process (or post Avrami process) which is observed by dilatometry. Errors may be introduced in this extrapolation. $h_{\infty 2}$ was used to calculate the volume contraction which occurred during crystallsation, using the accurately known capillary diameter. Volume contractions calculated were 5.1-5.3 x 10^{-2}cm.^{3}g.$^{-1}$. 93-96% of the contraction was due to the initial rapid process.

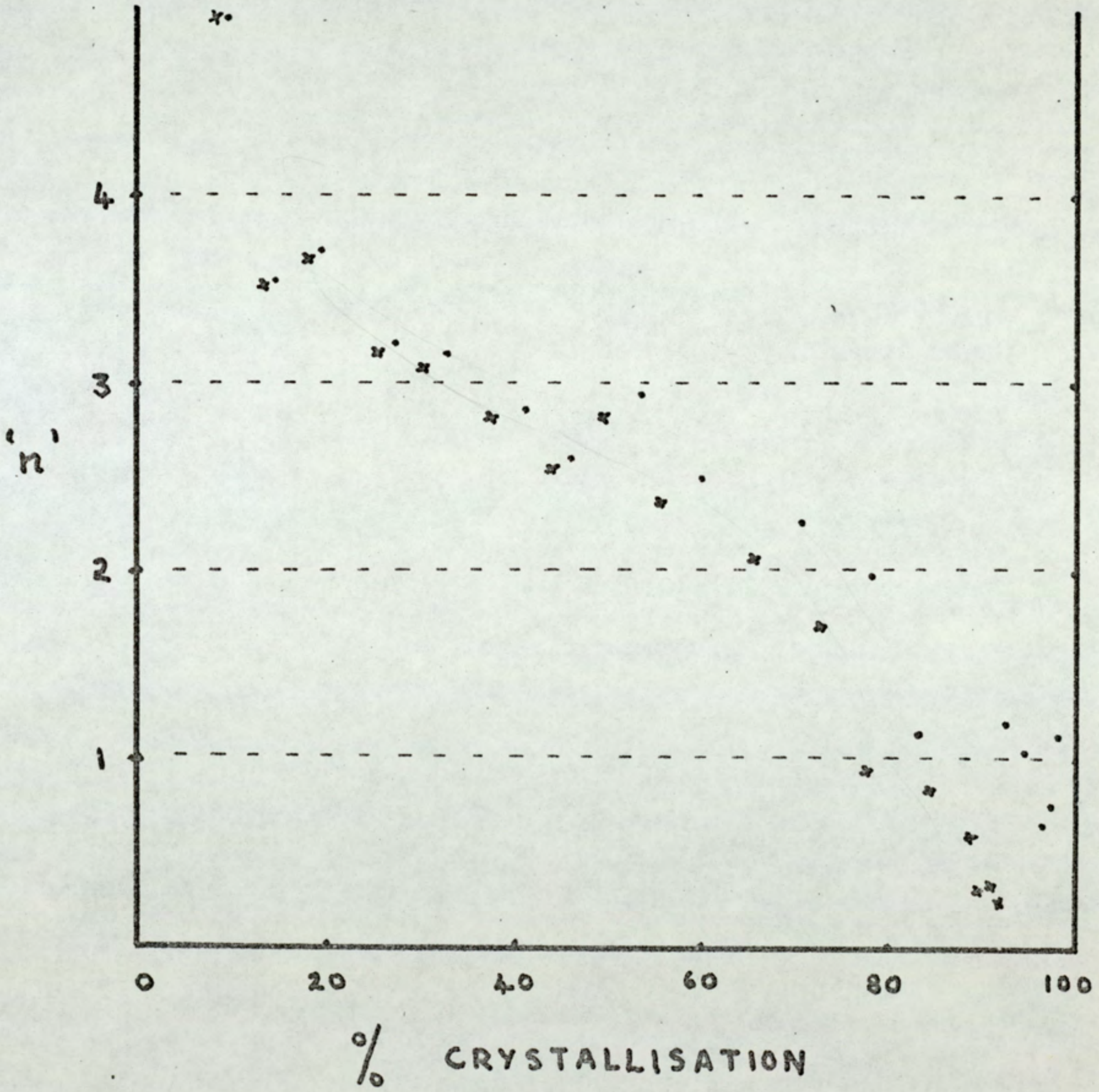
Plots of θ against log t obtained by DSC and dilatometry for sample 66/1 were different (Fig.6.2). The results obtained for polytetramethylene terephthalate (section 5.1.4) will show that comparable results can be obtained by the two techniques.

5.1.3. Polyethylene terephthalate.

DSC was used to measure crystallisation rates of polyethylene terephthalate. Due to the high temperatures required for melting and crystallisation, experimental difficulties were encountered. The high melt temperature required (295°C) tended to cause degradation. This was

FIG. 5.7. CALCULATED 'n' VALUES FOR POLYESTER 66/1.

- sample crystallised at 50·0°C.



× using h_∞ = 14·36 cm.
• using h_∞ = 14·86 cm.

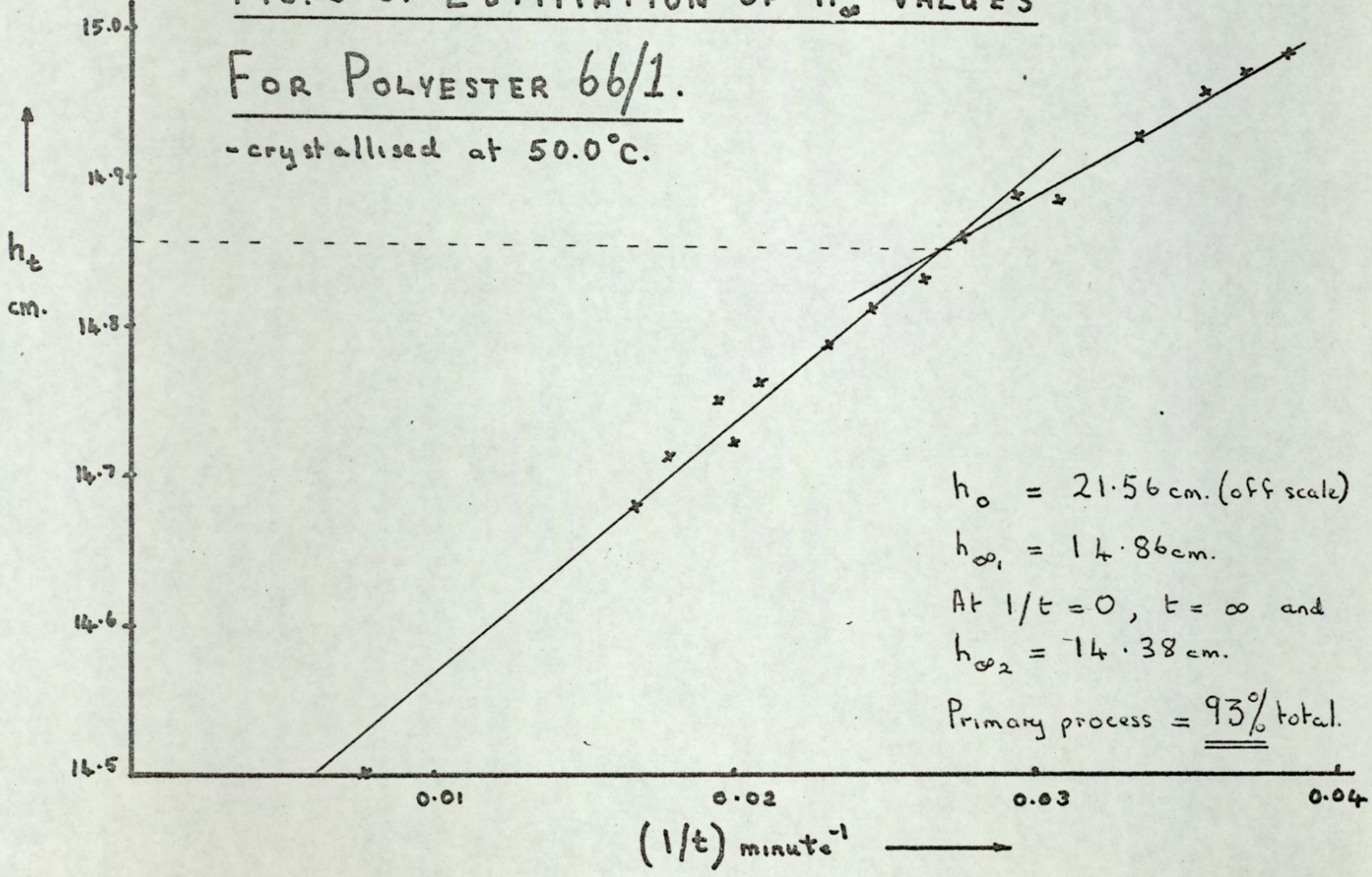


FIG. 5.8. ESTIMATION OF h_∞ VALUES FOR POLYESTER 66/1.

-crystallised at 50.0°C.

$h_o = 21.56$ cm. (off scale)

$h_{\infty_1} = 14.86$ cm.

At $1/t = 0$, $t = \infty$ and

$h_{\infty_2} = 14.38$ cm.

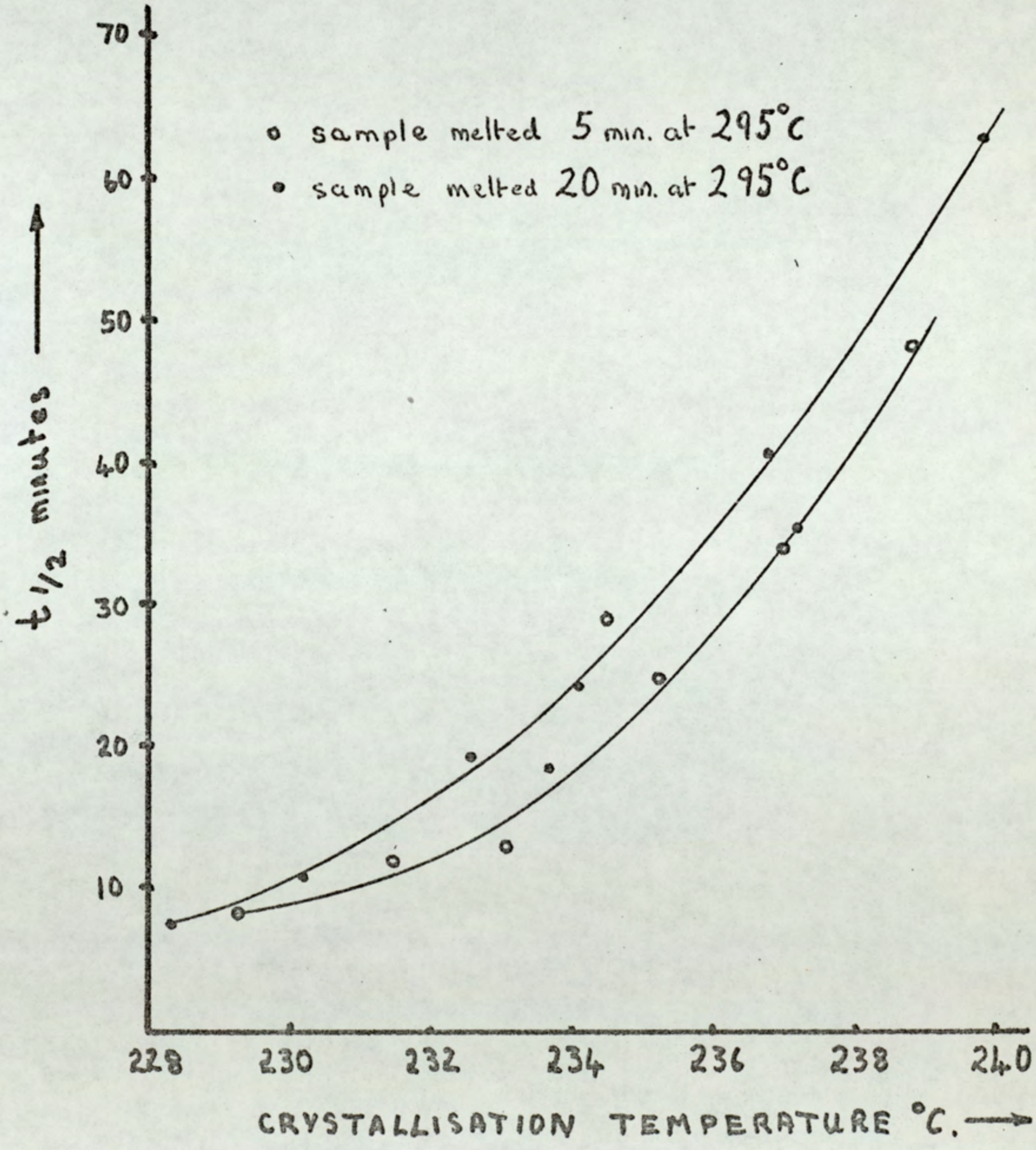
Primary process = 93% total.

reduced by performing the run in a nitrogen atmosphere and using each sample for only one crystallisation. The increased temperature of crystallisation also created problems as the constant voltage method used became less satisfactory when the temperature difference between the DSC cell and its surroundings increased. For rapid runs the difficulty lay in bringing the temperature into control quickly enough; for slower runs an increased recorder sensitivity was required, and the temperature fluctuations occurring (up to 0.5°C) were magnified until they were of the same order as the T_d signal. Instead of increasing the sensitivity it was possible to increase the sample size up to 25 mg. However, bubbling occurred in the melt, and the sample frequently overflowed out of the sample pan. This was avoided by crimping the edges of the pan and lid together. The appropriate balance of sample and reference weights appeared critical for this polymer. Without this, a considerable difference in baseline position on either side of the peak was observed.

The difficulties described resulted in a much greater scatter in $t_{\frac{1}{2}}$ values than that observed for the other polymers (Fig. 5.9). Many determinations were made and the best possible curve was drawn. To show that the scatter was not due to the particular sample used, (2T/1) some crystallisation measurements were made using the sample of polyethylene terephthalate supplied by I.C.I. A similar scatter was observed. Melting times of 5 minutes and 20 minutes were used as shown. The scatter appeared less in

FIG. 5. 9. CRYSTALLISATION HALF TIMES FOR POLYESTER 2T/1.

-measured by DSC.



the former case indicating that degradation could be the major cause. As analysis of isotherms obtained using the different melt times resulted in similar n values however, the results obtained after 20 minutes melting were used for comparison with the other polymers.

For the samples of polyethylene terephthalate available (2T/1 and the sample supplied by I.C.I.) it was not possible to measure spherulite growth rates as although melt conditions as stringent as 20 minutes at 320°C were used, the nucleation density was always too high. Spherulites have been observed for this polymer but some difficulty in obtaining these has been encountered. Keller et al[94] used samples from a polymer strip quenched directly after polymerisation. In later work Keller[96] crystallised the polymer as a plug in a glass tube, then sectioned it for examination purposes. He reported that spherulites in thin films were smaller and more difficult to study.

Crystallisation rates measured on samples melted for 20 minutes at 295°C in a nitrogen atmosphere are shown in Table 5.5. Crystallisation results approximated to an Avrami type equation with a constant n value applying to a large proportion ofthe process, as shown in Table 5.6.

n is close to 2, but appears to decrease at higher crystallisation temperatures.

Table 5.5. Crystallisation data for sample 2T/1.

$T_m = 276^\circ C$ $T_m^* = 283^\circ C$

$T^\circ C$	$\Delta T^\circ C$	$\Delta T^{*\circ} C$	$t_{\frac{1}{2}}$ min.	$1/t_{\frac{1}{2}}$ min^{-1}.
228.3	47.3	54.3	7.6	0.132
230.2	45.8	52.8	11.0	0.091
232.6	43.4	50.4	19.4	0.051
233.7	42.3	49.3	18.9	0.053
234.6	41.4	48.4	24.3	0.041
236.8	39.2	46.2	40.7	0.025
237.2	38.8	45.8	35.6	0.028
239.8	36.2	43.2	63.0	0.016

Crystallisation results approximated to an Avrami type equation with a constant n value applying to a large proportion of the process, as shown in Table 5.6.

Table 5.6. Kinetic analysis for sample 2T/1.

$T^{o}C$	K	n	% $cryst^{n}$ with constant n
228.3	5.33×10^{-3}	2.4	78
230.2	6.39×10^{-3}	2.0	97
232.6	8.80×10^{-4}	2.2	89
233.7	1.78×10^{-3}	2.0	68
234.6	9.20×10^{-4}	2.1	91
236.8	1.43×10^{-3}	1.7	82
237.2	2.94×10^{-3}	1.5	88
239.8	2.46×10^{-3}	1.9	83

Due to the decrease in n corresponding with an increase in $t_{\frac{1}{2}}$ the calculated rate constants are not meaningful, but of a similar order.

Since ΔH_f^* is available for this polymer a mean value ($\bar{\sigma}$) for the interfacial energies governing nucleus formation may be calculated.[9.28]. From equations (5) and (9) the slope of the plot of log $(1/t_{\frac{1}{2}})$ against $T_m^2/T\Delta T^2$ is equal to $-8\pi\sigma_s^2\sigma_e/n k \Delta H_u^2$, assuming only a primary nucleation process.

σ_e is the excess interfacial energy/repeating unit as it emerges from the crystal face normal to the chain direction.

σ_u is the lateral free energy/repeating unit.

$\bar{\sigma}$ is defined as $(\sigma_u^2\sigma_e)^{\frac{1}{3}}$, as σ_u and σ_e cannot be obtained separately.

ΔH_v is the heat of fusion/unit volume and is calculated from ΔH_f^* the heat of fusion of the gram repeat unit and its volume at the polymer melting temperature.

For polyethylene terephthalate[74],

amorphous density ρ at 20°C = 1.335g.cm^{-3}
coefficient of expansion α from 20°C - 70°C = 1.6×10^{-4} cm^3/°C
above 70°C = 3.7×10^{-4} cm^3/°C
ΔH_f^* = 5600 cal./repeat unit[59]
Then volume of the gram-repeat unit = 178.3 cm^3.
ΔH_v = 31.39 cal.cm^{-3}
slope of graph = -7.70°C
$\sigma_u^2 \sigma_e$ = 146 ergs^3 cm^6
$\bar{\sigma}$ = 5.3 ergs cm^2

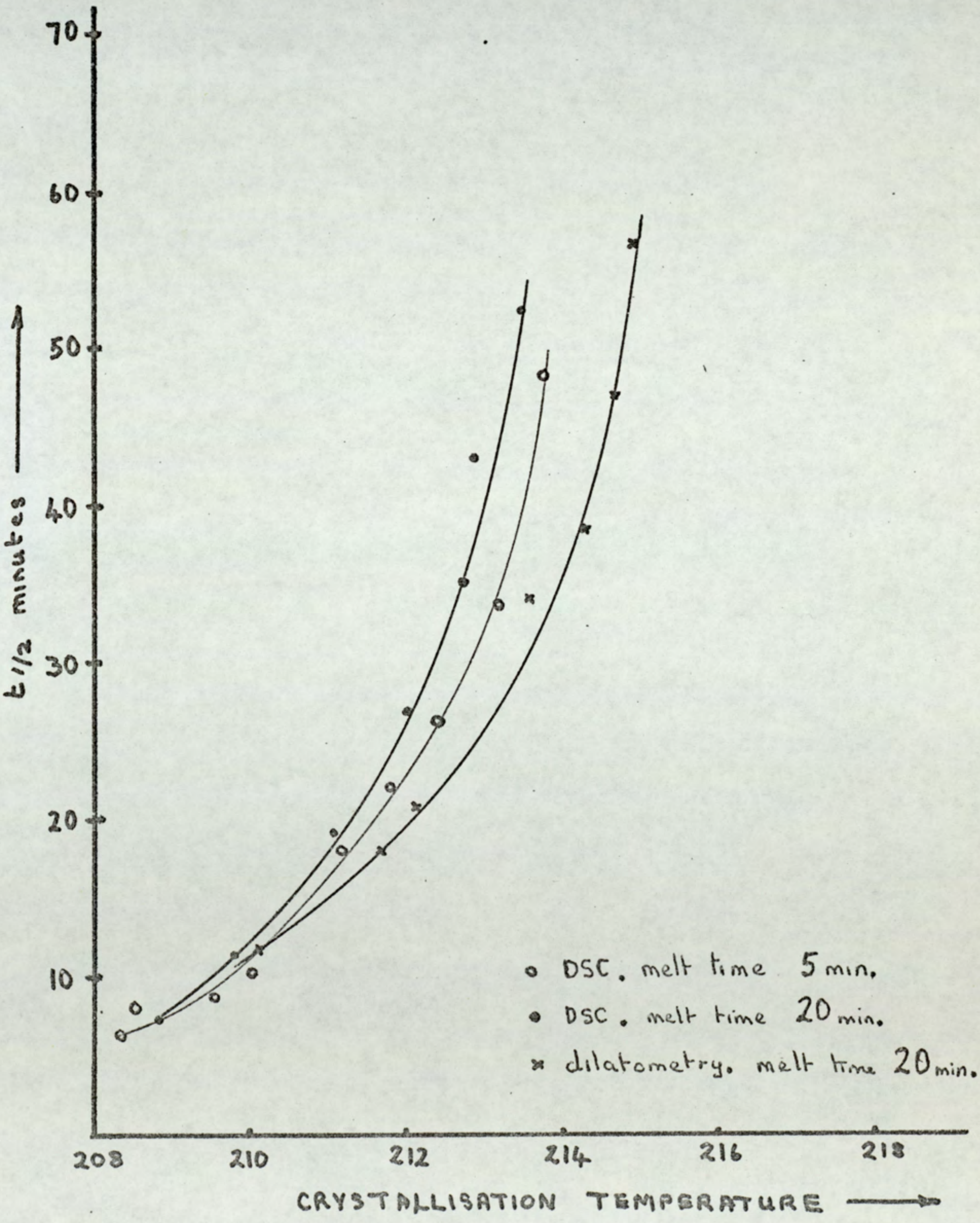
5.1.4. Polytetramethylene terephthalate.

Sample 4T/1 was studied by DSC and dilatometry. $t_{\frac{1}{2}}$ values obtained by the two methods are shown in Fig. 5.10.

Dilatometry samples (approximately 0.18g.) were initially dried at about 200°C and 10^{-4}mm.Hg pressure for 3 hours, before distilling mercury into the dilatometer. Prior to crystallisation samples were heated at 250°C for 20 minutes. On increasing the melting time to 30 minutes no change in the crystallisation rate was observed. Volume contractions calculated as for sample 66/1 (section 5.1.2) were between 5.1×10^{-2} and 5.4×10^{-2} cm^3 g^{-1}. 91-97%

FIG. 5.10. CRYSTALLISATION HALF TIMES FOR POLYESTER 4T/1.

- measured by DSC and dilatometry.



of the contraction was due to the initial rapid crystallisation process. Measurements on lower molecular weight samples of polytetramethylene terephthalate by dilatometry indicated that such samples crystallised more slowly.

Table 5.7. Effect of molecular weight on $t_{\frac{1}{2}}$ for polytetramethylene terephthalate.

Sample	M_n	$t_{\frac{1}{2}}$min. @ 210.7°C.
4T/1	13,400	16.2.
4T/2	11,100	19.9
4T/3	9,300	23.1

The molecular weight effect was not significant when crystallisation behaviour of different polymers was compared. Results obtained for the highest molecular weight sample were used.

DSC measurements were made on samples melted at 260°C for 5 minutes and 20 minutes. If the melt temperature was reduced to 250°C no change in the rate was detectable, so melt conditions were comparable with those used for dilatometry. Difficulties encountered in using the DSC technique for polyethylene terephthalate were not found for this polymer.

Crystallisation rates are shown in Table 5.8.

Table 5.8. Crystallisation data for sample 4T/1.

$T_m = 234^oC$ $T_m^* = 242^oC$

Dilatometry.					DSC.				
T^oC	ΔT^oC	$\Delta T^* C$	$t_{\frac{1}{2}}$ min.	$1/t_{\frac{1}{2}}$ min.$^{-1}$	T^oC	ΔT^oC	$\Delta T^{*o}C$	$t_{\frac{1}{2}}$ min.	$1/t_{\frac{1}{2}}$ min.$^{-1}$
210.1	23.1	31.1	11.9	0.084	208.8	25.2	33.2	7.5	0.133
211.7	22.3	30.3	18.3	0.055	209.8	24.2	32.2	11.6	0.086
212.1	21.9	29.9	20.9	0.048	211.1	22.9	30.9	19.5	0.051
213.6	20.4	28.4	34.3	0.029	212.0	22.0	30.0	27.0	0.037
214.3	19.7	27.7	38.7	0.026	212.7	21.3	29.3	35.4	0.028
214.7	19.3	27.3	47.4	0.021	212.9	21.1	29.1	43.2	0.023
214.9	19.1	27.1	56.8	0.018	213.5	20.5	28.5	52.5	0.019

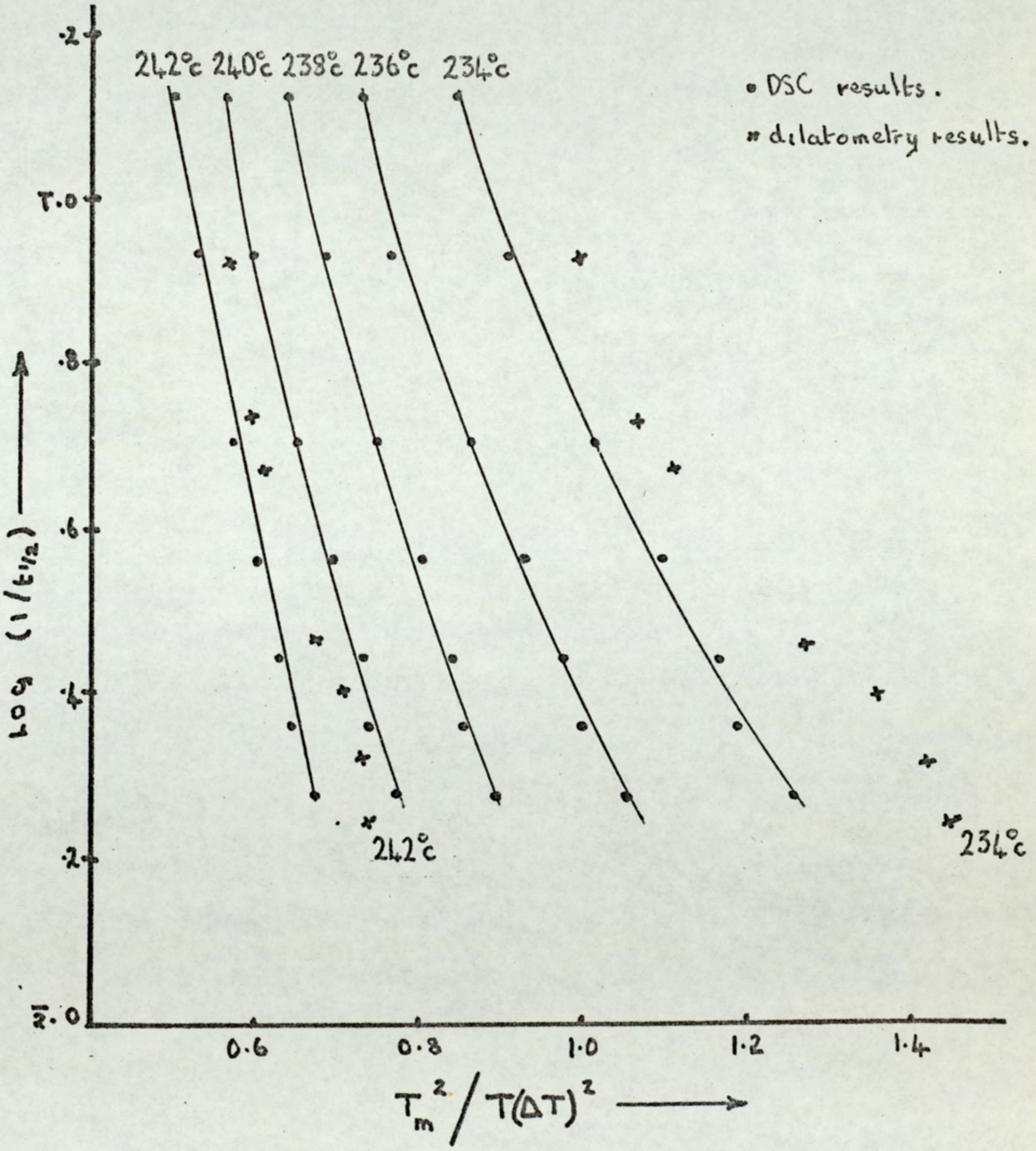
If $t_{\frac{1}{2}}$ values are compared as in Fig.5.10. it appears that rates observed by dilatometry are more rapid. This may be due to differences in sample temperature although this is not so apparent as for sample 66/1. (Fig.5.6). When n values are compared, as obtained by the two methods, they are found to be very similar indicating that the crystallisation mechanism detected by the two methods is the same. Plots of θ against log t from the two sets of results produce superimposable isotherms (Fig.6.3). Thus differences in dilatometry and DSC results for sample 66/1 are not due to major differences between the two techniques.

Results were also compared on a plot of log $(1/t_{\frac{1}{2}})$ against $T_m{}^2/T\Delta T^2$ (used to estimate $T_m{}^{*o}C$). (Fig.5.11). A greater scatter was observed for the dilatometry results. Due to the different $t_{\frac{1}{2}}$ values already discussed, dilatometry and DSC results did not lie on the same line. The DSC results were used to estimate $T_m{}^{*o}C$.

n values were constant and fractional for the major part of the process. These are shown in Table 5.9. n did not appear to be temperature dependent, but some scatter in n values was observed, so an average value of 2.7 was used to calculate corrected K values calculated using the computer. The experimental scatter is also shown by a poor fit to the Avrami equation in some cases. It is probably due to temperature fluctuation.

n values obtained by dilatometry tended to decrease during the later stages of the process. This was not observed by DSC and was due to the later slow crystallisation process, which was only detectable by dilatometry. Otherwise DSC and dilatometry results were in good agreement.

FIG. 5.11. PLOT OF LOG ($1/t_{1/2}$) AGAINST $T_m^2/T(\Delta T)^2$ FOR POLYESTER 4T/1.



[Temperatures shown refer to value used for T_m]

Table 5.9. Kinetic analysis for sample 4T/1.

	T°C	K	n	K(corrected)	%cryst^{n} with const. n.
Dilatometry.					
	210.1	5.29×10^{-4}	2.6	8.69×10^{-4}	78
	211.7	2.03×10^{-4}	2.9	2.72×10^{-4}	82
	212.1	8.24×10^{-5}	2.8	1.89×10^{-4}	71
	213.6	5.69×10^{-5}	3.0	4.98×10^{-5}	73
	214.3	3.39×10^{-5}	2.7	3.39×10^{-5}	75
	214.7	1.95×10^{-5}	2.7	1.95×10^{-5}	90
	214.9	1.52×10^{-5}	2.6	1.27×10^{-5}	67
DSC	208.8	2.92×10^{-3}	2.7	2.92×10^{-3}	92
	209.8	1.42×10^{-3}	2.5	9.29×10^{-4}	90
	211.1	2.38×10^{-4}	2.6	2.28×10^{-4}	40 - 98
	212.0	2.72×10^{-4}	2.4	9.48×10^{-5}	85
	212.7	7.06×10^{-5}	-	4.56×10^{-5}	n not const.
	212.9	5.84×10^{-5}	2.5	2.67×10^{-5}	83
	213.5	2.06 x 10-5	2.6	1.57×10^{-5}	30 - 92

It was possible to measure spherulite growth rates for sample 4T/1, although only within a temperature range of 3°C. An elevated melt temperature of 285°C was necessary to reduce the nucleation density. Growth rates were linear. Results are shown in Table 5.10. In all cases spherulites were numerous and small in size.

Table 5.10. Spherulite growth rates for sample 4T/1.

T°C	T°C	T^{*}°C	G /min.
211.5	22.5	30.5	0.85
212.2	21.8	29.8	0.52
213.0	21.0	29.0	0.33
213.3	20.7	28.7	0.28
214.3	19.7	27.7	0.09

$\bar{\sigma}$, the mean interfacial free energy governing nucleus formation was calculated for this polymer as in section 5.1.3, using the following information.

Density of polymer at melting temperature = 1.08 g.cm.$^{-3}$ (ref.3)

ΔH_f^{*} = 7.600 cal./repeat unit.

Volume of the gram-repeat unit = 203.7 cm.^{3}

ΔH_u heat of fusion/unit volume = 37.31 cal.cm.$^{-3}$

slope of graph = - 4.75°C

$\sigma_u^{2}\sigma_e$ = 172 ergs^{3}cm.6

$\bar{\sigma}$ = 5.6 ergs cm.^{2}

5.1.5. Polypentamethylene terephthalate.

Sample 5T/1 was studied by DSC Due to the low maximum crystallisation rate for this polymer measurements could be made above and below the temperature of maximum rate, T_{max} which was 68-70°C (Fig.5.12). A melt temperature of 165°C was used; decreasing the melt time from 20 minutes to 5 minutes did not significantly alter the rate. However thermal history did alter the total amount of crystallisation which occurred. A polymer sample as prepared was melted for 5 minutes at 165°C, then crystallised at 82°C. The process was repeated twice, using the same sample. The heat evolved during the first crystallisation was only 60% of that evolved during subsequent crystallisations. The crystallisation rate was unchanged. It appeared that nuclei were produced during the first crystallisation which were not destroyed on melting. In order to obtain the maximum peak area in all measurements, samples were first crystallised at a suitable temperature in the DSC cell.

Using similar melt conditions to those used for DSC measurements it was possible to grow large well defined spherulites, although only at temperatures higher than those at which overall crystallisation rates were measured. In order to obtain large spherulites it was necessary to ensure that the cover slips and polymer samples were dust free. A range of spherulite sizes could be seen within a single sample crystallised isothermally. Typical plots of spherulite size against time at different temperatures are shown in Fig. 5.13. It appears that most spherulites have a finite size of about 10 μ at zero time, indicating

Table 5.11. Crystallisation data for sample 5T/1.

$T_m = 142^{\circ}C$ $T_m^* = 150^{\circ}C$

$T^{\circ}C$	$\Delta T^{\circ}C$	$\Delta T^{*\circ}C$	$t_{\frac{1}{2}}$min.	$1/t_{\frac{1}{2}}$min.$^{-1}$	$G\mu$/min.
42.2	99.8	107.8	58.7	0.017	-
51.2	90.8	98.8	26.9	0.037	-
62.4	79.6	87.6	15.9	0.063	-
71.0	71.0	79.0	14.8	0.068	-
80.2	61.8	69.8	18.5	0.054	-
89.5	52.5	60.5	28.4	0.035	-
99.9	42.1	50.1	51.5	0.019	-
104.5	37.5	45.5	-	-	2.40
107.0	35.0	43.0	-	-	1.85
110.0	32.0	40.0	-	-	1.20
111.8	30.2	38.2	-	-	0.97
115.2.	26.8	34.8	-	-	0.65

Note. T_m^* was obtained as described from a plot of log $(1/t_{\frac{1}{2}})$ against $T_m^2/T\Delta T^2$ using only the measurements made on the higher temperature side of the maximum rate. From the theory only these have the temperature dependence predicted by such a plot.

FIG. 5.12. CRYSTALLISATION HALF TIMES FOR POLYESTER 5T/1 - measured by DSC

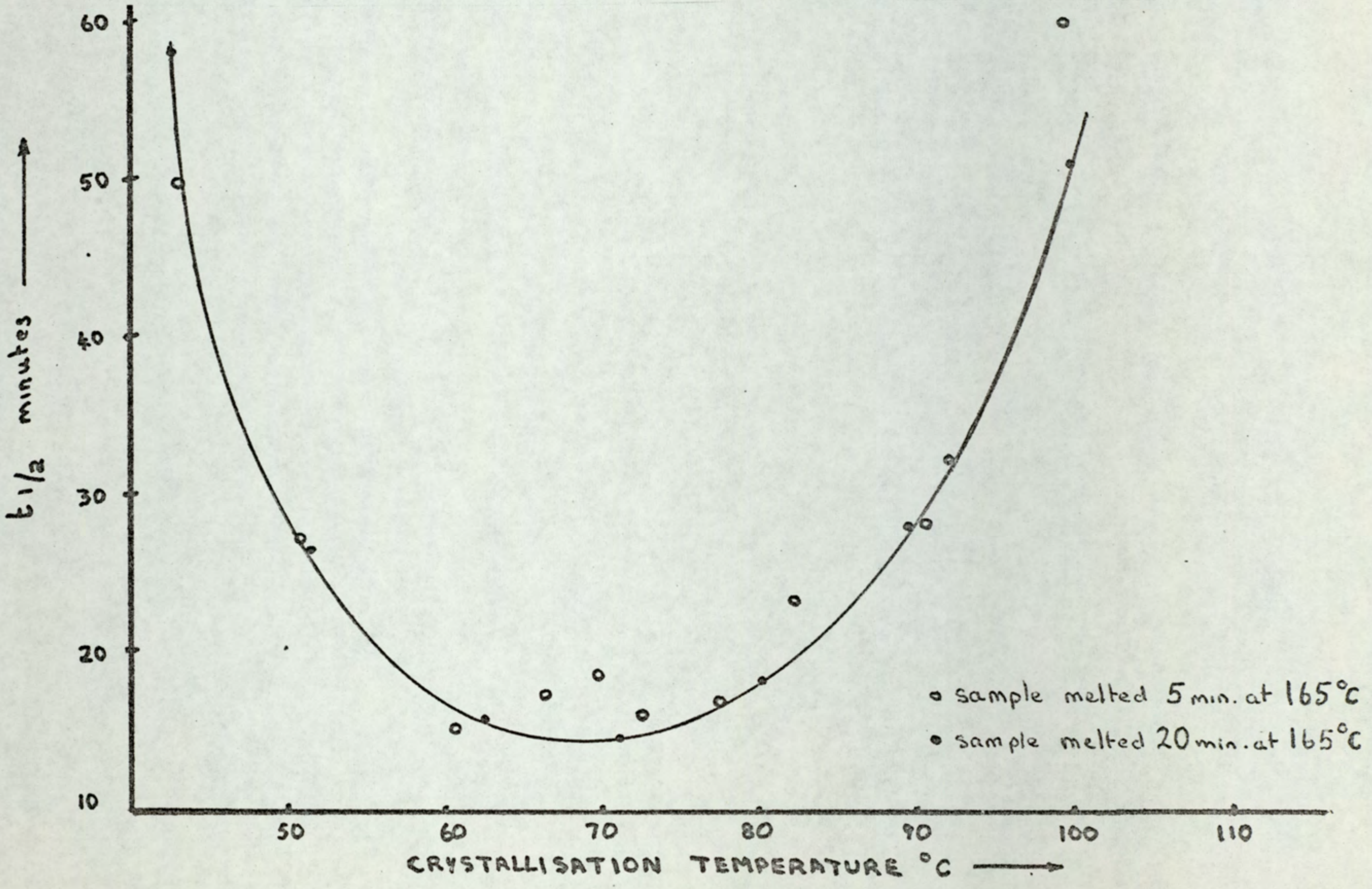
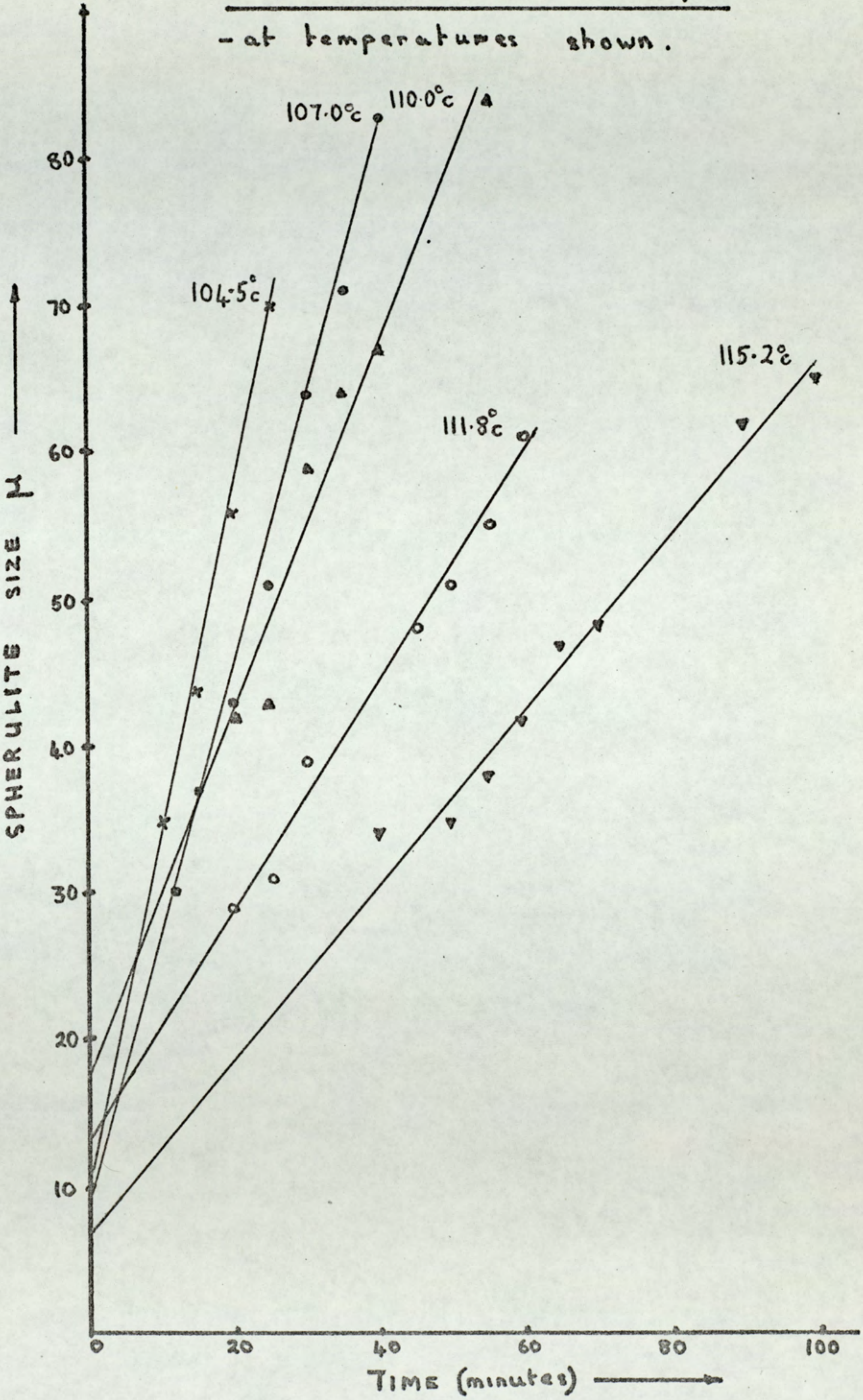


Fig. 5.13. Spherulite Growth Rates for Polyester 5T/1.

- at temperatures shown.



heterogeneous nucleation.

Crystallisation data for samples of polypentamethylene terephthalate, first melted at 265°C for 20 minutes are shown in Table 5.11.

Analysis of results using the computer program did not fit an Avrami type equation. They were generally rather inconsistent, although n appeared to increase in most cases.

5.1.6. Polyhexamethylene terephthalate.

Overall crystallisation rates of sample 6T/1 were measured by DSC, after melting for 5 minutes or 20 minutes at 186°C. Reduction of the melt temperature to 175°C did not alter the crystallisation rate. $t_{\frac{1}{2}}$ values are shown in Figure 5.14.

Spherulite growth rates could not be measured for sample 6T/1 although melt temperatures up to 230°C and melt times up to 3 hours were used. In all cases a very large number of small spherulites was observed.

$t_{\frac{1}{2}}$ values obtained for samples first melted for 20 minutes at 186°C are shown in Table 5.12.

Calculated n values were constant and fractional for the major part of the crystallisation and are shown in Table 5.13. Since n did not appear to be temperature dependent, the average value (2.9) was used to calculate the corrected K values, also shown.

FIG. 5.14. CRYSTALLISATION HALF TIMES FOR POLYESTER 6T/1.

-measured by DSC.

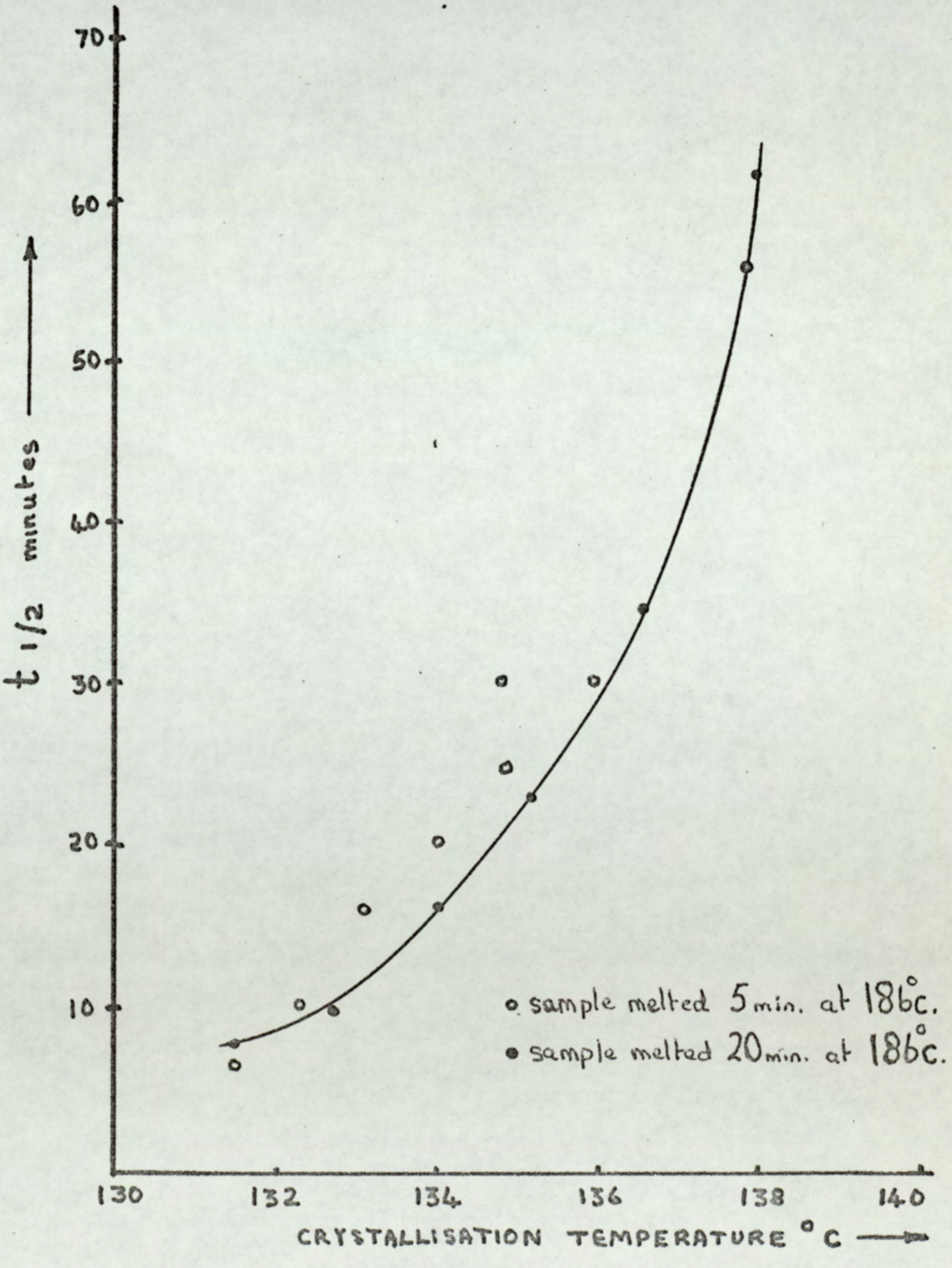


Table 5.12. Crystallisation data for sample 6T/1.

$T_m = 156^\circ C$ $T_m^* = 162^\circ C$

$T^\circ C$	$\Delta T^\circ C$	$\Delta T^{*\circ} C$	$t_{\frac{1}{2}}$ min.	$1/t_{\frac{1}{2}}$ min.$^{-1}$
131.5	24.5	30.5	8.0	0.125
132.7	23.3	29.3	10.0	0.100
134.0	22.0	28.0	16.5	0.061
135.2	20.8	26.8	23.2	0.043
136.6	19.4	25.4	34.9	0.029
138.0	18.0	24.0	61.9	0.016

Table 5.13. Kinetic analysis for sample 6T/1.

$T^\circ C$	K	n	K(corrected)	%cryst^n with const. n.
131.5	3.16×10^{-3}	2.6	3.46×10^{-3}	86
132.7	1.34×10^{-3}	2.7	9.74×10^{-4}	86
134.0	3.25×10^{-4}	2.7	4.94×10^{-4}	76
135.2	3.5×10^{-5}	3.1	9.46×10^{-5}	94
136.6	2.8×10^{-6}	3.5	5.65×10^{-5}	76
138.0	1.6×10^{-5}	2.6	8.09×10^{-6}	87

Figure 5.15 shows the actual variation in n for the crystallisation at 138.0°C. This is typical for DSC results approximating to an Avrami type equation. The limits fixed in the computer program are also shown in this diagram. The scatter in the initial and final stages is largely due to the magnification of experimental error which occurs when n is calculated at these points.

$\bar{\sigma}$ was calculated for this polymer as in section 5.1.3, using the following information.

Specific volume = 0.858 $cm.^3\ g.^{-1}$ (ref.13)
ΔH_f^* = 8500 cal./repeat unit
Volume of the gram-repeat unit = 212.8 $cm.^3$
ΔH_u, heat of fusion/unit volume = 39.95 $cal.cm.^{-3}$
slope of graph = -2.98°C

$$\sigma_u^2\sigma_e = 123\ ergs^3 cm.^6$$
$$\bar{\sigma} = 5.0\ ergs\ cm.^2$$

5.1.7. Polytetramethylene isophthalate.

For this polymer crystallisation rates were too slow for measurement by DSC, so dilatometry was used. Samples were melted for 5 minutes and for 20 minutes at 185°C. The effect of change in melting time was not significant compared to the experimental scatter observed. (Fig.5.16). The scatter was not due to poor temperature control as the temperature dependence of rate is low for this polymer. As large spherulites were observed the erratic results may be due to the formation of very small voids between spherulites. These have been observed for

FIG. 5.15. CALCULATED n VALUES FOR POLYESTER 6T/1.

-sample crystallised at 138·0°C.

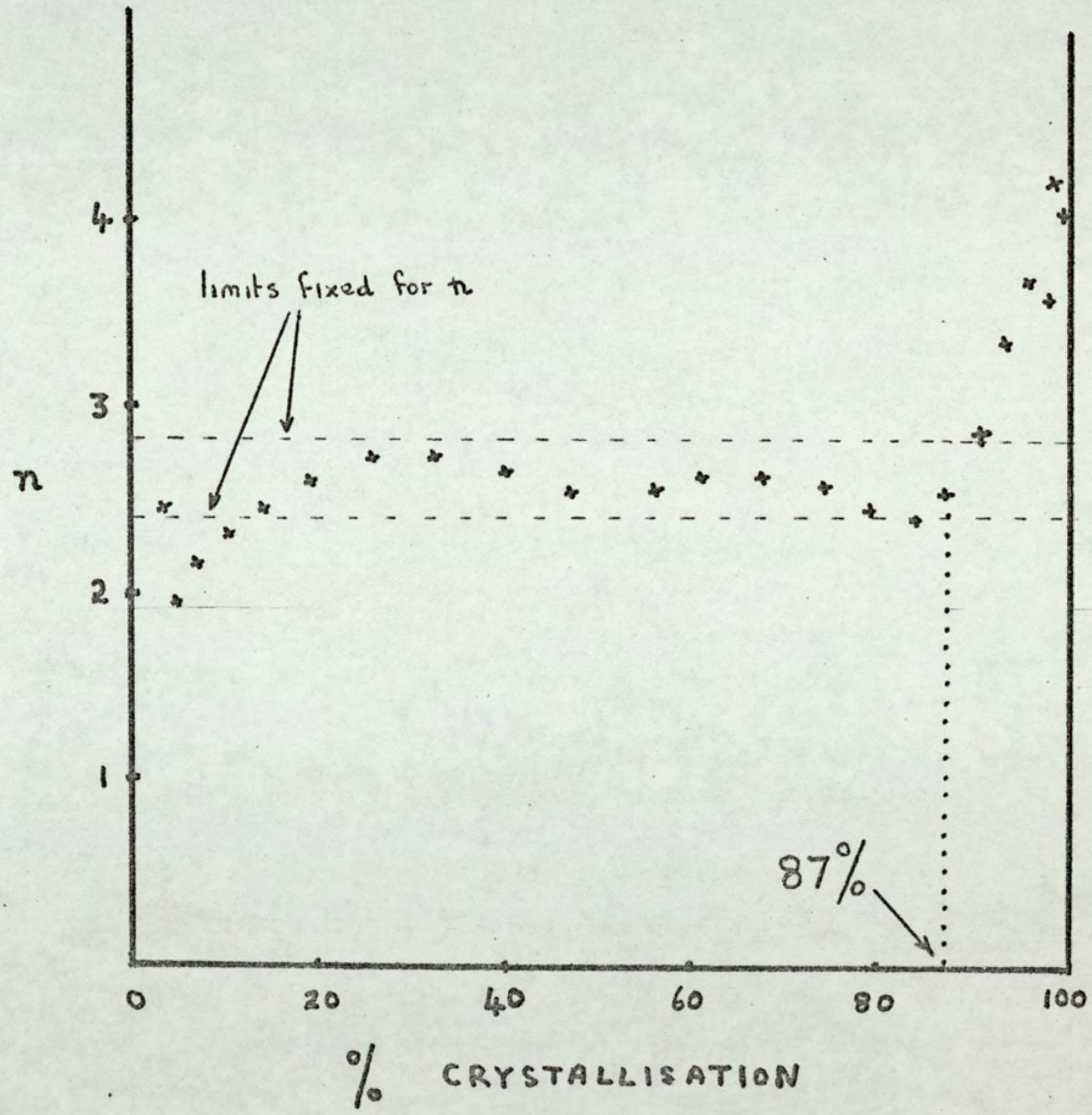
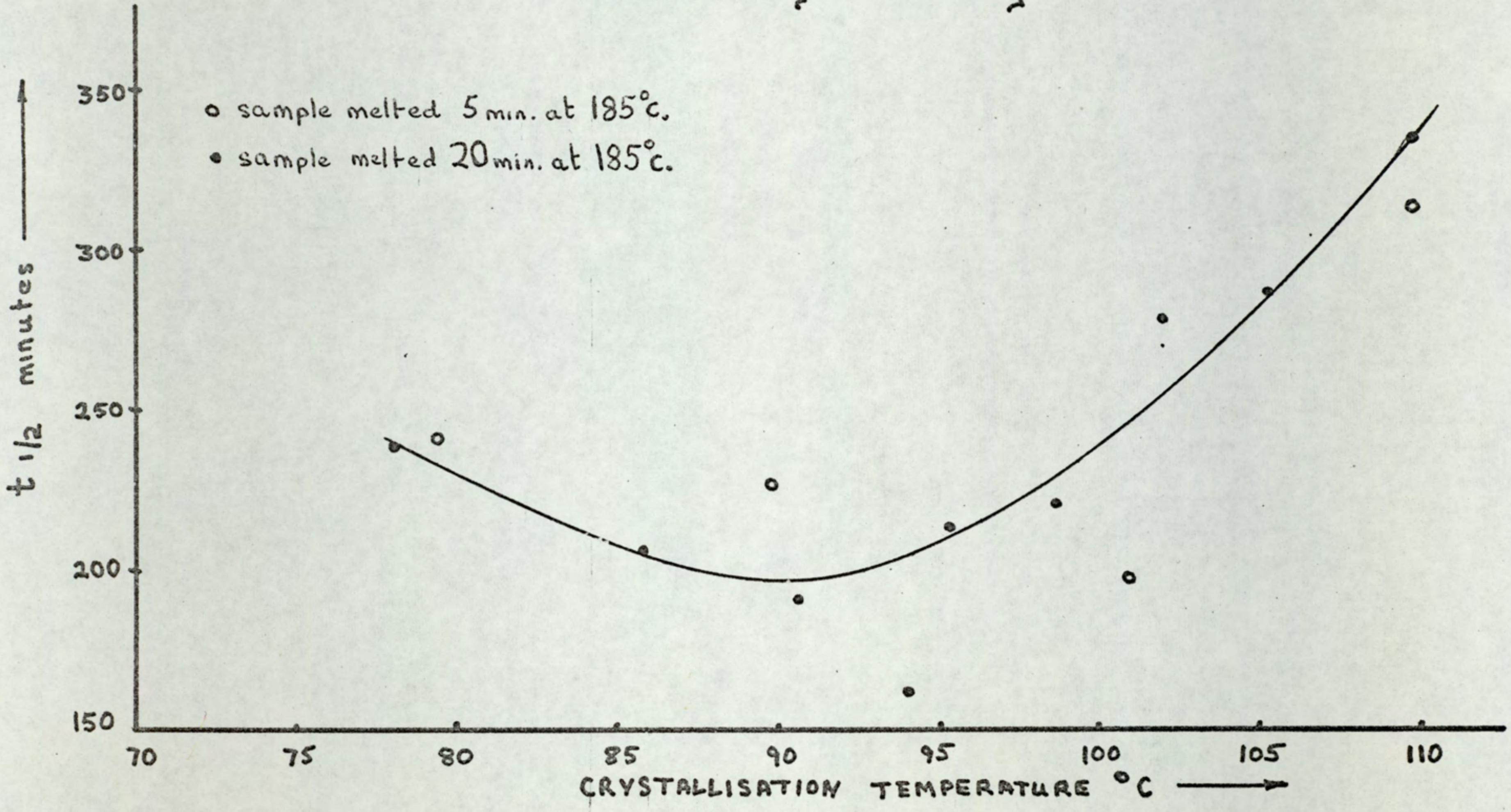


FIG. 5.16. CRYSTALLISATION HALF TIMES FOR POLYESTER 4I/1.

-measured by dilatometry.



poly-(tetramethyl-p-silphenylene)-siloxane and were considered to give erroneous dilatometry results[123]. Alternatively the irreproducibility may be due to non-random nucleation behaviour.

Approximately 0.18g.samples were used. Each sample was melted in the dilatometer for 3 hours at 155°C and 10^{-4}mm.Hg pressure before filling the dilatometer with mercury. Crystallisation rates were measurable over a wide temperature range (35°C) above and below the temperature of maximum rate. As the crystallisations were slow the h_∞ value was taken as the height of the mercury column after crystallisation overnight. (ie. Each crystallisation was continued for almost 24 hours). The method used previously to obtain $h_{\infty 1}$ and $h_{\infty 2}$ could not be used as the process was not followed beyond $h_{\infty 1}$ at all temperatures as shown in Fig. 5.17. Due to the large supercoolings required the polymer was assumed to be at the crystallisation temperature 5 minutes after the dilatometer was placed in the crystallisation bath. Volume contractions were between 3.4 and 4.0×10^{-2} $cm.^3g.^{-1}$.

Spherulite growth rates could be measured over the same temperature range as overall crystallisation rates, using the same melt conditions. The temperature of maximum rate was found to be 90-92°C by both types of measurement. The growth of spherulites was linear with time. All spherulites appeared to have a finite size of about 10μ at zero time, indicating that nucleation was due to heterogeneities in the

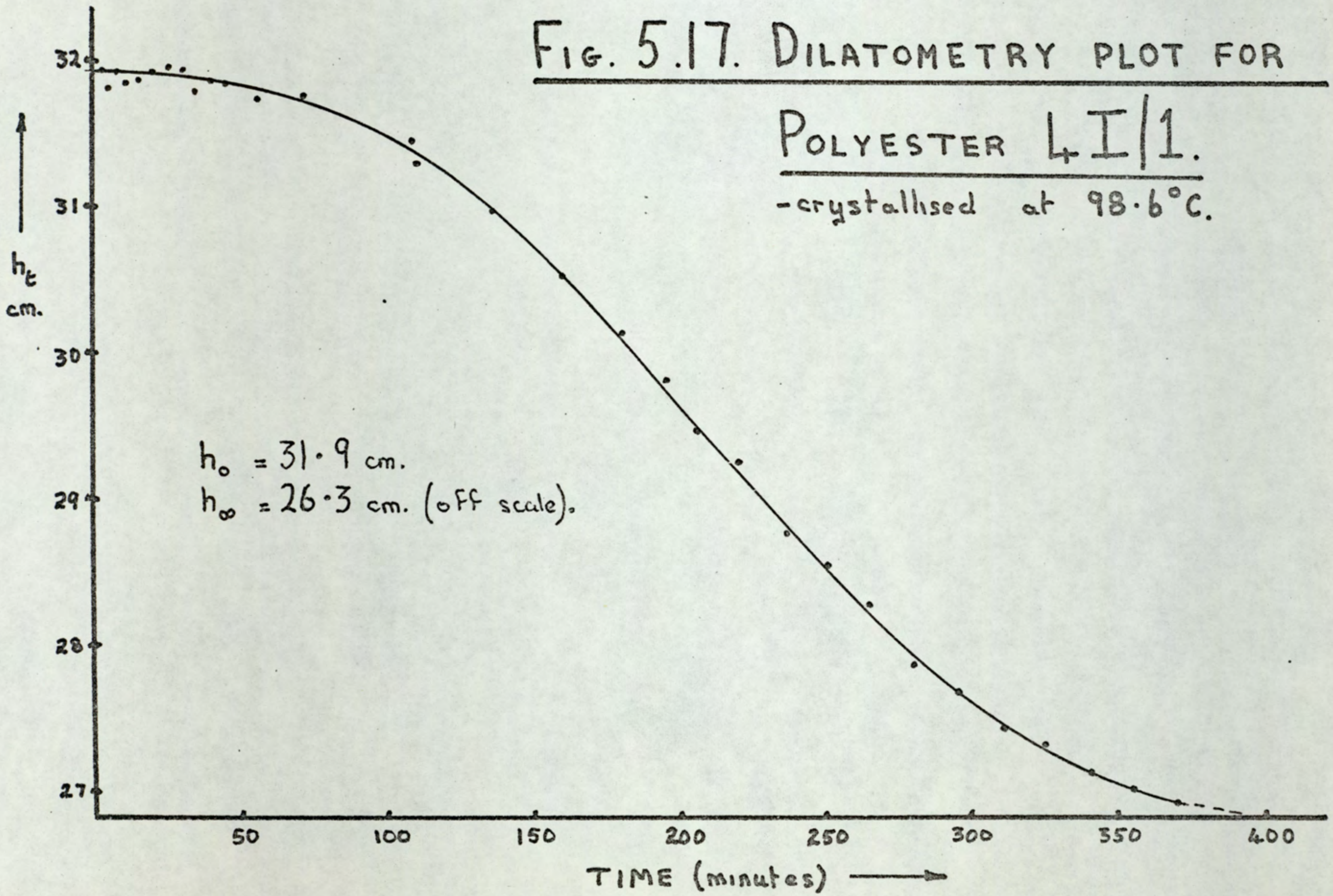


FIG. 5.17. DILATOMETRY PLOT FOR POLYESTER 4I/1.
-crystallised at 98·6°C.

polymer. If a sample was quenched during crystallisation isolated spherulites were present within the amorphous material. Spherulites were well defined and highly birefringent.

Crystallisation results for samples first melted for 20 minutes at 185°C are shown in Table 5.14.

Table 5.14. Crystallisation data for sample 4I/1.

$T_m = 150^\circ C$ $T_m^* = 160^\circ C$

T°C	ΔT°C	ΔT*°C	$t_{\frac{1}{2}}$min.	$1/t_{\frac{1}{2}}$min.$^{-1}$	G_ρ/min.
78.0	72.0	82.0	238	0.0042	-
85.8	64.2	74.2	206	0.0049	-
90.7	59.3	69.3	192	0.0052	-
95.3	54.7	64.7	213	0.0047	-
98.6	51.4	61.4	220	0.0045	-
102.0	48.0	58.0	278	0.0036	-
105.3	44.7	54.7	287	0.0035	-
109.7	40.3	50.3	334	0.0033	-
76.7	73.3	83.3	-	-	0.13
83.0	67.0	77.0	-	-	0.17
88.3	61.7	71.7	-	-	0.21
93.5	56.5	66.5	-	-	0.25
99.2	50.8	60.8	-	-	0.19
105.1	44.9	54.9	-	-	0.16
114.0	36.0	46.0	-	-	0.15

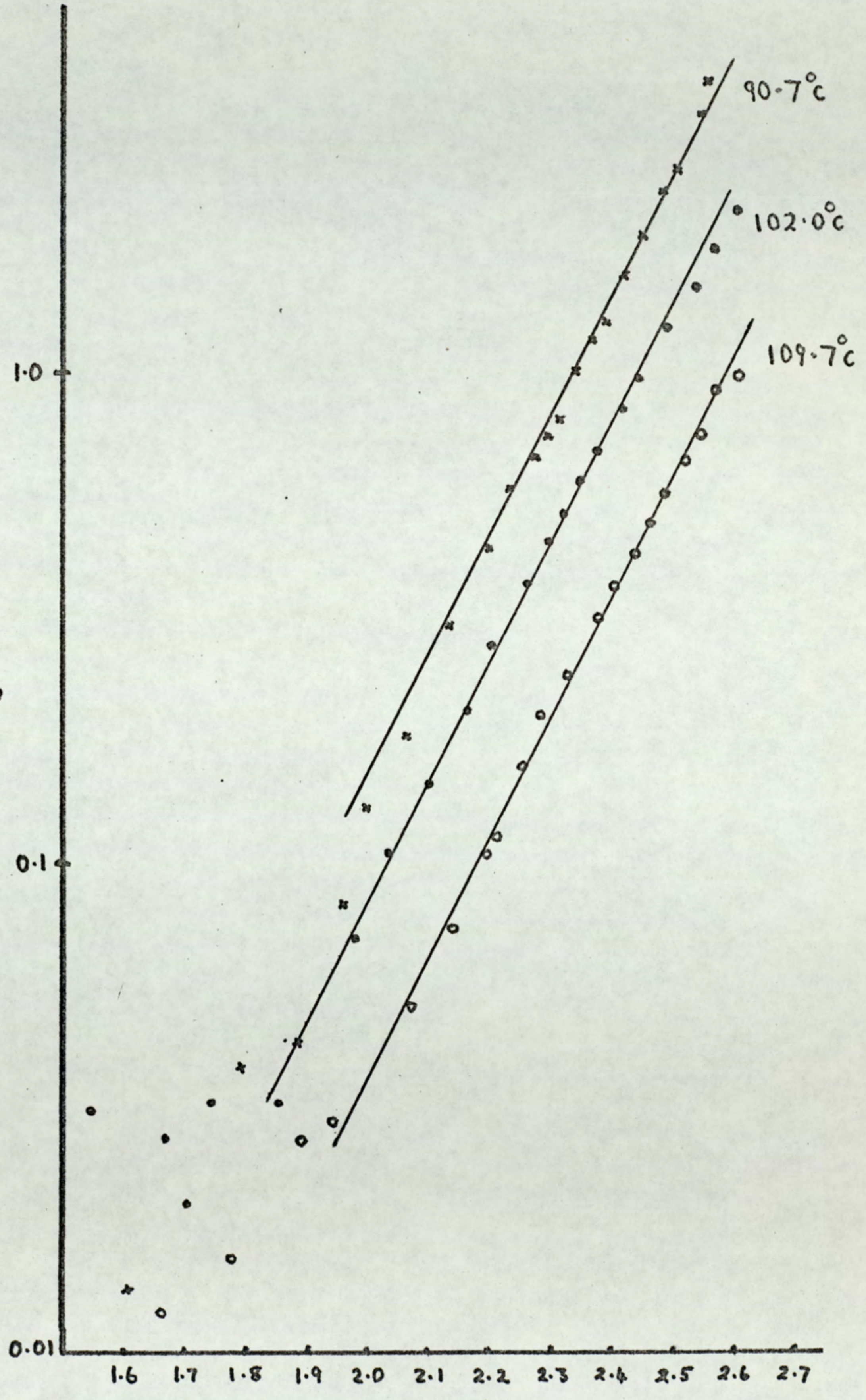
Only the $t_{\frac{1}{2}}$ values at temperatures above T_{max} were used to estimate T_m^*.

The selection procedure for n used in the computer program was unsuitable for these results, as a scatter in values was observed, probably due to small temperature fluctuations during the long crystallisations. For DSC results this type of scatter was eliminated, or averaged by the use of the automatic integrator. In this case the scatter in calculated n values was aggravated by the fact that many of these were within the first 20% of the crystallisation, when errors are magnified. In several experiments the process was not followed beyond 80% of the crystallisation. Avrami plots were drawn; some are shown in Figure 5.18. These plots indicated that to obtain a value of n which applied to the majority of the process, it was reasonable to average all the n values calculated after the first 10% of crystallisation occurred. Thiswill be referred to as $\bar{n}$. K was also calculated. Results are shown in Table 5.15.

Table 5.15. Kinetic analysis for sample 4I/1.

$T^{o}C$	$\bar{n}$	K	K(corrected)
78.0	2.6	8.20×10^{-7}	9.54×10^{-7}
85.8	2.5	1.14×10^{-6}	1.14×10^{-6}
90.7	2.5	1.36×10^{-6}	1.36×10^{-6}
95.3	2.4	1.79×10^{-6}	1.05×10^{-6}
98.6	2.5	9.68×10^{-7}	9.68×10^{-7}
102.0	2.3	1.66×10^{-6}	5.38×10^{-7}
105.3	2.8	9.10×10^{-8}	4.97×10^{-7}
109.7	2.3	1.09×10^{-6}	3.38×10^{-7}

Fig. 5.18. Avrami plots for Polyester 4I/1.



The first column of K values were calculated using the n values shown; the corrected K values were calculated from the average n (2.5). The very small change in rate with temperature is indicated by these results.

$\bar{\sigma}$ was calculated for this polymer as in section 5.1.3, using the following information.

Density of polymer at melting temperature = 1.14 g.cm.^{3}(ref.3)

ΔH_f^* = 10100 cal./repeat unit

Volume of the gram-repeat unit = 193.0 cm.^{3}

ΔH_u heat of fusion/unit volume = 52.34 cal.cm.$^{-3}$

slope of graph = -2.80

$\sigma_u \sigma_e^2$ = 184 ergs^{3}cm.^{6}

$\bar{\sigma}$ = 5.7 ergs cm.^{2}

5.2. DSC melting and crystallisation temperatures.

Each sample was melted in nitrogen for 5 minutes at the temperature shown in Table 5.16, column 2, and then cooled at 5°C/minute. The DSC crystallisation temperature is shown. The sample was then heated at 5°C/minute and the DSC melting temperature recorded. Under these conditions sample 5T/1 and 4I/1 did not crystallise; the melting temperature of previously crystallised samples is listed. For polyesters 46, 4T and 6T double melting peaks were observed; for 5T and 4I the melting peaks were very broad. (see also section 5.3.2.)

Table 5.16. DSC melting and crystallisation temperatures.

Polymer sample	Melt temperature°C	DSC crystallisation temperature°C	DSC melting temperature°C
46/1	80	31	53,58
66/2	80	47	62
2T/1	295	193	259
4T/1	260	197	214,224
5T/1	165	-	134
6T/1	180	124	140,149
4I/1	180	-	141

The DSC melting temperature represents the melting of the bulk of the sample. Since the melting temperature measured by microscopy represented the disappearance of of the last trace of crystallinity in the sample, and slower crystallisation and cooling rates were used in the latter case, T_m values were higher. (Table 2.4).

5.3. Heats of fusion.

5.3.1. DSC cell calibration.

Pure samples of gallium, indium, tin and lead were used. Gallium melts at 30°C so the DSC cell was cooled using solid carbon dioxide before melting the samples, in order to record the baseline before the transition. Lead samples were heated in nitrogen. Results used for calibration are recorded in Table 5.17. The calibration coefficient E is calculated as described in section 3.2.3.

(The temperatures recorded are the peak temperatures T_p. These are higher than the actual melting temperatures as the temperature recording thermocouple monitors the reference temperature. The start of the transition appears at the sample melting temperature).

Table 5.17. Calibration of DSC cell.

Sample	ΔH mcal.mg.$^{-1}$	Weight mg.	Area units	E mcal/area unit	Peak temperature T_p °C
Ga	19.1[149]	10.50	1125	0.178	35
Ga	19.1	12.83	1373	0.179	35
Ga	19.1	11.68	1043	0.214	35
In	6.79[149]	8.71	260	0.228	161
In	6.79	8.71	276	0.214	161
In	6.79	19.46	579	0.228	161
In	6.79	19.46	587	0.225	161
Sn	14.2[149]	14.47	878	0.234	237
Sn	14.2	14.47	836	0.246	237
Sn	14.2	11.14	646	0.245	237
Sn	14.2	11.14	666	0.242	237
Sn	14.2	7.36	430	0.243	237
Sn	14.2	7.36	450	0.232	237
Pb	5.5[152]	22.18	490	0.247	333
Pb	5.5	20.06	434	0.254	333
Pb	5.5	20.18	405	0.274	333
Pb	5.5	19.02	381	0.274	333

Fig. 5.19 is the calibration plot for the DSC cell. The average E, and the upper and lower limits observed at each temperature are shown. Although a straight line calibration was not reported for the DSC cell[149], it

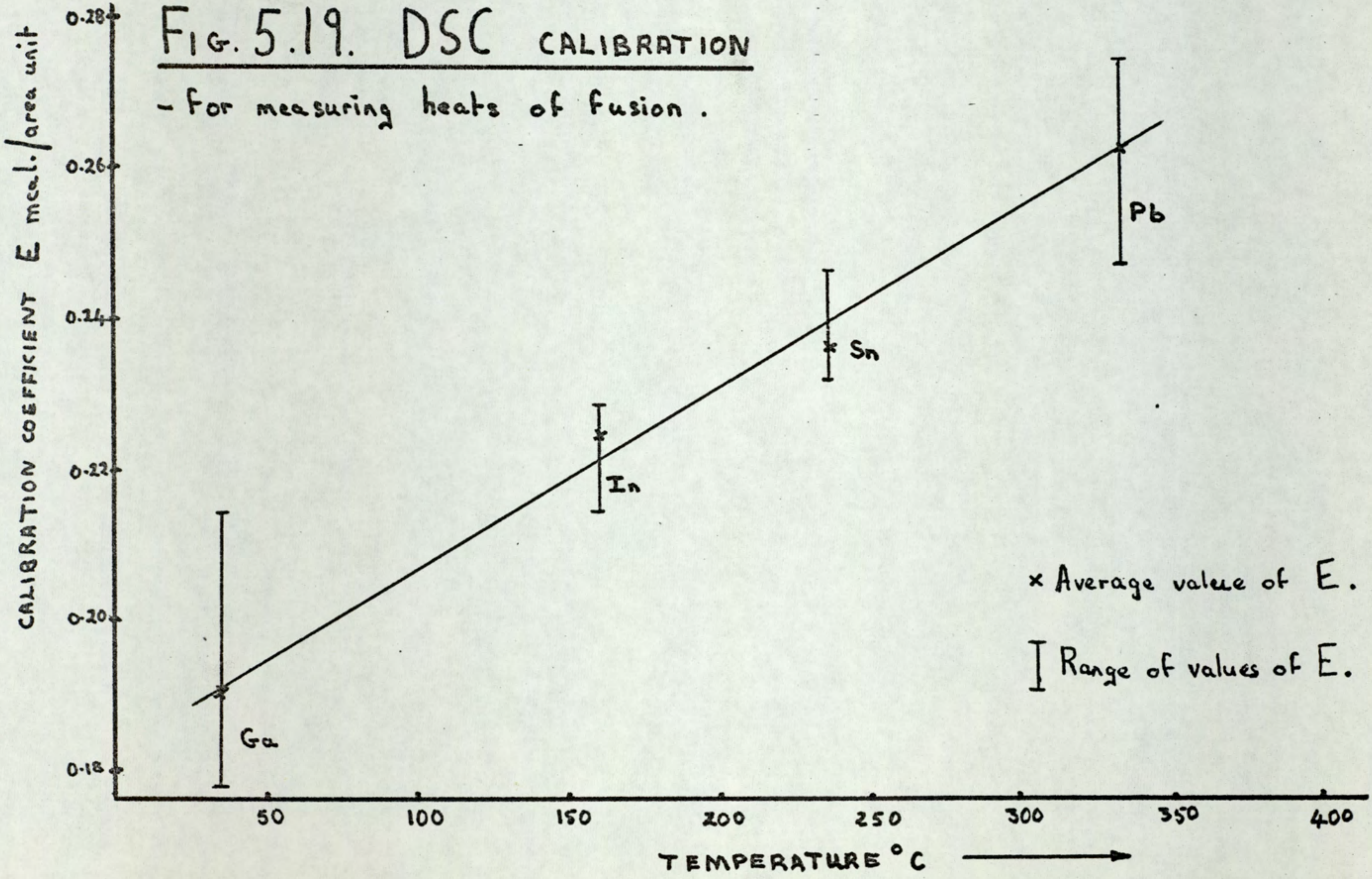


FIG. 5.19. DSC CALIBRATION

– for measuring heats of fusion.

cooled in the cell, then reheated. Again one peak, in the same position, but having a smaller area, was observed.

Sample 2T/1.

This sample was crystallised overnight at 240°C in a stream of nitrogen, having first been melted for 5 minutes at 295°C. After crystallisation one melting peak was observed at 272°C. The sample was then cooled to about 190°C. On reheating the area of the crystallisation peak was negligible with the recorder sensitivity used.

Sample 4T/1.

After melting for 15 minutes at 260°C this sample was crystallised overnight at 215°C. To obtain a level baseline before the melting transition, the sample was cooled to 180°C before heating. On heating one peak (T_p= 228°C) was observed. After cooling to 180°C and reheating, an additional small peak was present at 218°C

Sample 5T/1.

This sample was melted for 15 minutes at 165°C then crystallised overnight at 100°C. It was cooled to 70°C (no further crystallisation occurred), then heated. One melting peak (T_p= 136°C) was observed. On cooling no crystallisation occurred, so the sample was allowed to crystallise for several days at room temperature. Again a single melting peak was observed at 136°C.

Sample 6T/1.

Sample 6T/1 was melted for 15 minutes at 180°C, then crystallised overnight at 142°C. On cooling to 120°C no further crystallisation occurred. The sample was heated, one melting peak being observed (T_p = 153°C). Crystallisation was observed when the sample was cooled to 100°C. On melting two overlapping peaks (T_p = 142,152°C) were present. The two types of melting trace are shown in Fig. 5.20.

Sample 4I/1.

After melting for 15 minutes at 180°C this sample was crystallised overnight at 90°C. A small peak (T_p = 109°C) and two overlapping larger peaks (T_p= 131,144°C) were observed on heating. On cooling the sample did not crystallise. After several days at room temperature the sample was reheated. Melting peaks were present at 131°C and 144°C. The peak at 109°C was no longer present.

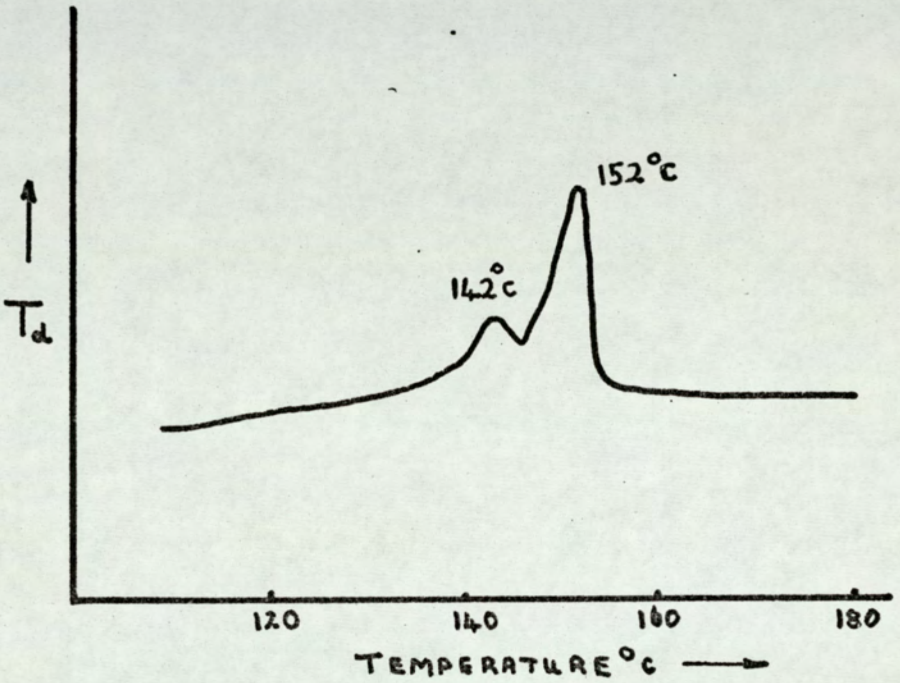
5.3.3. Heats of fusion of polyesters.

The information used in calculation of heats of fusion of polyesters is given in Table 5.18. In cases where two peaks overlap, the total area is measured.

Errors in these results will be due to errors in the calibration coefficient already discussed, to determination of the peak baseline which is always difficult for polymers 61, and due to the fact that there was only time available for one determination of heat of fusion in each case. The error introduced by the value used for E may be assessed as follows. If the E value of 0.20 used to calculate ΔH for sample 46/1 is replaced by a possible E = 0.21 ΔH is increased by 5% to 12.7 $mcal.mg.^{-1}$. This is not too

Fig. 5.20. DSC Melting Traces for Polyester 6T/1.

A. Rapidly cooled sample.



B. Slowly crystallised sample.

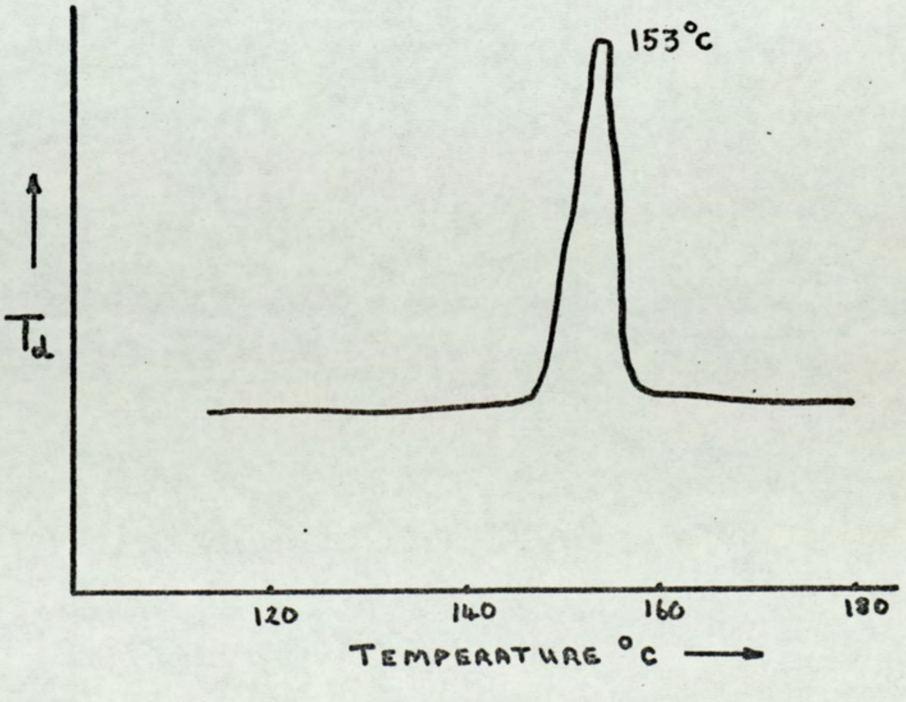


Table 5.18. Calculation of heats of fusion for polyesters.

Polymer sample	T_p °C	E mcal./area unit	Weight mg.	Area units	ΔH mcal.mg.$^{-1}$	Sample conditions.
46/1	62	0.20	14.26	861	12.1	Cryst. overnight @ 51°C
46/1	54,59	0.20	14.26	867	12.2	Air cooled.
66/2	62	0.20	10.86	823	15.2	Cryst. overnight @ 53°C
66/2	62	0.20	10.86	782	14.4	Air cooled.
2T/1	272	0.25	15.71	1137	18.1	Cryst. overnight @ 240°C
4T/1	228	0.24	15.94	900	13.5	Cryst. overnight @ 215°C
4T/1	218,228	0.24	15.94	648	9.7	Air cooled.
5T/1	136	0.21	15.45	615	8.4	Cryst. overnight @ 100°C
5T/1	136	0.21	15.45	639	8.7	Cryst. several days @ room temp.
6T/1	153	0.22	15.62	930	13.1	Cryst. overnight @ 140°C
6T/1	142,153	0.22	15.62	668	9.4	Air cooled
4I/1	109 131,144	0.21	14.18	31 411	6.5	Cryst. overnight @ 90°C
4I/1	131,144	0.21	14.18	406	6.0	Cryst. several days @ room temp.

significant when larger differences between polymers are being considered, and does not appear to be the main source of error. That the results obtained are of some value is indicated by the observed reduction in ΔH which would be expected when slowly crystallised and more rapidly crystallised samples of the same polymer are compared. (i.e. for samples 66/2, 4T/1 and 6T/1.)

In Table 5.19 the highest heats of fusion obtained for each polymer (in cal.g^{-1} and cal./repeat unit) are listed. Values of ΔH_f*, the heat of fusion for the 100% crystalline polymer, are available for some of the polyesters studied as shown. The sources from which these values are taken are listed in column seven of the table. They were obtained using the diluent method proposed by Flory[51]. Values of ΔH_f^* have been used to indicate the % crystallinity achieved in the polymer samples studied.

Table 5.19 Heats of fusion and % crystallinity.

Polymer sample	ΔH cal.g.$^{-1}$	ΔH cal./repeat unit	ΔH_f^* cal./repeat unit	%cryst.	Ref.no.
46/1	12.2	2440	-	-	-
66/2	15.2	3470	-	-	-
2T/1	18.1	3470	5600	62	59
4T/1	13.5	2970	7600	39	3
5T/1	8.7	2040	-	-	-
6T/1	13.1	3250	8500	38	13
4I/1	6.0	1320	10100	13	3

5.4. X-ray diffraction results.

5.4.1. X-ray powder photographs.

The powder type photographs obtained are shown in Figure 5.21. The broader lines observed for some of the polymers indicated that these samples had less perfect crystalline structures. As the number of lines was relatively few, and d values were not very accurate where lines were broad, attempts to obtain any independent evidence concerning crystal structure were unsuccessful. However for 46 and 66 polyesters some indication of structure may be obtained if d values are compared with those available in the literature for other aliphatic polyesters. d values and line intensities were comparable to those obtained for 26 and 2 10 polyesters[72,73,78].
The latter polyesters have been shown to have a monoclinic structure. The length of the unit cell, which contains two adjacent chains, is slightly less than the length of one fully extended repeat unit. From the similarity of the powder photographs it is likely that 46 and 66 polyesters have a similar structure.

Calculated d values are shown in Table 5.20. A visual estimate of relative intensity is also given.

(w-weak, m-medium, s-strong, v.s-very strong, b-broad.)

Table 5.20. d values from powder photographs.

Polymer sample	d A^{o}	Intensity.
46/1 and 66/2	2.1	w
	2.2	m

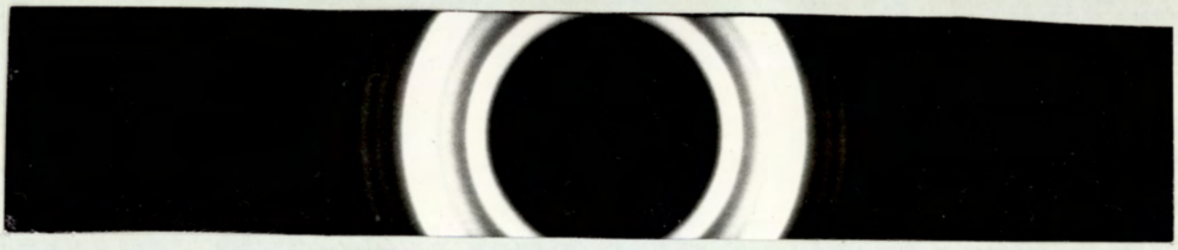
Polymer sample	d A°	Intensity
46/1 and 66/2	2.5	w
	3.0	m
	3.68	s
	4.18	v.s
2T/1	1.7	w,b
	1.8	w
	1.9	w
	2.1	m,b
	2.7	m
	3.4 (d_{100})[85]	v.s,b
	4.0 (d_{110})	v.s,b
	5.1 (d_{010})	v.s,b
4T/1	1.7	w
	1.9	w
	2.0	m,b
	2.2	w
	2.3	w
	2.8	m,b
	3.0	w
	3.50	s
	3.90	s
	4.3	m
	5.12	s
	5.56	s
5T/1	1.1	w
	2.2	w
	3.18	s

Polymer sample	d A^o	Intensity
5T/1	3.44	s
	3.75	s
	4.10	s
	5.14	s
	5.63	s
6T/1	1.8	w
	2.1	w
	2.2	w
	2.3	w
	2.5	w
	3.51	v.s
	3.94	s
	4.84	v.s
	7.0	w
4I/1	1.8	w
	1.9	w
	2.0	w
	2.1	m
	2.6	w,b
	3.3	m,b
	3.60	s
	4.0	w
	4.5	m
	5.27	s
	6.3	m
	7.8	w

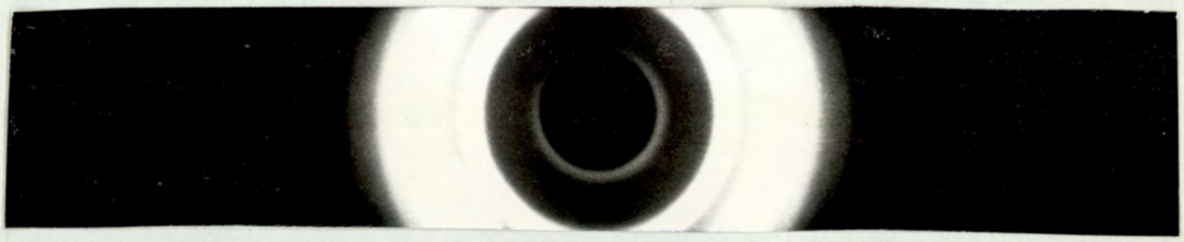
FIG. 5.21. X-RAY POWDER PHOTOGRAPHS.

46/1

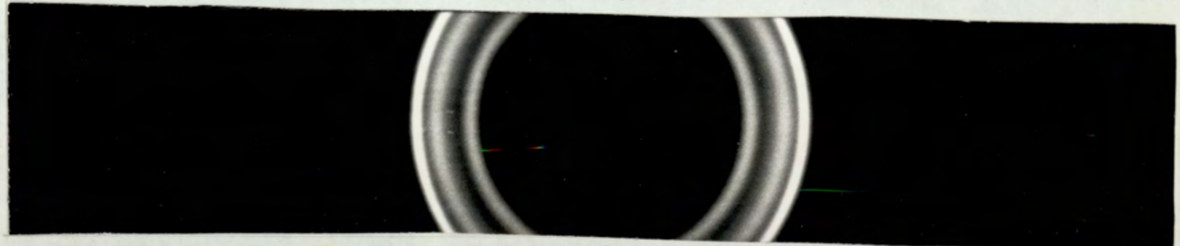
2T/1



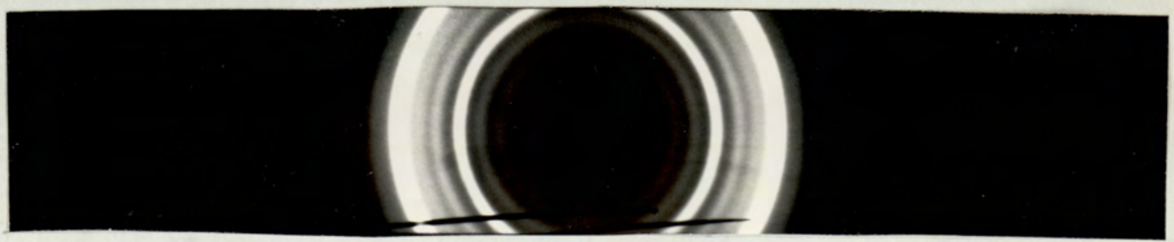
4T/1



5T/1



6T/1



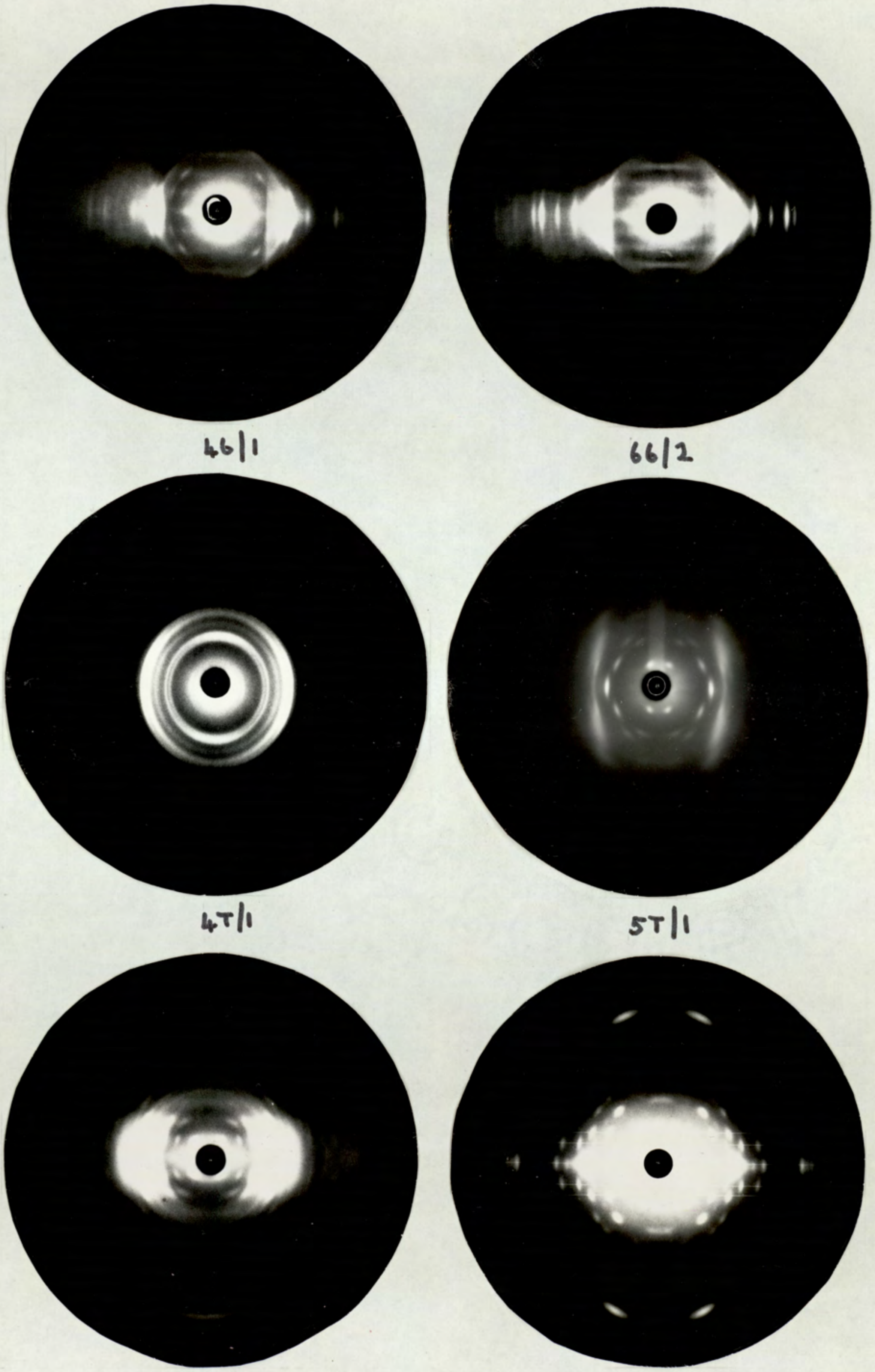
4I/1

5.4.2 X-ray fibre diagrams.

Photographs obtained are shown in Figure 5.22. For samples 4T/1 and 2T/1 the fibres were not drawn sufficiently, so no layer lines were observed. For the remaining samples the identity period, or c distance, was calculated. Results are shown in Table 5.21, together with the crystallographic data available for the polyesters studied, and the length of the extended chain calculated as in Figure 3.8. For polyesters 46, 66, 2T and 6T c is found to be equal to 0.1-1.1 A^{o} less than the calculated repeat distance, indicating a slightly distorted planar zig zag configuration with the indentity period almost corresponding to one chemical repeat unit. For the 4I polyester, when the zig zag structure is drawn out the repeat distance would be expected to correspond to two chemical repeat units. The measured c distance again indicates a distorted planar zig zag configuration. For the 5T polyester again the repeat distance would be expected to correspond to two chemical repeat units. However the measured c distance of 12.2 A^{o} can neither be explained in this way, nor related to one chemical repeat distance, as the distortion would be much higher than that usually observed. Further investigation would be required to account for this value. It is possible that the fibre was not drawn sufficiently to produce a true fibre diagram.

The reduction in chain length in a unit cell has been reported to be constant for a series of aliphatic polyesters, and equal to approximately 0.5 A^{o}.[72,73,75-78] It is thought

FIG. 5.22. X-RAY FIBRE DIAGRAMS.



46/1

66/2

4T/1

5T/1

6T/1

4I/1

Table 5.21 Crystallographic data for polyesters.

Polymer sample.	Unit cell dimensions.						Ref. no.	Crystal system.	Calculated repeat distance A^{o}
	aA^{o}	bA^{o}	cA^{o}	α^{o}	β^{o}	γ^{o}			
46/1			13.7				this work	monoclinic?	14.82
66/1			16.2				this work	monoclinic?	17.34
2T/1	4.56	5.94	10.75	98.5	118	112	82,83	triclinic	10.86
4T/1									13.37
5T/1			12.2						14.62
6T/1	4.57	6.10	15.40	105.5	98.5	114.5	82	triclinic	15.88
			15.3				this work		
4I/1			26.0				this work		13.58

to be due to distortion of the glycol part of the chain[72,73]. For the aromatic polyesters 2T, 6T and 10T the chain length reduction is greater when the number of methylene groups is greater[82]. For the 6T polyester the identity period measured was close to the reported value.

CHAPTER 6.

Discussion.

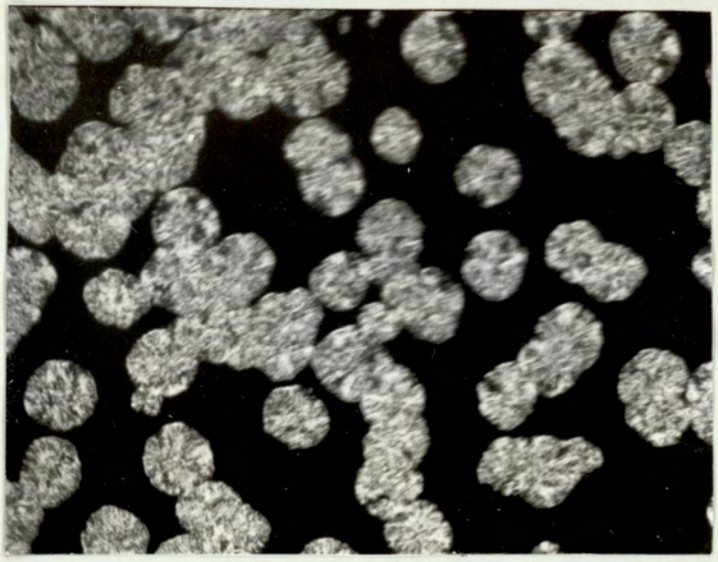
6.1. Crystallisation kinetics of linear polyesters.

6.1.1. Polytetramethylene adipate.

Crystallisation of the 46 polyester appears to be dominated by a primary process having an n value close to 3. According to the Avrami theory this may be explained by heterogeneous nucleation followed by three dimensional growth, or homogeneous nucleation followed by two dimensional growth. The actual situation cannot be determined unequivocally although microscope observations point to the former case, as well developed spherulites present at a given time appear similar in size. Fig. 6.1 shows spherulites which have been grown for 16 hours at 48°C. The predominating effect of a single primary process detected by this method is further indicated by the DSC curves which have $t_{\frac{1}{2}} \triangleq t_{max}$, and are symmetrical in appearance. Although the growth of distinct spherulites could not be observed using those melting conditions used for overall crystallisation rates, this may be merely due to their small size.

Using the programmed microscope it was observed that the large spherulites grown isothermally melted 1-2°C lower than the remaining material, which crystallised on quenching. The latter material melted at 61°C. On cooling the molten sample this crystallised first. As cooling continued, small spherulites developed within the outlines

FIG. 6.1. SPHERULITES IN 46/1 POLYESTER.



Sample crystallised at 48°C.

of the original large ones. The total amount of birefringence was less than that present originally.

The formation of annealed material having a melting temperature lower than a more rapidly crystallised sample has been observed previously by thermal methods[35-39,44]. It has been suggested that the higher melting material is kinetically preferred, while the lower melting material is thermodynamically preferred. This is supported by the microscope observations described for the 46 polyester. Bell and Dumbleton[38] described the higher melting material as form I, and the latter material as form II. The melting temperature of form I is constant, while that of form II increases with increased annealing time or temperature. Bell and Dumbleton showed that the presence of double peaks cannot be explained by the presence of two different crystallite size distributions, as larger crystallites formed by annealing would have a higher melting temperature. They suggested that form I was due to folded chain crystallites while form II was due to crystallites containing extended chains. The increasing melting temperature of form II was then attributed to the increasing size and perfection of crystallites containing linear molecules.

Results for the 46 polyester showed that the material in the form of large spherulites did not crystallise first due to any structural difference (e.g. molecular weight). In such a case the same material would be again expected to crystallise first after melting and subsequent cooling ; in practice the reverse was true. The remaining material crystallises first, probably due to the large number of nuclei present, then nucleation occurs within the outline of the large spherulites. Thus a difference in the actual crystallite form is indicated. Further investigation of this difference is required.

When a sample was crystallised slowly in the DSC cell, then melted, one peak (T_p=62°C) was observed. From the treatment used this would be expected to correspond to form II material. The sample was cooled, then reheated. After the relatively rapid cooling two melting endotherms (T_p=54,59°C) were observed. Further work would be required to determine the nature of these two peaks. It is likely that the peak at 59°C corresponds to that originally observed at 61°C for the quenched material, since rapid cooling was used. Then the peak at 54°C would be due to thermodynamically preferred material, in a less perfect form than that observed by microscopy. No large spherulites would be produced under these conditions. The two peaks were similar in size with the cooling conditions used. According to many of the reported results for different polymers[35-40,42,44] the size and melting temperature of the peak initially at 54°C would be expected to increase on annealing, possibly accounting for the single peak observed at 62°C in the slowly crystallised sample.

Spherulite growth rates were analysed according to the method described by Mandelkern et al[26], and equations (14a) - (17a). Straight line plots were obtained in all four cases using $T_m = 70^\circ C$, indicating nucleation controlled spherulite growth. However the slopes of these lines were not those suggested by Mandelkern to be universal for all polymers. These slopes are a function of the heat of fusion and the surface free energies between the crystal nucleus and liquid. No reason for the constancy of the slope for different polymers has been proposed.

6.1.2. Polyhexamethylene adipate.

An important feature in the crystallisation behaviour of this polymer was a very high nucleation density which prevented the measurement of spherulite growth rates under any of the conditions used. Although this was the case, more stringent melting conditions did reduce the nucleation density. A greater reduction in the rate was observed for this polyester when the melt time was increased from 5 to 20 minutes, than in any other case. (The effect of changing melt time was least in the cases where nucleation density was low, and large spherulites were grown. i.e. 5T, 4I).

For samples 66/1 and 66/2 the crystallisation measured by DSC corresponded to an Avrami equation with n = 2 only at the lowest temperatures used. Price[134] has indicated that n values below 3 often have no significance except during the initial stages of the crystallisation due to assumptions made in the Avrami theory. However in this case the entire process was governed by n = 2, which may then be attributed to fibrillar growth, spherulite formation being prevented by impingement of crystallising centres.

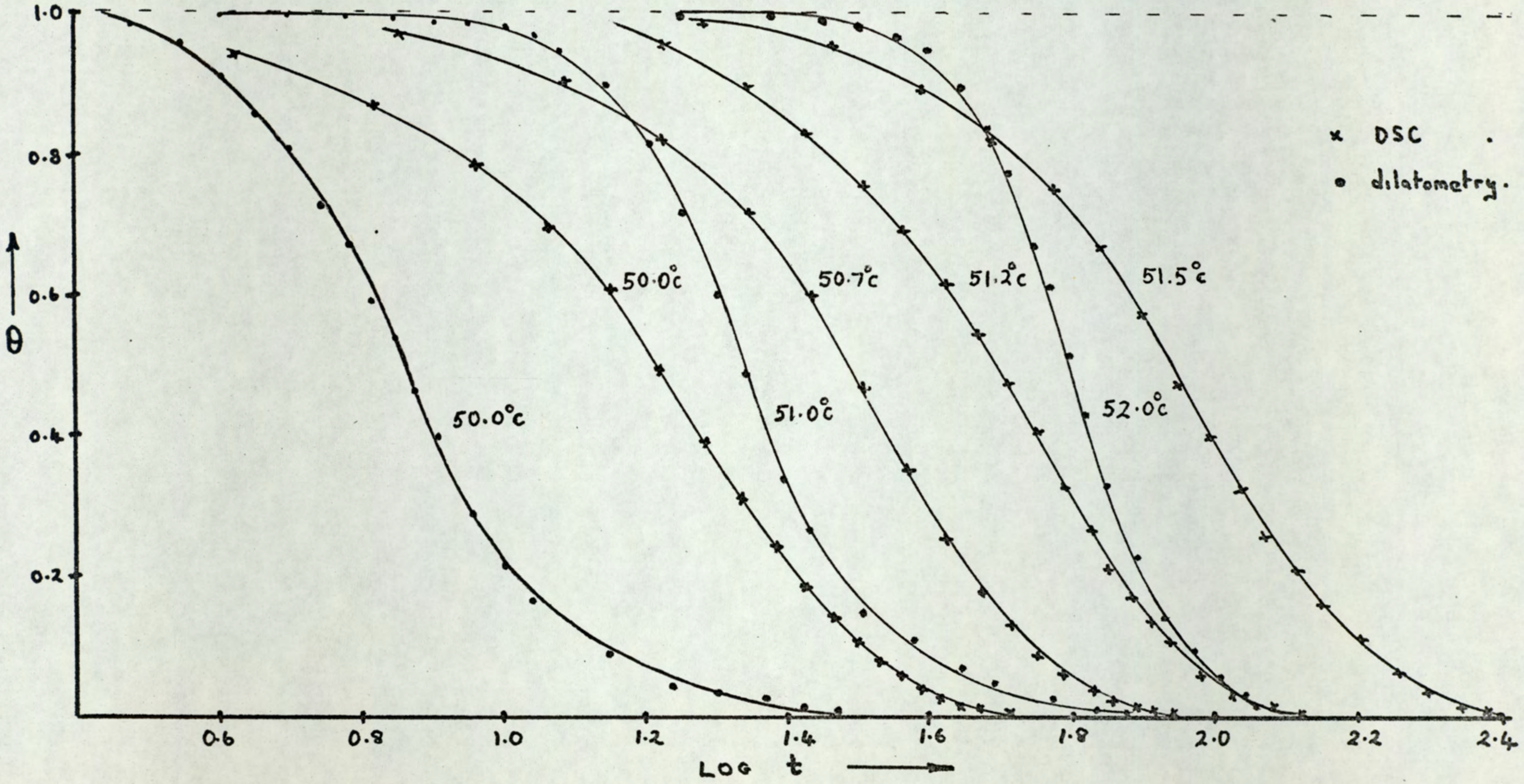
Except for the more rapid crystallisations the behaviour of this polymer was not described by a simple Avrami equation. The calculated 'n' values decreased continuously. This behaviour has been discussed by Hillier [131], who attributes it to two concurrent processes. A primary process with n = 3 or 4 involving spherulite growth is immediately followed by a secondary process when the density within the spherulites increases according to an Avrami equation with n = 1[129,131] or 2[132]. Hillier has tested his theory by fitting experimental results to a modified Avrami equation using a computer program. The secondary crystallisation proposed here is not the slow process normally considered to be proportional to log (time) which continues long after the initial rapid process is completed and will be referred to as the post Avrami process. Results obtained in this work indicate that this is not detected by DSC, which is not sensitive enough to measure very slow changes in crystallinity.

The theory described above may account for the behaviour observed for polyhexamethylene adipate. For sample 66/2 a discontinuity in the Avrami plots occurred in the later stages of the crystallisation (Fig.5.5) and n approached 2. It is possible that the primary process is complete at this stage, and the secondary process alone is being observed. This would indicate a situation similar to that observed for polypropylene [132]. No evidence is available concerning the nature of the secondary process. At lower crystallisation temperatures where $n = 2$ it is possible that the crystallisation is too rapid for spherulite formation. Thus impingement of crystallising centres may occur while these are still in a sheaf-like form.

Sample 66/1 was studied by DSC and dilatometry, but the behaviour observed was different in the two cases as shown in Fig. 6.2, where θ is plotted against log t. This was also shown by Avrami plots; the slopes of lines (although not constant) approximating to the dilatometry results were greater than those fitted to the DSC result.

For polyhexamethylene adipate and polytetramethylene terephthalate which were both studied by the two methods, it was observed, and has been reported previously [115,116] that DSC did not follow the crystallisation to such a high conversion as dilatometry. The post Avrami type of crystallisation, shown by results for 66 and 4T polyesters to account for about 5% of the total volume change, was not detected by DSC. Since results obtained by the two methods for polytetramethylene terephthalate were comparable, this slow crystallisation did not account for the different behaviour detected in the two cases for

FIG. 6.2. CRYSTALLISATION ISOTHERMS FOR POLYESTER 66/1.



polyhexamethylene adipate. It appeared that the difference was due to the high temperature coefficient of crystallisation for the 66 polyester. Using dilatometry it is likely that crystallisation occurred as the polymer sample was cooled to the crystallisation temperature, so the crystallisation was not isothermal and attempts to analyse results would not be meaningful. This was also indicated by the isotherms. Those obtained by dilatometry were not entirely superimposable. Using DSC cooling could be effected much more easily, as the sample was much smaller, and the aluminium sample pan could be cooled much more rapidly than the bulky dilatometer. The DSC results were considered to be more valid.

Godovskii and Slonimiskii[113] discussed differences between dilatometry and thermal results for isotactic polypropylene. They found n values of 3 and 2 in the two cases respectively and they suggested that dilatometry detected spherulite formation, while the thermal method detected the formation of individual crystallites. However, different samples of polypropylene were studied by the two techniques, and that used for dilatometry was extracted in n-heptane. It seems likely that different results could be due to different nucleation characteristics of the samples rather than due to the different techniques.

For a slowly crystallised sample of 66/2 one melting endotherm at 62°C was observed. A similar peak was observed after the sample was allowed to cool, then re-melted. For this polymer the crystallisation kinetics indicated that some transformation of the crystalline region occurs during crystallisation. It is possible that no further reorganisation occurs during slow crystallisation, so no change in the melting behaviour is detected.

6.1.3. Polyethylene terephthalate.

Results obtained by DSC for sample 2T/1 indicated that the crystallisation was governed by an Avrami type equation with n close to 2. It has been reported[93,133] that n is 2 or 3 for crystallisation at temperatures below that of maximum rate, and 3 or 4 at temperatures above T_{max}. The actual value of n depends on the fusion conditions. Measurements in this work were only made at the higher temperatures. The difference in n values appears to be due to nucleation density. Morgan[133] observed that samples crystallised at the lower temperatures had a birefringent granular structure when n = 2, while distinct spherulites were observed in those crystallised at higher temperatures. In the case where n = 2 he assumed that fibrillar growth occurred, and that spherulite growth was prevented by the impingement of crystallising centres. The n value of 2 obtained in the present work may be attributed to the same cause as in all cases the nucleation density was high and distinct spherulites were not observed. The high nucleation density was not due to fusion conditions which were similar to those used by Morgan et al. However these workers used samples from polymer which had been quenched immediately after preparation to prevent thermal history effects. It appears that the high nucleation density observed in this work may be due to the catalyst used in preparation (there was no mention of a catalyst in the preparation used by Morgan et al). Alternatively the crystallisation of the polymer which occurred after preparation created nuclei which were not subsequently destroyed. A high nucleation density was also observed in the sample of polyethylene terephthalate supplied by I.C.I.

In view of the above discussion the more rapid crystallisation rates observed in this work were not unexpected. Results are shown in Table 6.1. The fusion conditions were similar in the two cases. The K values obtained in this work were not considered to be very accurate as n was found to decrease as $t_{\frac{1}{2}}$ increased. However, they may be used for purposes of comparision. It appears that discrepancies are very large, but since in this work the K values were measured at degrees of supercooling from 35°-50°, it is obvious from Fig. 1.4 that behaviour of the different polyesters may still be compared irrespective of different nucleation behaviour from sample to sample.

Table 6.1. Measured and literature values of crystallisation rate for polyethylene terephthalate.

$T^{o}C$	K (this work)	K^{93}
234.6	9.20×10^{-4}	-
235	-	5.57×10^{-7}
236	-	6.04×10^{-7}
236.8	1.43×10^{-3}	-
239.8	2.46×10^{-3}	-
240	-	5.05×10^{-8}

Mitsuishi and Ikeda[153] also observed the growth of spherulites, and n values of 3 for samples of polyethylene terephthalate crystallised at 238°C. Cobbs and Burton[69] obtained an n value close to 2 at temperatures of 210°C, and 230°C but their samples were initially at room temperature. It has been reported [119,123] that a higher nucleation is observed when samples are crystallised after heating from room temperature, instead of after cooling from the melt. This supports the theory that a higher nucleation density causes a change in n from 3 or 4 to 2.

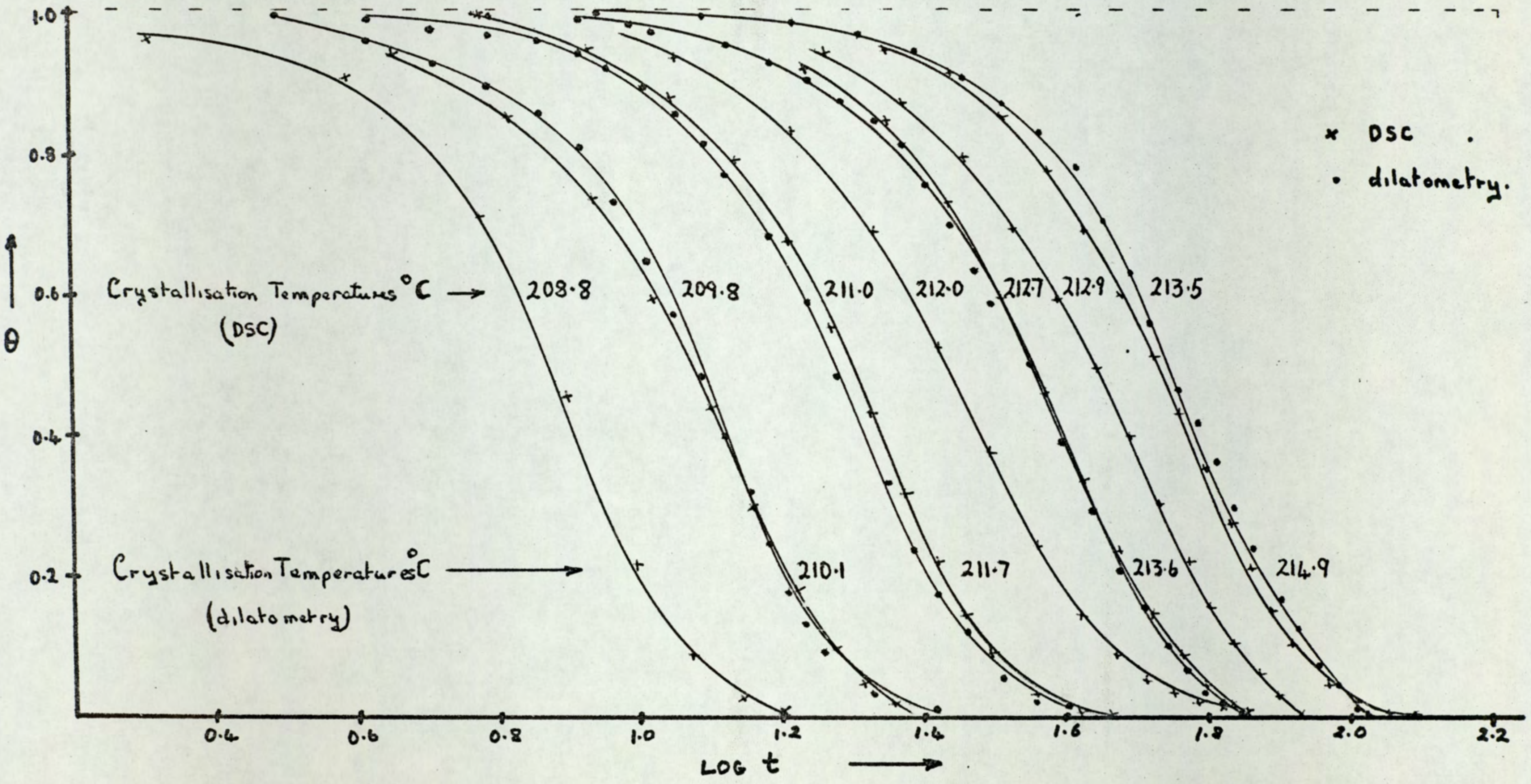
When a sample of 2T/1 was crystallised overnight at 240°C, then melted, one endotherm was observed at T_p=272°C. After cooling and reheating the amount of crystallisation which occurred was so small that the position and number of endotherms could not be distinguished. Multiple melting peaks have been reported for this polymer[36,44,46]. A lower temperature melting peak increases in size and perfection as the polymer is annealed. Cates and Lawton[44] reported that after crystallisation at a lower temperature, followed by several hours annealing at 235°C, a single sharp peak is observed at 271°C as in the present work. This was due to the melting of form II material. The same melting peak was observed when the sample was crystallised directly at 235°C[44] or 238°C[153]. Similar observations were made by Roberts[46] who made a detailed study of the melting behaviour of this polymer. It appears that at sufficiently high crystallisation temperatures the more stable crystalline form is produced directly.

Mitsuishi and Ikeda[153] compared samples of polyethylene terephthalate crystallised at 120°C and 238°C. They found that the crystallite thickness in the (100) direction was $\leqslant 40$ A° for samples crystallised at 120°C, which have an unchanging melting temperature, and may therefore be considered to be of form I. Crystallites formed at 238°C had a thickness of more than 200 A°. Thus the thermodynamically preferred crystalline form contains larger crystallites when time is allowed for perfection of these. As this form initially has a lower melting temperature crystallites must at first be smaller than those in the form I material. Two different types of crystallites are indicated. Since spherulite formation was observed by these workers, but not in the present work, and different n values were found in the two cases, although the melting temperature was the same, it does not seem likely that the different forms can be explained by differences on the scale of spherulites. Again, different types of crystallites are suggested.

6.1.4. Polytetramethylene terephthalate.

For sample 4T/1 crystallisation fitted to an Avrami equation with a constant but fractional n value of 2.6-2.7. Using a value for h_∞ obtained as described previously (i.e. excluding the slow, post Avrami crystallisation) the same n values were obtained by DSC and dilatometry. Crystallisation isotherms obtained by the two methods were of the same shape (Fig.6.3.). Considerable controversy has arisen in the assignment of fractional n values. They have been attributed to the presence of potential nuclei having a specific probability of developing[9,119], and to the occurrence of an Avrami process with $n = 3$ or 4, followed by an increase of crystallinity within the spherulites[131].

FIG. 6.3. CRYSTALLISATION ISOTHERMS FOR POLYESTER 4T/1.



Banks et al[154] suggested that two simultaneously occurring processes do not, in general, account for a constant fractional value of n although the combination of processes governed by n=3 and n=4 fitted the experimental data for polydecamathylene terephthalate[32].

From the results available for polytetramethylene terephthalate it is not possible to draw definite conclusions to account for the fractional n value. From the linear growth rate of spherulites observed an n value of 3 or 4 would be expected. It is possible that the observed results may be explained in a similar way as those for polymethylene [119,130]. ie. heterogeneous nucleation followed by a first order process by which the density of the spherulites increases.

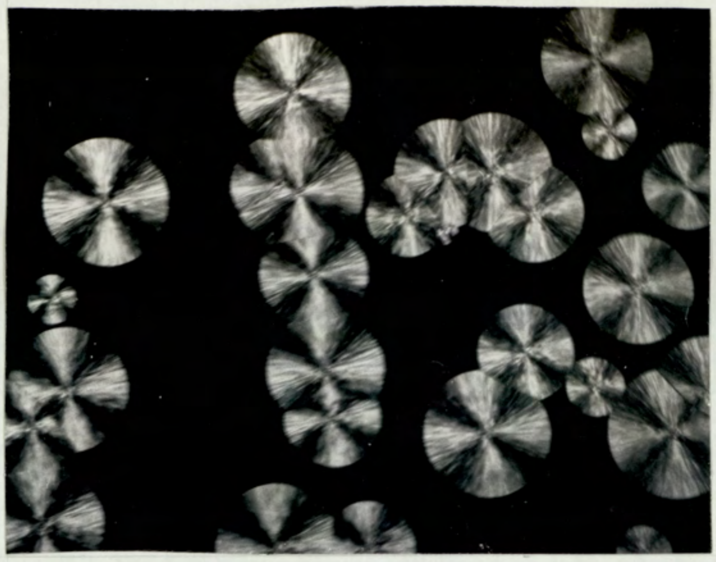
On melting a slowly crystallised sample of polytetramethylene terephthalate, one peak was obtained at T_p= 228°C. When the sample was cooled, then reheated, peaks were obtained at 218°C and 228°C. The latter was larger in area. Further experiment was required to show whether the lower temperature peak was due to the more stable form, as for polyethylene terephthalate. A single peak was obtained for all the isothermally crystallised samples. From the fractional n value it is possible that some transformation of the crystalline material occurs during these crystallisations. Again, further evidence is required.

Spherulite growth rate results were analysed according to equations (14a) - (17a). In this case straight line plots, having the slopes indicated by Mandelkern et al[26] were obtained with $T_m = 242^\circ C$. This was the estimated melting temperature from similar plots with log $(1/t_{\frac{1}{2}})$ as ordinate (Fig.5.11). Mandelkern concluded that the melting temperature used in their analyses to yield straight lines of given slope was a reasonable estimate for the thermodynamic polymer melting temperature. They compared results with independently estimated values where possible. Results for sample 4T/1 indicate that the method used in this work may also be considered to give reasonable values for T_m^*.

6.1.5. Polypentamethylene terephthalate.

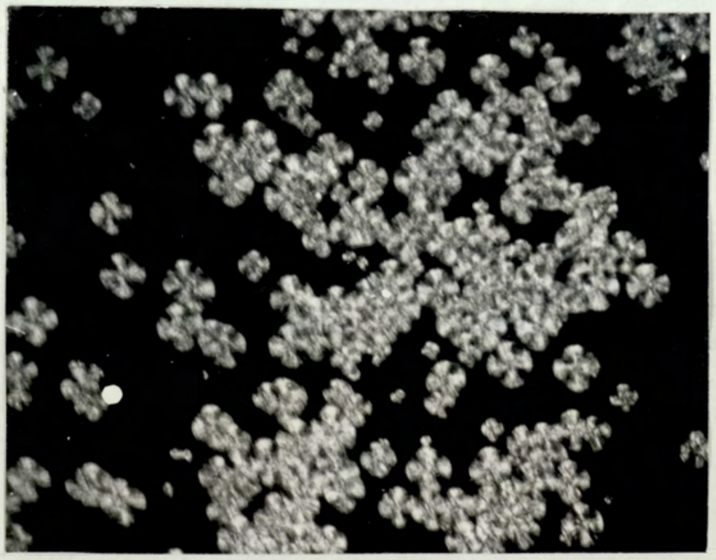
The crystallisation of this polymer did not follow a simple Avrami type equation. n Values were found to be rather inconsistent. Other experimental observations indicated that the crystallisation kinetics were complex. It has been reported (section 5.1.5) that the amount of crystallisation occurring increases on repeated crystallisation. From plots showing spherulite growth (Fig.5.13) spherulites appear to have a finite size at zero time. Both these observations support a heterogeneous nucleation process. However if a crystallising sample is observed under the microscope during isothermal crystallisation many different sizes of spherulites are seen, indicating a homogeneous process. (Fig. 6.4). Some of these are relatively large (100μ) and well defined. It seems that a relatively small number of heterogeneous nuclei are present, and that additional nuclei are formed during the

Fig. 6.4. Spherulites of 5T/1.



Sample crystallised at 110°c.

Fig. 6.5. Spherulites of 4I/1.



Sample crystallised at 110°C.

course of crystallisation. Therefore lack of Avrami behaviour in this polymer is probably due to variations in nucleation throughout the sample, leading to different mechanisms.

Only one peak at $T_p = 136^\circ C$ was observed when a slowly crystallised sample of 5T/1 was melted. It appeared that this sample had not been crystallised rapidly enough to obtain any different crystalline form.

For polypentamethylene terephthalate the temperature of maximum crystallisation rate was estimated to be 68-70°C. Then $T_{max}/T_m^* = 0.83$. Such a value is predicted by equations of type (8)[9,28].

Spherulite growth rates were analysed according to equations (14a) - (17a). Straight lines were obtained if a melting temperature of 155°C was used. This is rather high compared to the observed melting temperature. The slopes of plots (14a) and (15a) did not correspond to the reported values[26]. Plots of (16a) and (17a), which represented the dependence of spherulite growth rate on $T_m^2/T\Delta T^2$ only had the predicted slope if a melting temperature as high as 158°C was used.

61.6. Polyhexamethylene terephthalate.

Crystallisation was governed by an Avrami type equation with a constant but fractional n value of 2.6 - 2.7. The significance of such a value has been discussed for polytetramethylene terephthalate (section 6.1.4). For this sample spherulite growth rates were not obtainable.

On melting the slowly crystallised polymer one peak was observed at 153°C; on melting the cooled sample peaks were present at 142°C and 152°C. Previously only one peak was reported for this polymer[82]. Again, the melting behaviour is analogous to that of sample 4T/1. Only one endotherm was observed when isothermally crystallised samples were melted.

6.1.7. Polytetramethylene isophthalate.

Allowing for experimental scatter, crystallisation of this polymer was governed by an Avrami type equation with n equal to 2.5. Large distinct spherulites could be obtained (Fig. 6.5), and growth rates were linear, so an n value of 3 or 4 would be expected, as for sample 4T/1. Since spherulites appeared to have a finite size at zero time, heterogeneous nucleation with $n = 3$ seemed most likely. An additional secondary process is again indicated.

Crystallisation rate and spherulite growth rate measurements were made above and below the temperature of maximum rate which was 90-92°C. Then $T_{max}/T_m^* = 0.84$ as predicted by equations of type (9).

The 4I polyester did not crystallise when it was air cooled from the melt. When a sample was crystallised overnight at 90°C melting peaks were observed at 109°C, 131°C and 144°C. When the same sample was crystallised for several days at room temperature the smallest peak at 109°C was absent. All the material had crystallised in the higher melting forms. In both cases the peak at 131°C was smaller that that at 144°C; after the slower crystallisation the lower temperature peak was relatively smaller than after overnight crystallisation indicating that this was due to a less perfect form. This was confirmed when a sample which had been at room temperature for several months was melted. One broad peak was present at the higher temperature.

An attempt was made to analyse spherulite growth rates obtained at temperatures above T_{max} in terms of equations (14a)-(17a). It did not appear that results would fit to straight lines having the reported slope[26]. Thus the behaviour suggested to be typical for all polymers only applied to polytetramethylene terephthalate among those studied.

6.1.8. Correlation between crystallisation mechanism and melting behaviour.

The observations made indicate that there may be some correlation between the crystallisation mechanism and melting behaviour. Further experimental evidence is required, but the available results will be summarised.

1. For the 66 polyester n decreased. One melting peak was observed for slowly crystallised and quenched samples. This may be due to two crystallisation processes both too rapid for separation by quenching the polymer.
2. For the 46 polyester n was constant and equal to 3. One melting peak was obtained for a slowly crystallised sample; two were observed when crystallistion was more rapid. It is possible that the more stable crystalline

form is produced directly on isothermal crystallisation.

3. For the 2T polyester n was constant and equal to 2. One melting peak was observed for the slowly crystallised sample. Two melting endotherms have been reported for more rapidly crystallised samples. The single peak has been shown to represent the more stable crystalline form, which is known to be produced directly under the crystallisation conditions used.
4. For 4T and 6T polyesters n was constant and equal to 2.6-2.7. One melting peak was obtained from a slowly crystallised sample, and two from more rapidly crystallised samples. Results are not available to show whether the more stable form is produced directly, or by transformation of the kinetically preferred material in these cases.
5. For the 5T polyester n was not constant. Only one melting peak was observed with the conditions used, but these favoured slow crystallisation in both cases.
6. For the 4I polyester n was constant and equal to 2.5. Crystallisations were necessarily slow. It appeared that the lower temperature melting peaks were due to less perfect (and probably smaller) crystallites. This behaviour was probably due to the much slower crystallisation of this polymer.

6.2. Effect of structural changes on crystallisation and melting.

Parameters used in comparing crystallisation behaviour include the degree of supercooling and the crystallisation range, defined as follows.

The degree of supercooling corresponding to a given crystallisation half time will be smallest for the polymers which crystallise most readily. ΔT_{40}, for example, will be used to represent the degree of supercooling corresponding to $t_{\frac{1}{2}}$ = 40 minutes. These values were obtained from Fig. 6.6 which shows the variation of $t_{\frac{1}{2}}$ with ΔT for the polyesters studied. A similar plot of $t_{\frac{1}{2}}$ against ΔT^* could have been used, but this would not have altered the comparison between the different polyesters.

The crystallisation range may be represented as the temperature difference which changes the rate from one selected value to another. For example, the crystallisation range $_{20-50}$ $^{\circ}$C is used to refer to the difference in crystallisation temperature between isothermal runs with $t_{\frac{1}{2}}$ equal to 20 minutes and 50 minutes. Such a value may be used as a measure of the temperature coefficient of crystallisation rate. From the graph showing the temperature dependence of $t_{\frac{1}{2}}$, when this can be measured over a wide range of temperature (Fig.5.12), the slope is greatest where $t_{\frac{1}{2}}$ is furthest from the maximum rate. It follows that, when the temperature difference between selected $t_{\frac{1}{2}}$ values is compared, the highest maximum rate would be expected when this difference is smallest. Thus it may be shown which polymers are potentially capable of crystallising the fastest, although the maximum rates are much too fast for measurement. Experimentally, only the same range of rates may be measured for each polymer.

6.2.1. Effect of increasing chain length in aliphatic polyesters.

Some of the features of the crystallisation behaviour of polytetramethylene adipate and polyhexamethylene adipate are shown in Table 6.2.

Table 6.2. Crystallisation and melting behaviour of aliphatic polyesters.

Polyester	46/1	66/2
T_m °C	60	61
T_m^{*} °C	70	65
ΔT_{40} °C	14	9
Cryst^{n}range$_{20-50}$ °C	2.5	0.9
Avrami number	3	-

Observed melting temperatures of the two polyesters are similar, although the estimated melting temperature of the 46 polyester is higher. The similarity is due to two opposing factors affecting the melting temperatures of linear aliphatic polyesters. As the number of carbonyl groups in a chain decreases, the polarity decreases and also the melting temperature. However polyethylene has a higher melting temperature than the aliphatic polyesters. This is approached as the concentration of carbonyl groups is reduced, so the melting temperature tends to increase. On a plot of melting temperatures against the number of methylene groups in the glycol, for a series of polymethylene adipates, the 46 and 66 polyesters appear to lie close to the minimum in the curve. From the results quoted for various aliphatic polyesters[155], the glass transition temperatures are also likely to be similar.

The crystallisation behaviour of the two polymers was found to differ. For the 66 polyester a lower value of ΔT_{40}, and a smaller crystallisation range, compared with the 46 polyester indicate that the former polymer crystallises more readily and more rapidly. This is not due to differences in crystal structure as the X-ray powder photographs for the two samples are identical. The structure implied has already been discussed.

It appears that nucleation occurs more readily in the 66 polyester. This is supported by the high nucleation density observed by microscopy. Since an increased melt time (from 5 to 20 minutes) decreases crystallisation rate more for this polymer than any of the others, residual order in the melt was indicated. However the very stringent melting conditions described did not decrease the nucleation density sufficiently to observe spherulite growth.

As the high nucleation density was found for samples 66/1 and 66/2 it was not considered to be due to molecular weight, or to the preparative conditions used. (Sample 66/1 was prepared by reacting adipic acid and hexamethylene glycol in the absence of a catalyst for a total time of 50 hours; it had a molecular weight of 5000. Sample 66/2 was prepared from the glycol and dimethyl terephthalate with a catalyst present, and had a molecular weight of 16,500. The reaction time was 7 hours.) Thus the higher nucleation density in the 66 polyester compared to the 46 polyester was attributed to molecular structure.

The greater flexibility of the longer glycol chain must significantly affect the crystallisation behaviour. The 66 repeat unit is more flexible as the concentration of ester groups is lower. These groups have been shown to be stiffer, i.e. they have a greater energy barrier to rotation than methylene groups[14]. Results for polyethylene[27,128] indicate that flexibility is not the only factor which facilitates the nucleation process. The crystallisation range$_{20-50}$ was found to be 1.5-2.0°C and ΔT_{40} was 11°C for this polymer. Therefore polyethylene crystallises more readily than polytetramethylene adipate, but less readily than polyhexamethylene adipate., although the overall differences are only small. It appears that ease of crystallisation, like melting temperature depends on a number of factors. In this case chain flexibility and polarity both appear to be contributing factors. It is conceivable that polar groups which enhance interchain cohesion also favour crystallisation.

It is considered that the rapid crystallisation of the 66 polyester also affects the crystallisation kinetics. For the 46 polyester, where the nucleation density is lower distinct spherulites may be observed, and the Avrami integer n is equal to 3.

The change in crystallisation behaviour caused by the introduction of two methylene groups is also observed for the aromatic polyesters. It demonstrates the sensitive balance of factors which affect crystallisation.

Reported results for related aliphatic polyesters may be considered briefly. The measurement of spherulite growth rates, and observation of different types of spherulites for polyethylene adipate[90,92] indicate that this has a lower nucleation density, and is more like the 46 than the 66 polyester, which would be expected. Although overall crystallisation rates have been quoted for polydecamethylene adipate[28], direct comparison of results is not possible, as slower rates were measured using dilatometry.

6.2.2. Effect of increasing aliphatic chain length in aromatic polyesters.

These are compared in Table 6.3.

Sample 5T/1 involves an additional effect and is discussed in section 6.2.4.

When the 2T, 4T and 6T polyesters are compared the decreasing melting temperature and glass transition temperature with increasing aliphatic content is noted. While the greatest change in T_m and T_g occurs after the 4T polyester in the series, the main change in crystallisation behaviour occurs immediately after the 2T polyester. The crystallisation behaviour of the 4T and 6T polyesters is similar. While these samples crystallise rapidly, the 2T polyester may be quenched without crystallisation occurring.

The differences in crystallisation and melting behaviour with increasing aliphatic chain length must again be due to the balance of factors on which these depend. The high melting and glass transition temperatures of polyethylene terephthalate are due to the rigidity of the molecule; this also makes crystallisation more difficult. When the number of methylene groups in the glycol is increased to 4, the increased flexibility of the molecule promotes ready crystallisation at the expense of melting temperature. As for the aliphatic polyesters it appears that flexibility has

Table 6.3. Crystallisation and melting behaviour of aromatic polyesters.

Polyester	2T	4T	5T	6T
T_m ^{o}C	276	234	142	156
T_m^{*} ^{o}C	283	242	150	162
T_g ^{o}C	115[81] 110[156]	80[81,156]	45[81,156]	50[156] 45[81]
ΔT_{40} ^{o}C	38	21	46	19
cryst^{n} range$_{20-50}$ ^{o}C	4.9	2.3	16.7	2.8
Avrami number	2	2.6-2.7	-	2.6-2.7
Mean interfacial free energy $\bar{\sigma}$ erg.cm^{2}.	5.3	5.6	-	5.0
ΔH_f^{*} cal./repeat unit	5600	7600	-	8500
ΔH_f^{*} cal.g.$^{-1}$	29.2	34.6	-	34.3
ΔS_f^{*} cal./^{o}K/repeat unit	10.2	15.0	-	19.5
ΔS_f^{*} cal./^{o}Kg.$^{-1}$	0.053	0.068	-	0.079

(The value of 45^{o}C for the glass transition temperature of the 5T polyester seems rather high as crystallisation rates were measured below this temperature.)

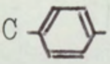
ΔS_f^{*} is the entropy of fusion and is equal to $\Delta H_f^{*}/T_m^{*}$.

Both ΔH_f^{*} and ΔS_f^{*} are expressed per gram of polymer for comparison purposes.

more effect on crystallisation than on melting temperature. Farrow et al[81] have shown that configurational changes in the glycol unit in 2T, 6T and 10T polyesters occur on crystallisation. The increased possibility for such changes in a longer glycol chain may contribute to the crystallisation behaviour.

When the number of methylene groups in the glycol is increased from 4 to 6, a large decrease in melting temperature is observed, but the change in crystallisation behaviour is only small. Further increase in the number of methylene groups has very little effect on the melting temperature (Table 1.2). The length of various chain units appears critical. These are shown in Table 6.4. They were calculated assuming the normal bond lengths and angles (section 3.4.2.)

Table 6.4. Lengths of chain units.

Unit	Length A^{O}
$-O(CH_2)_2O-$	3.63
$-O(CH_2)_4O-$	6.13
$-O(CH_2)_6O-$	8.65
-OC  CO-	4.87

The sharp contrast in crystallisation behaviour between the 2T polyester and the 4T and 6T polyesters may occur because the flexible unit is the shorter one in the former case, and the longer one in the two latter cases. This would not expected to be so significant when melting temperatures are considered. These will be affected by the concentration of ester groups in the chain. Additional evidence concerning the effect of the proportion of rigid groups in the repeat unit would be of interest..

Differences in behaviour were not considered to be due to crystal structure. 2T, 6T and 10T polyesters are known to crystallise with a triclinic unit cell[81-83]. It seems unlikely that a different crystal system would be observed for 4T.

As for the aliphatic polyesters a non-fractional Avrami integer is obtained where the crystallisation may be described as less rapid.

The value of the mean interfacial free energy $\bar{\sigma}$ may be expected to give some information concerning nucleation processes for the different polyesters, but all the values calculated were of a similar order. It is possible that separate values of σ_u, the Lateral free energy/repeating unit and σ_e, the excess interfacial energy/repeating unit as it emerges from the crystal face normal to the chain direction, are required before any conclusions can be drawn.

When thermodynamic properties are considered, the heat of fusion appears to be significant in determining the crystallisation and melting behaviour. Comparison of the heats of fusion expressed in calories per gram indicates that the value for the 2T polyester is smaller than the values for the 4T, 6T (and 10T) polyesters which are similar to one another. This is not a reflection on the experimentally determined quantities, which have been obtained by independent methods[3,13,59,60].

The significance of the value of ΔH_f^* has been discussed by Allen[157], but no definite conclusions were reached. It appears in the present work that factors determining this value also determine the crystallisation behaviour, as 2T, having a lower ΔH_f^* behaves differently from the other aromatic polyesters studied. Once again it seems that the balance of factors should be considered, including flexibility and intermolecular forces. These forces may be measured in terms of molar cohesion energies[4]. They decrease steadily as the number of methylene groups in the chain increases, so do not alone account for the lower heat of fusion of polyethylene terephthalate, or its slower crystallisation. Thus the rigidity of the molecule appears to be the major factor.

Allen has attributed the decrease in melting temperature in the terephthalate series of polyesters to a faster increase in the entropy of fusion than the heat of fusion. This is explained by identifying large heats of fusion with strong intermolecular forces, and the entropy of fusion with chain flexibility. It is then assumed that molecular cohesion is not greatly affected by the introduction of more methylene units, while the number of possible configurations available to the molecule will increase, and account for the change in ΔS_f^*. Results in Table 6.3 show that ΔS_f^* (expressed in cal./^oK g.$^{-1}$) increases steadily with the number of methylene groups in the aliphatic chain, while ΔH_f^* increases from the 2T to the 4T polyester, then attains a constant value. Thus the melting temperatures also require an explanation in terms of ΔH_f^*.

For polyethylene terephthalate it has been indicated that the growth of sizeable spherulites is dependent on the thermal history of the sample. For this reason the presence of measurable spherulites in the 4T polyester only was not felt to be significant. Even in this polymer an increased melt temperature was required, and the nucleation density was high.

Sharples and Swinton[32] measured overall crystallisation rates for polydecamethylene terephthalate. These workers reported high nucleation densities in some of their samples, but selected for measurement samples in which resolvable spherulites were obtained. They prepared the 10T polyester from decamethylene glycol and terephthaloyl chloride, so did not use a catalyst. The crystallisation range$_{20-50}$ was found to 2.3°C and ΔT_{40} was 17°C in agreement with the observations for 4T and 6T polyesters in the work. ΔT_{40} decreases on increasing the number of methylene groups in the chain. Thus as the aliphatic unit increases in length the crystallisation behaviour approaches that of the aliphatic polyesters.

For the 10T polyester n was found to be temperature dependent and varied between 2.7 and 4.0 as the crystallisation temperature increased. The results obtained at the higher temperatures (i.e. n between 3 and 4) were attributed by Hillier[131] to the rapid growth of spherulites corresponding to $n \simeq 4$, followed by an increase in density within these according to a first order process. At the lowest temperatures used, where n was between 2 and 3 it is possible that a heterogeneous process predominates. This situation was observed at all crystallisation temperatures for the 4T and 6T polyesters studied. Overall crystallisation rates measured for these corresponded to those obtained at the lower temperatures for polydecamethylene terephthalate.

6.2.3. Effect of introducing an aromatic ring.

This effect may be observed by comparing 46 with 4T and 66 with 6T polyesters. It should be noted that there is also a reduction in the length of the chemical repeat unit of $1.45\ A^{o}$ brought about by the introduction of the aromatic group (Table 5.21).

Features of the crystallisation behaviour of the polymers are shown in Tables 6.2 and 6.3. The considerable increase in the melting temperatures on introducing an aromatic group has already been discussed. It is thought to be due to a much lower entropy of fusion resulting from the reduced number of conformations available to the aromatic chain in the molten state.

When the crystallisation behaviour of samples 46 and 4T is compared ΔT_{40} is found to be larger for the aromatic polymer, while the crystallisation range is found to be
20-50
of a similar order. The larger supercooling required for the same crystallisation rate would be expected for the more rigid polymer. A similar crystallisation range indicates that the polymers are potentially capable of

crystallising at a similar maximum rate. This behaviour appears to be related to the critical nucleus formation. It seems that a nucleus of critical size is not achieved so easily for the 4T polyester. Its formation must depend on chain flexibility. Once a nucleus is formed, crystallisation proceeds equally rapidly in the two cases, and does not appear to be hindered by the more rigid chain in the 4T polyester. Other factors such as polarity and chain length which are similar for the two polymers may then be significant.

Since it is not known whether the structure of the nucleus is related to the crystal structure of the polymer, it is not obvious whether the latter affects crystallisation rate. However since similar maximum rates are indicated it seems rather unlikely that the different crystal structures of the polyesters are having any effect.

The 66 and 6T polyesters crystallise faster than the 46 and 4T polyesters respectively, although the difference is smaller for the aromatic polyesters. When 66 and 6T polyesters are compared a larger degree of supercooling to achieve the same rate of crystallisation is again observed for the aromatic polymer. In this case a greater maximum rate is indicated for the 66 than the 6T polyester. Thus flexibility possibly has some effect on the growth of nuclei as well as on nucleation.

6.2.4. Effect of an odd number of methylene groups.

This is shown by the series of polyesters 4T, 5T and 6T (Table 6.3). The presence of an odd number of methylene groups in either the acid or glycol forming a polyester is known to result in a lower melting temperature than that of related 'even' polyesters. This is thought to be due to the increased difficulty in packing which occurs in the 'odd' polyesters resulting in reduced interchain cohesion. It was therefore expected that crystallisation would not proceed so easily in the 5T polyester as in the 4T and 6T polyesters.

In practice the crystallisation behaviour was changed even more than might have been expected. 5T could readily be obtained in an amorphous form, unlike the other two polyesters which crystallised on cooling in liquid nitrogen. In 5T well defined spherulites could be grown, and isolated in an amorphous matrix if a crystallising sample were quenched. ΔT_{40} was 46°C, compared to about 20°C for the 'even' aromatic polyesters, and the crystallisation range$_{20-50}$ for 5T was also larger. The maximum rate corresponding to $t_{\frac{1}{2}} = 15$ minutes at 68-70°C was measurable; rate measurements could be made above and below this temperature.

It is apparent that an odd number of methylene groups has an even more significant effect on crystallisation than on melting. There are various possible causes and the information available is not sufficient to indicate the major one.

Courtaulds models of 4T and 5T repeat units indicate that rotation in the latter is more restricted due to steric hindrance, so it is possible that chain rigidity is again an important factor in determing crystallisation rate. The other factors in reducing rate depend on the chain configuration in the crystalline 5T polymer. Two separate experiments resulted in an identity period of 12.2A$^{\circ}$. The length of the chemical repeat unit is 14.62A$^{\circ}$. There are two possible explanations. If this value is the true identity period, a severely distorted zig-zag configuration, probably to the extent of helix formation is indicated. In such a case interchain cohesion would be considerably reduced, which could cause reduction in crystallisation rate. Alternatively, it is possible that samples used to obtain the fibre diagrams were not fully drawn so did not give the true identity period. If the chain was actually in a planar zig-zag configuration, the identity period would be expected to approximate to two chemical repeat units. This reduced symmetry may be effective in reducing crystallisation rate. The former situation seems to be more likely with the results available at present.

6.2.5. Effect of introducing a m-substituted aromatic ring.

Conix and Van Kerpel[3] have discussed the effect of a m-substituted aromatic ring in reducing melting temperature and hindering crystallisation. They concluded that the difficulty in crystallising these compounds was due to the shape of the molecules rather than their reduced symmetry. They attributed the slow crystallisation to the bulk of the benzene nucleus protruding from the main chain. The reduction in melting temperature from the 4T (234°C) to the 4I (156°C) polyester was found to be due to a higher entropy offusion in the latter case. The heat of fusion is lower for the 4T polyester, so does not account for its higher melting temperature. The different heats of fusion for the two polymers were suggested[3] to be due to different chain configurations but this work has indicated that the 4I chain has a planar zig-zag form. The same form is expected for the 4T polyester by analogy with other aromatic polyesters.

Conix and Van Kerpel attributed the higher entropy of fusion of isophthalates to a greater degree of configurational freedom achieved on melting. This may now be accounted for in terms of the greater volume change which occurs when the 4I polyester melts. Kirshenbaum[60] discusses the calculation of the entropy of fusion of various polymers. This may be considered to consist of two contributions. One, ΔS_{exp} is associated with the increase in volume which occurs on melting, andthe other $(\Delta S_c)_v$ with the increase in the number of conformations a macromolecule can assume on passing from a solid to a liquid state[60,157]. From the method given by Kirshenbaum for calculating the latter contribution, $(\Delta S_c)_v$ for 4T would be expected to be equal to, or greater than that for 4I. Thus the larger entropy of fusion for 4I must be due to a larger volume change on melting. The volume contraction on crystallising this polymer was actually found to be less (0.03-0.04 cm ^{3}g.$^{-1}$) than that for the 4T polyester (0.05cm.^{3}g.$^{-1}$). However crystallinity of the latter polymer was about 15%, or less; that of the 4T polyester was nearer 40% (Table 5.19). Estimation of the volume contractions on crystallising (or increase in volume on melting) for the 100% crystalline polymer in the two cases shows that this may be almost twice as large for the 4I polyester. It can be visualised that the more bulky chain occupies more space than that of the 4T polyester when not packed in a regular structure.

The vast difference in crystallisation behaviour between the 4I and 4T polyesters is readily seen. Crystallisation of the 4I polyester was too slow for measurement by DSC, the maximum rate being $t_{\frac{1}{2}}$-195 minutes at 90-92°C. The polymer could be quenched readily and growing spherulites could be isolated within an amorphous matrix. Crystallisation rates and spherulite growth rates only changed slightly with temperature, again typifying a polymer which crystallised slowly. Conix and Van Kerpel commented that for isophthalates the temperature interval over which crystallisation occurred was narrow compared to that for terephthalates This type of statement can be misleading. In this work it was shown that crystallisation actually occurred over a very wide temperature range at a slow rate.

The very slow crystallisation of the 4I polyester was considered to be mainly due tothe benzene nucleus protruding from the chains, and restricting their movement. Since other results have indicated that the crystal structure is not important in determining crystallisation behaviour, the increased repeat unit length due to reduced symmetry would not be expected to produce the vastly different behaviour observed here. It is implied that spherulite nuclei do not have the crystal structure observed in crystalline polymers.

6.2.6 Model to assess effect of structure on crystallisation rate.

Such a model was proposed by Bunn[2] in 1954. He suggested that factors which reduced T_m reduced the temperature difference between T_m and T_g which, in turn, reduced the crystallisation range. If T_1 and T_2 are the temperature limits within which crystallisation will occur (Fig.1.1), he also suggested that any factors which increase (T_1-T_g) or (T_m-T_2) are likely to reduce the probability of nucleation.

T_g was not available for 4I. Using the values available for the other polymers[81,155,156], (T_m-T_g) was found to be in the following order.

$$5T < 6T < 66 \doteq 46 < 4T < 2T$$

Thus although the slow crystallisation observed for 5T is predicted by this theory, other results do not lie in the order indicated, so the model is not a useful one in predicting crystallisation behaviour. This may be partly due to uncertainties in the values of T_g, but the more likely cause is the different factors which affect T_g and T_m, and the crystallisation behaviour. The crystallisation range mentioned requires definition.

Bunn also suggested that increased chain length increased (T_1-T_g) and therefore reduced the probability of nucleation Results for the 46 and 66 polyesters show that this is not an important factor.

It is suggested that the balance of factors involved in predicting crystallisation behaviour is too complex for representation by a simple model. Consideration of each of the possible factors is probably a more useful approach.

6.3. Summary of data obtained for linear polyesters.

6.3.1. Overall crystallisation rates.

Crystallisation half times are collected in Fig. 6.6 to show the relative significance of different effects. From the results shown for 4I polyester it is obvious that the reduction in rate caused by the bulky isophthalate groups is a major one. The differences between 46 and 66 and 4T and 6T are seen to be relatively insignificant.

Fig. 6.7 shows the variation of log K with the degree of supercooling. Only the corrected K values, calculated in the cases where n was constant are shown. Similar trends are observed to those in Fig. 6.6. Results in Fig. 6.7 may be compared with those reported in the literature (Fig.1.4). The same features are confirmed, although samples have different molecular weights, and different methods of measurement were used. The aliphatic polyesters crystallised at the lowest degree of supercooling. The behaviour of the 10T polyester, with a relatively long aliphatic chain approached that of the aliphatic polyesters. The 2T polyester was again shown to crystallise more slowly.

6.3.2. Spherulite growth rates.

The spherulite growth rates measured are shown in Fig. 6.8. Reported growth rates for polyesters were plotted in

FIG. 6.6. CRYSTALLISATION HALF TIMES FOR POLYESTERS.

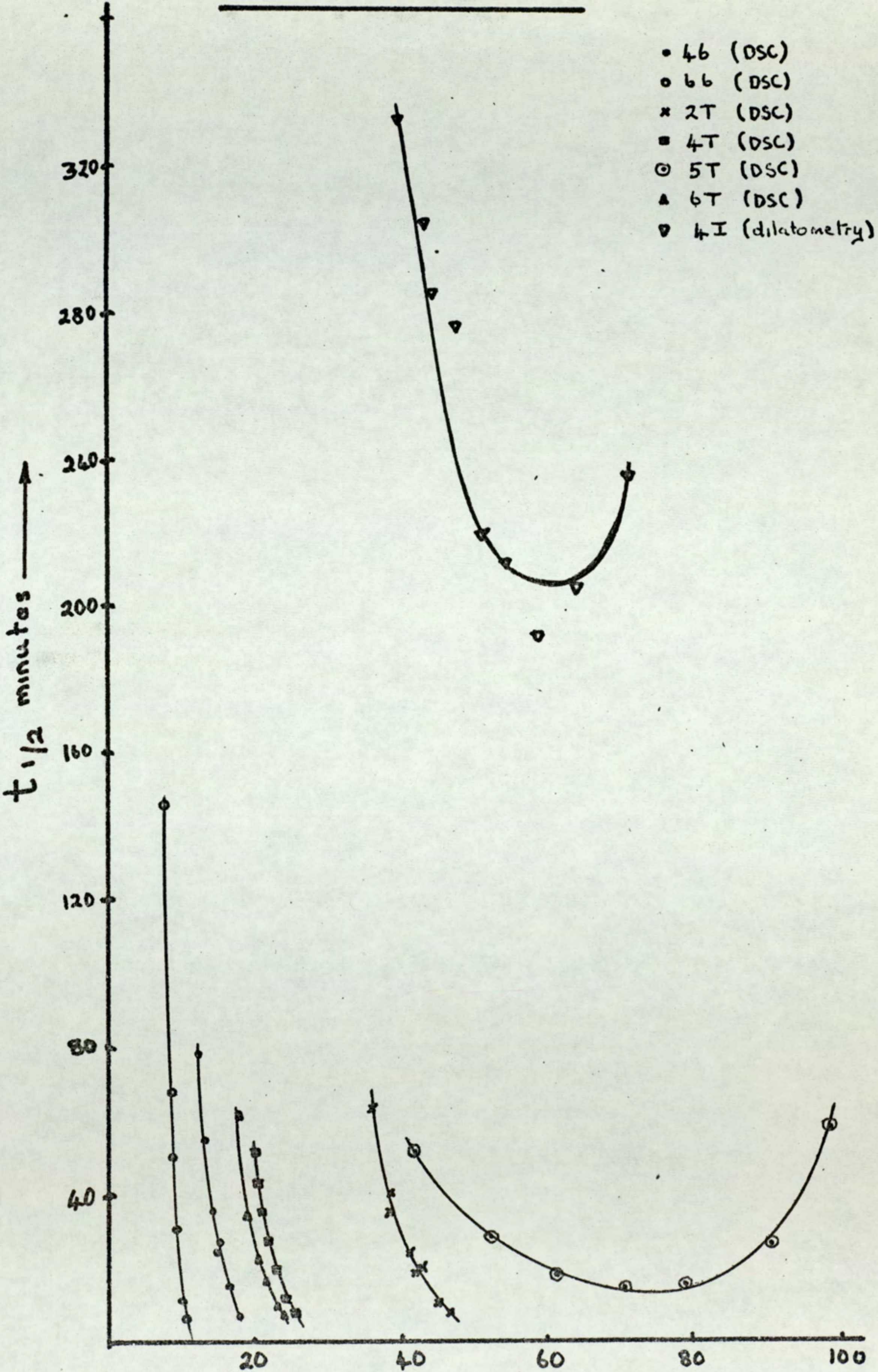


Fig. 6.7. Crystallisation Rate Constants for Polyesters.

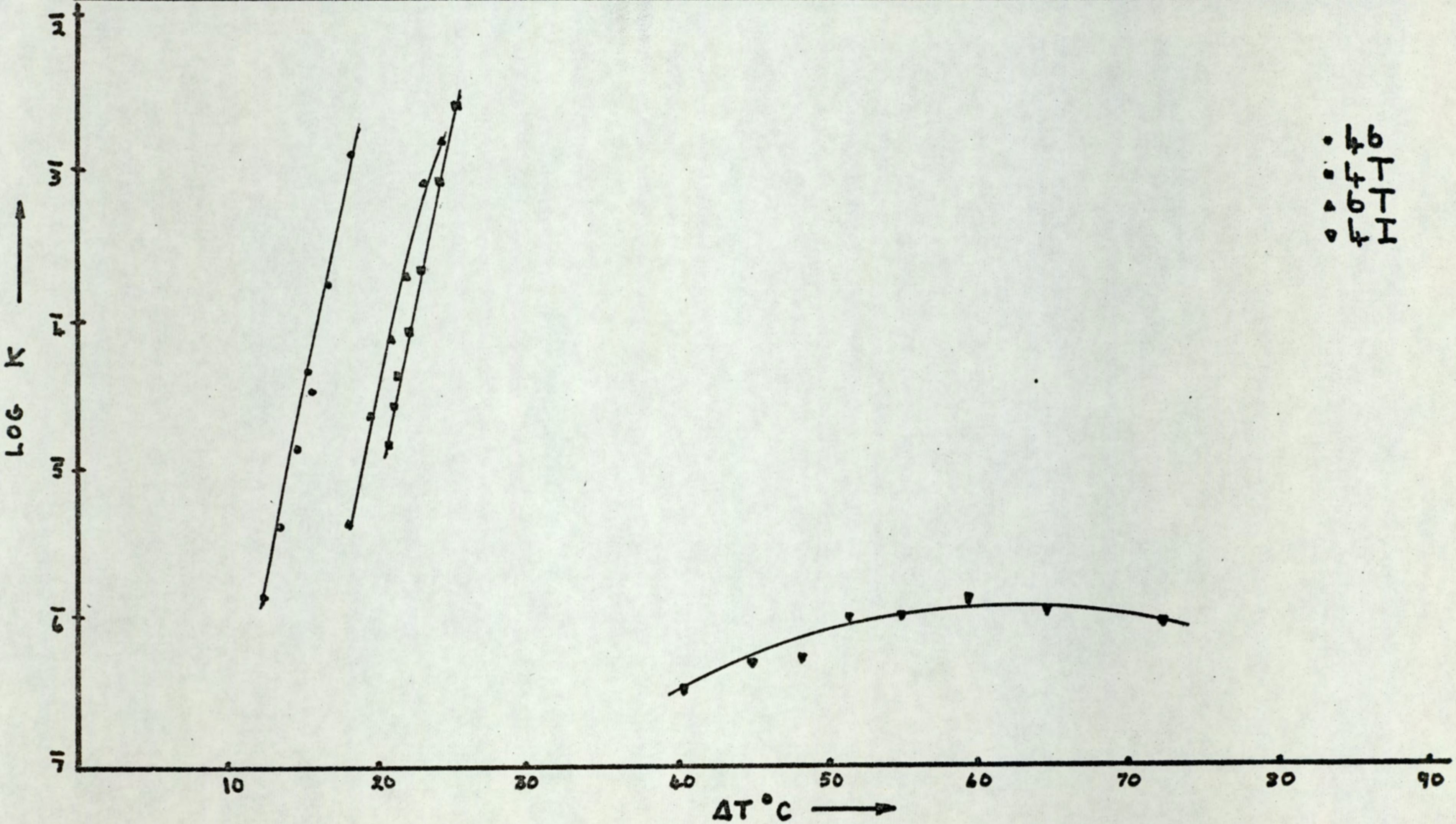


FIG. 6.8. SPHERULITE GROWTH RATES FOR POLYESTERS.

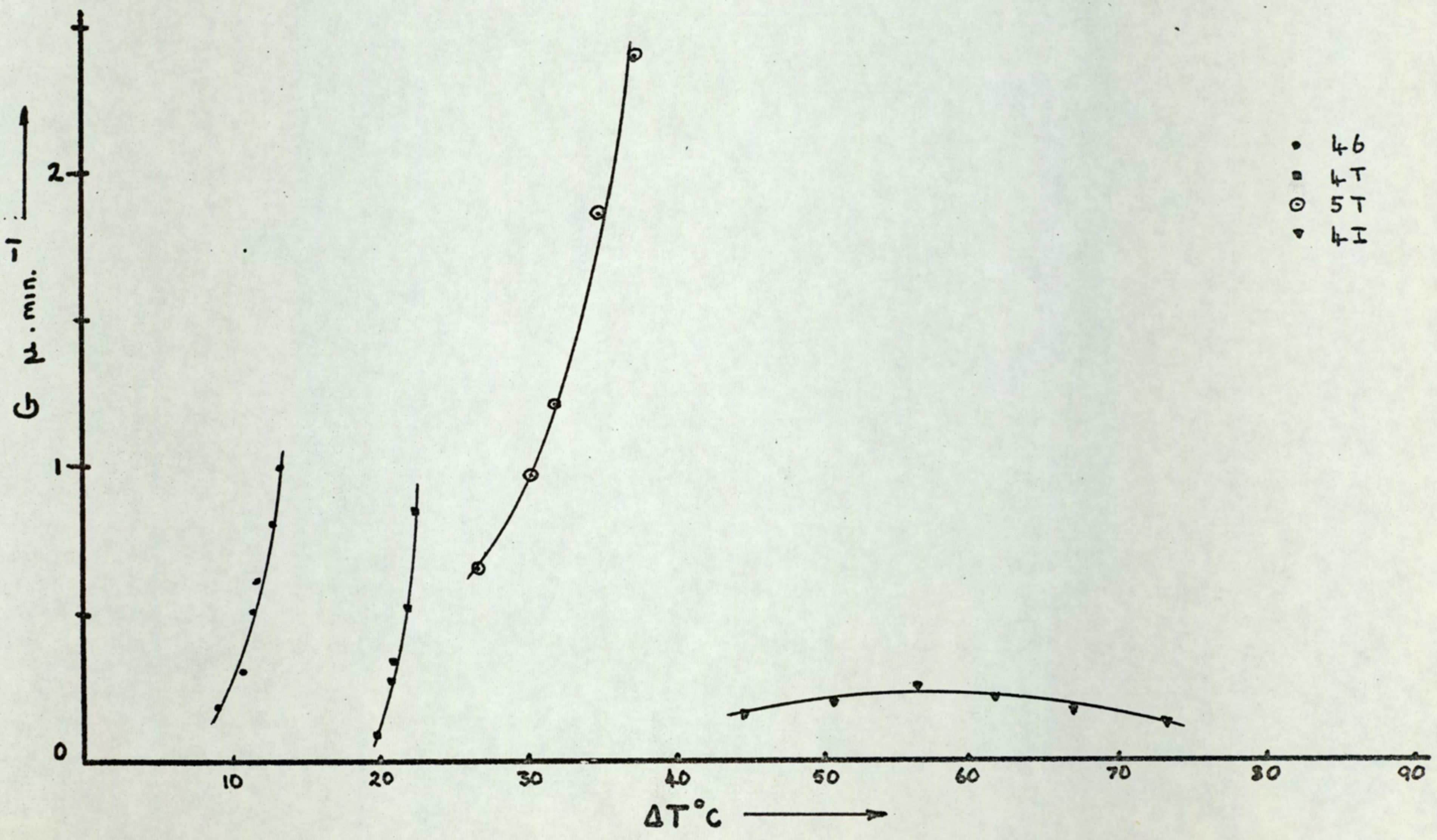


Fig. 1.5. Again, more rapid rates at lower degrees of supercooling are observed for the flexible aliphatic polyesters. The similar behaviour of 46 and 4T polyesters (except for the different amount of supercooling required) is illustrated in this diagram.

A significant effect in reducing the number of methylene groups in the chain is shown in Fig. 1.5. Results for the 24 and 26 polyesters indicate that these polymers have slower growth rates than the 46 and 10 10 polyesters such that growth rates for 24 polyester may be measured above and below the temperature of maximum rate. It is suggested that chain length is one of the factors governing spherulite growth.

Table 6.5. Maximum rates of spherulite growth[126]

Polymer	G_{max}/μ min.$^{-1}$
polyethylene	5,000
66 nylon	1,200
polyoxymethylene	400
6 nylon	150
polychlorotriflouroethylene	30
Isotactic polypropylene	20
polyethylene terephthalate	10
isotactic polystyrene	0.2
polycarbonate from bisphenol A	0.01
polyethylene succinate[102]	10
polytetramethylene isophthalate (this work)	0.25

(The G_{max} values were either reported in the literature or estimated by Boon et al). The method of estimation was not described. Similar structural effects already described are illustrated by the values listed. The low growth rate of the 4I polyester is comparable with that reported for isotactic polystyrene which has phenyl groups pendant from the main chain. Although the aromatic ring is actually part of the main chain in the 4I polyester the effect of bulky groups in reducing rate is illustrated. ref?

The very rapid growth rate for polyethylene, with its regular flexible chain would be expected. The much slower rates for isotactic polypropylene and polychlorotrifluoroethylene with their increased bulk are also likely. Other features such as the much slower rate for 6 nylon than 66 nylon still require complete explanation. Thus although the effects of major structural changes are predictable, when minor changes are made, the balance of factors determining the crystallisation behaviour is important.

6.3.3. Degrees of crystallinity of polyesters.

The information available wasnot sufficient to allow quantitative comparison of degrees of crystallinity obtainable in all the polyesters studied. ΔH_f^* was known for 2T, 4T, 6T and 4I polyesters (Table 5.19). ΔH was measured for slowly crystallised samples of all the polymers. It was hoped to use these values to estimate the relative crystallinity of these samples.

The value of 62% obtained for the 2T polyester was comparable to that reported by Roberts for slowly crystallised samples of the same polymer, using DSC[46]. It appeared that a higher degree of crystallinity could be achieved in this polyester than for the 4T and 6T, for which the crystallinities were 39% and 38% respectively. A possible explanation for this is the shorter repeat unit for 2T. It is likely that greater difficulty is experienced in aligning the longer units as crystallisation proceeds, due to chain entanglement.

For 10 6 and 10T polyesters ΔH_f^* (expressed in cal.g.$^{-1}$) is identical[9]. This suggests that similar values may be expected for the 46 and 4T, and 66 and 6T polyesters resulting in 30-40% crystallinity for the two aliphatic polymers. Therefore, these having a similar repeat distance to the 4T and 6T polyesters, develop a similar degree of crystallinity. Howard and Knutton[47] reported crystallinities of about 90% obtained by DSC for 10 6 and 10 10 polyesters, compared to 30% by density determination. The present work supports the latter results.

The value of 13% for 4I is not unexpected with the bulky aromatic nucleus preventing chain movement.

ΔH_f^* was not available for the 5T polyester. However assuming that it does not vary much from the remaining polyesters (this is true for 'odd' aliphatic polyesters), the low value of ΔH indicates that a low degree of crystallinity (about 20%)is present. Again this is likely when the other crystallisation behaviour of the polymer is considered.

ΔH was also measured for more rapidly crystallised samples where possible (Table 5.18). For the aliphatic polyesters, due to rapid nucleation, this was similar to that for slowly crystallised samples. For 4T and 6T samples only 28% crystallinity was developed on cooling due to the slower nucleation rates implied.

X-ray diffraction photographs (Fig. 5.21 and 5.22) did not give much further indication concerning the crysallinities of the polyesters, since the appearance of these depended on the sample preparation. The most notable feature of these photographs was the well-defined crystallites indicated by the sharp reflections in the photographs of the 4I polyester. This demonstrates that although the bulky aromatic groups protruding from the main chain considerably reduced crystallisation rate, they did not prevent the formation of a well-defined crystal structure. Conditions used to provide samples for the photographs (i.e. the presence of solvent orientation) would be expected to facilitate chain motion.

CHAPTER 7.

CONCLUSIONS AND RECOMMENDATIONS.

7.1. Conclusions.

1. The Du Pont thermal analyser and DSC cell, modified as described, could be used to measure isothermal crystallisation rates at temperatures up to 220°C. At higher temperatures the heating system used resulted in rather inadequate temperature control. For polyhexamethylene adipate, where the crystallisation rate is very temperature dependent, the DSC technique was found to be more suitable than dilatometry due to the smaller sample size used. DSC was not sensitive to the very slow, post Avrami crystallisation observed by dilatometry.

2. Parameters relating to ease of crystallisation and rate of crystallisation depended primarily on the structure of the actual polymer; parameters concerned with the crystallisation mechanism, for example, the Avrami exponent n varied from sample to sample of the same polymer. The changes in n were caused by differences in nucleation attributable to sample preparation and thermal history. These factors were less significant when the overall crystallisation behaviour of different polymers was compared.

3. The effect of molecular weight on crystallisation rate was not significant when structural changes were being compared.

4. There was no indication that homogeneous nucleation occurred in any of the polyesters. It is possible that catalysts used in their preparation served as centres for heterogeneous nucleation. Spherulite growth rates indicated the presence of particles as large as 10 μ in the polymer melt.

5. By comparing literature results with observations made in this work a decreased value of n (approaching 2) is found in some cases where a high nucleation density is observed. This suggests that the development of growing fibrils into spherulites is restricted by impingement between the many growing centres.

6. For polytetramethylene adipate and polyhexamethylene adipate the identity period was due to a slightly distorted planar zig-zag configuration of the chains. A monoclinic structure similar to that for polyethylene adipate was indicated. A planar zig zag configuration was also observed for polytetramethylene isophthalate.

7. Nucleation is not governed by crystal structure. It is suggested that crystal nuclei do not have the structure observed in larger crystallites.

8. Chain flexibility appears to be the major factor governing nucleation. It is more important than chain cohesion. Flexibility has more effect on crystallisation than on melting behaviour.

9. The growth of nuclei beyond the critical size is less dependent on chain flexibility. It appears to be related to the length of the repeat unit or to the concentration of polar groups. For the polyesters growth is more rapid when the repeat unit is longer and the concentration of carbonyl groups correspondingly lower. This effect becomes less significant with increasing length of repeat unit.

10. The degree of crystallinity obtainable is less when the repeat unit is longer. This is thought to be due to chain entanglement. Factors causing a considerable reduction in crystallisation rate also reduce crystallinity.

11. The presence of bulky groups causes very severe reduction in crystallisation rate.

12. Multiple melting peaks were observed for all the polyesters except polyhexamethylene adipate and polypentamethylene terephthalate.

7.2. Recommendations for further work.

The results from this work have indicated certain areas where further investigation may be useful.

1. Further X-ray work to find the chain configuration in polypentamethylene terephthalate. The measurement of ΔH_f^* and hence ΔS_f^* for this polymer may also provide further information to account for its crystallisation

behaviour. Results obtained in this work do not distinguish between several possible explanations.

2. The study of the crystallisation behaviour of an aliphatic polyester having an odd number of methylene groups in the glycol unit (eg. polypentamethylene adipate). In such a polymer the steric hindrance occuring in polypentamethylene terephthalate would be absent. By comparing results for an 'odd' aliphatic polyester with those for the polytetramethylene and polyhexamethylene adipates it should be obvious whether the increased rigidity cause by steric hindrance in polypentamethylene terephthalate reduces its crystallisation rate.

3. Further study of the presence of multiple melting peaks aimed at finding whether it could be related to the crystallisation mechanism as suggested in section 6.1.8. Microscopic observations of the type described for polytetramethylene adipate (section 6.1.1) may be useful.

4. The development of suitable conditions to obtain single crystals from the polyesters studied. Could these be related to the different nucleation behaviour observed in the bulk polymers?

5. The extension of this work to include additional structural features which are known to affect polymer melting temperatures (eg. side chains, ether linkages in the main chain, hydrogen bonding etc.)

6. The effect of the structural changes described on suitable mechanical properties.

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