# HETEROGENEOUS NUCLEATION IN POLYMER CRYSTALLIZATION

A Thesis Submitted For The Degree of Doctor of Philosophy

BY

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"WE SHALL NOT CEASE FROM EXPLORATION
AND THE END OF ALL OUR EXPLORING
WILL BE TO ARRIVE WHERE WE STARTED
AND KNOW THE PLACE FOR THE FIRST TIME"

T. S. Eliot, "Little Gidding" (from: The Four Quartets), Collected Poems, 1909-1962. (Faben & Faben, London, 1974, p.222).

TO MY PARENTS AND ANIBAL

# ABSTRACT

The effect of talc, sodium benzoate, boron nitride, saccharin and sorbitol on the nucleation and crystallisation of PP, PE, PB, POM, PHB, PET and Nylon 66 has been investigated by DSC, light microscopy and electron microscopy.

The effectiveness of the nucleating agent has been evaluated by the study of the interfacial layer between the polymer and the substrate of densely packed particles using light microscopy and by quantitative analysis of the DSC cooling exotherms, obtained from polymers with homogeneously dispersed nucleating agent.

It has been found that the crystallisation temperature of the nucleated polymer is exponentially dependent on the concentration of the nucleating particles. This has been explained solely by the decrease in the average distance between the nuclei, with no changes in the crystallization kinetics. The extent of the shift in the crystallisation temperature of a heterogeneously nucleated polymer has been found to be related to the initial number of spherulites present in the un-nucleated polymer. The highest shift in the crystallization temperature has been obtained from partially molten polymers (selfnucleation); the shift which can be obtained with the best nucleating agents is approaching this level.

Electron microscopy studies, especially the diffraction patterns obtained from the nucleating interface, have shown a good crystallographic correlation between the polymer matrix and the nucleant. Thus, the correlation between the growth direction of the spherulite lamellae and the nucleating facet is good for all active nucleants, but a perfect match of the molecular spacing in this plane (epitaxy) has been observed only for very strong nucleants.

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# CHAPTER 1

# 1. INTRODUCTION

The solidification process during the manufacturing of moulded polymeric components will influence not only the speed of production but also very extensively the mechanical properties of the finished product. In semicrystalline polymers the solidification is affected by the nucleation and the rate of crystallization. From the practical point of view it is easier to control the nucleation than the rate of crystallization and it is the purpose of this study to evaluate the parameters influencing the nucleation mechanism of different polymer compounds.

There are two basic nucleation processes: first, there is the birth of the new solid phase or nucleus within the melt, this is called primary nucleation; then follows the process of crystal growth which requires nucleation at the growing interface and this is called secondary nucleation. Once the nucleus is formed it will initiate the growth of the crystalline phase, most often in all directions, and a morphological structure called spherulite is formed. This structure is composed of lamellae or small crystalline structures that grow in a radial direction from the central nucleus until it impinges on another spherulite. The size and number of spherulites formed can be controlled by the rate of nucleation of the polymer. This modification is very important as it can influence the tensile and impact properties of the polymer.

The primary nucleation can be initiated by several different ways. It is called homogeneous nucleation when it involves a spontaneous aggregation of polymer chains in a reversible way up to the point where a critical size is reached; beyond this point, the addition of chains is irreversible and crystal starts to grow. Homogeneous nucleation occurs in the absence of a second phase and requires a large degree of supercooling. Vonnegut's[1] experiments on small molecule droplets indicate degrees of supercooling of 60°C to more than 100°C for homogeneous nucleation.

Primary nucleation is called heterogeneous nucleation when it involves the aggregation of polymer chains at the interface with a foreign phase; be it adventitious impurities or a purposely added nucleating agent. The addition of nucleating agents increases the rate of nucleation and leads to the formation of a larger number and therefore smaller spherulites. This modification can improve several physical properties of the polymer. Heterogeneous nucleation requires a small degree of supercooling, usually only 10°C to 30°C. This suggests that most crystallization of macromolecules is initiated by heterogeneous nucleation.

A special type of primary nucleation is called self-nucleation. This term describes primary nucleation caused by polymeric crystals which are chemically identical to the crystallizing polymer, but have survived the prior dissolution or melting step.

The crystallization of macromolecules presents additional difficulties compared to small molecules. When estimating the volume of a nucleus one finds that for typical degrees of supercooling, it is less than the volume of a macromolecule. Thus nucleation can involve only part of one macromolecule or even smaller portions of several macromolecules.

In principle, the flexibility of linear macromolecules permits two different nucleation paths for crystallization from macromolecular melts or solutions. The first type of nucleation is intermolecular and is called fringe micelle nucleation. The second type of nucleation is intramolecular and is called chain-folded nucleation. Experimental evidence for homogeneous fringed micelle nuclei is scarce. Flory[2] has pointed out the limitations of this model.

Instead, a direct proof of the concept of chain-folding was obtained by Bittiger and Husemann[3] who crystallized cellulose tricarbonilates from dilute solution. For a sufficiently high molecular weight, folded chain lamellae were formed. The lamellae were about 550 A thick and their volume corresponded to the volume of a single molecule. It has been concluded that nucleation was homogeneous and that the lamellae must consist of folded polymer molecules. Other evidence supporting the chain-folding concept has come from low angle x-ray diffraction which gives dimensions corresponding to lamellae thickness. A more detailed review can be found in Keller[4].

Although there have been many attempts to control the nucleation process and predict the effectiveness of potential nucleating agents, the present knowledge is mainly empirical. The various mechanisms of nucleation will be reviewed below.

## 1.1 HOMOGENEOUS NUCLEATION

### 1.1.A HOMOGENEOUS NUCLEATION CONCEPT

The classical concept of crystal nucleation was developed by Gibbs[5] and Volmer[6] and has been reviewed by Turnbull[7], Zettlemoyer[8] and Robertson and Pound[9].

It is based on the assumption that fluctuations in a supercooled melt (phase A) occur, which lead to the formation of embryos (phase B). These embryos are aggregates of molecules having the configuration representative of phase B to be formed, and most of them will decay and only a few will grow to form a stable phase.

At constant pressure and temperature the probability of an embryo being present is, according to Boltzman's law, proportional to the Gibbs free energy of its formation.

Considering the simplest case, the homogeneous formation of a spherical embryo of radius r, the standard Gibbs free energy may be written as:

$$\Delta G_{HOM} = - \frac{4}{3} \Pi r^3 \Delta G_v + 4 \Pi r^2 \sigma \qquad (1.1)$$

where $\Delta G_v$ is the difference between the standard Gibbs free energy per unit volume in phase B and A and $\sigma$ is the surface free energy of the interface between the embryo and the matrix. When the free energy becomes negative, a stable growth of the embryos formed will occur.

Figure 1.1 represents the process schematically. The figure shows that before a thermodynamically stable phase B of sufficient size can be grown, a primary nucleus must be formed

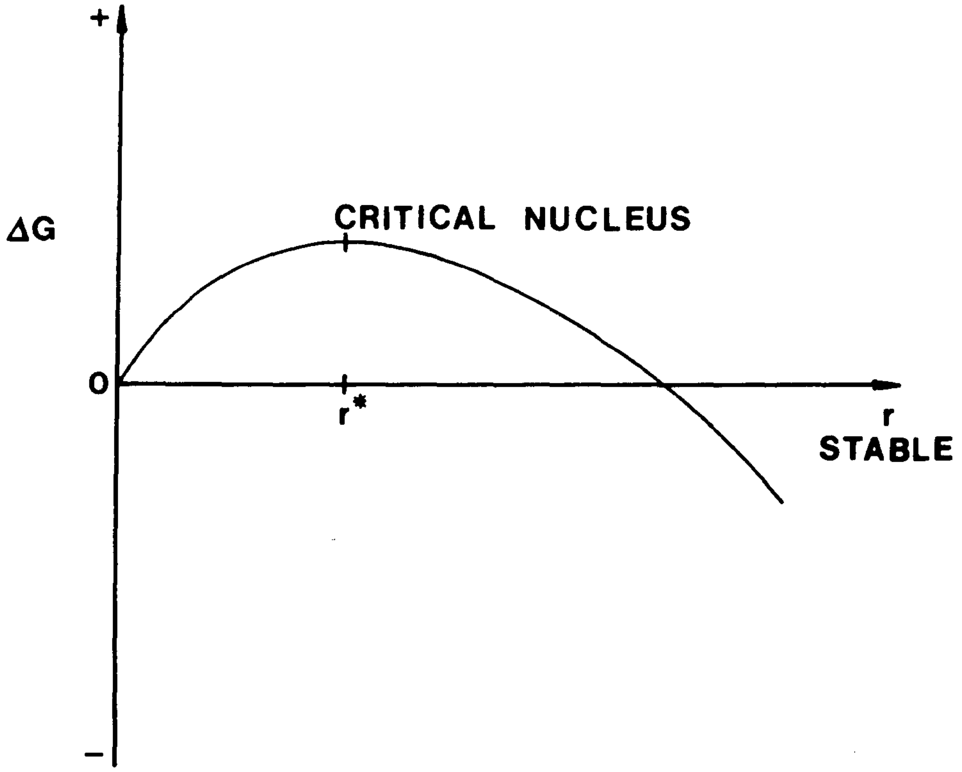


Fig.1.1. Schematic representation of the change in free enthalpy ΔG as a function of nucleus size r.

via a path of positive $\Delta G$. The maximum in $\Delta G$ corresponds to the critical size nucleus. Nuclei to the left are called subcritical nuclei or embryos, nuclei to the right are called supercritical as long as their $\Delta G$ is still positive. Nuclei with a negative $\Delta G$ are called stable nuclei or small crystals.

The time needed for a nucleation process will depend on the size that is required to form a stable nucleus. The maximum value of $\Delta G$, designated $\Delta G^*$, occurs at a critical size $r^*$ and can thus be computed by differentiation of Equation (1.1).

$$\frac{d(\Delta G_{HOM})}{dr} = -4 \Pi r^2 \Delta G_v + 8 \Pi r \sigma$$

Setting this equation equal to zero for $r=r^*$

$$r^* = \frac{2\sigma}{\Delta G_v} \qquad (1.2)$$

Substituting into Equation (1.1) gives

$$\Delta G^*_{HOM} = \frac{16\Pi}{3} \frac{\sigma^3}{(\Delta G_v)^2} \qquad (1.3)$$

Equation (1.3) assumes a spherical shape of the nucleus, such a shape representing the resistance to nucleation for a given volume.

Binsbergen[10] found that when different nucleus geometries are considered, the difference from Equations (1.2) and (1.3) lies in an arithmetic factor.

When a polymeric system is taken into account, Equation (1.1) has to be modified to consider the formation of an asymmetrical nucleus.

Hoffman and Lauritzen[11] and Price[12] developed a rectangular parallelepiped model to describe a chain-folded polymer nucleus. Adjacent segments are connected by loops or folds which are assumed to be as short as possible, consistent with crystallography and the energetic requirements for a particular chain configuration. The most regular arrangement that may occur is sketched in Fig. 1.2.

The standard Gibbs free energy of formation of the nucleus from the melt is then given by:

$$\Delta G_{HOM} = - ab\ell\ \Delta G_v + 2a\ell\sigma + 2b\ell\sigma + 2ab\sigma_e \tag{1.4}$$

where $\Delta G_v$ is the bulk free energy change disregarding surface effects, $\sigma$ and $\sigma_e$ are the side and end surface free energies respectively and a, b and $\ell$ are the dimensions of the nucleus.

The critical nucleus size can, once again, be computed from Equation (1.4) by differentiation with respect to the dimensions a and $\ell$. The critical nucleus dimensions a* $\ell$* are obtained by equating the partial derivatives $\partial G_{HOM}/\partial a$, $\partial G_{HOM}/\partial b$ and $\partial G_{HOM}/\partial \ell$ to zero

$$a^* = b^* = \frac{4\ \sigma}{\Delta G_v} \tag{1.5a}$$

and $$\ell^* = \frac{4\sigma_e}{\Delta G_v} \tag{1.5b}$$

The free energy of crystallization of a nucleus of critical size is then

$$\Delta G^*_{HOM} = \frac{32\ \sigma^2\sigma_e}{\Delta G_v{}^2} \tag{1.6}$$

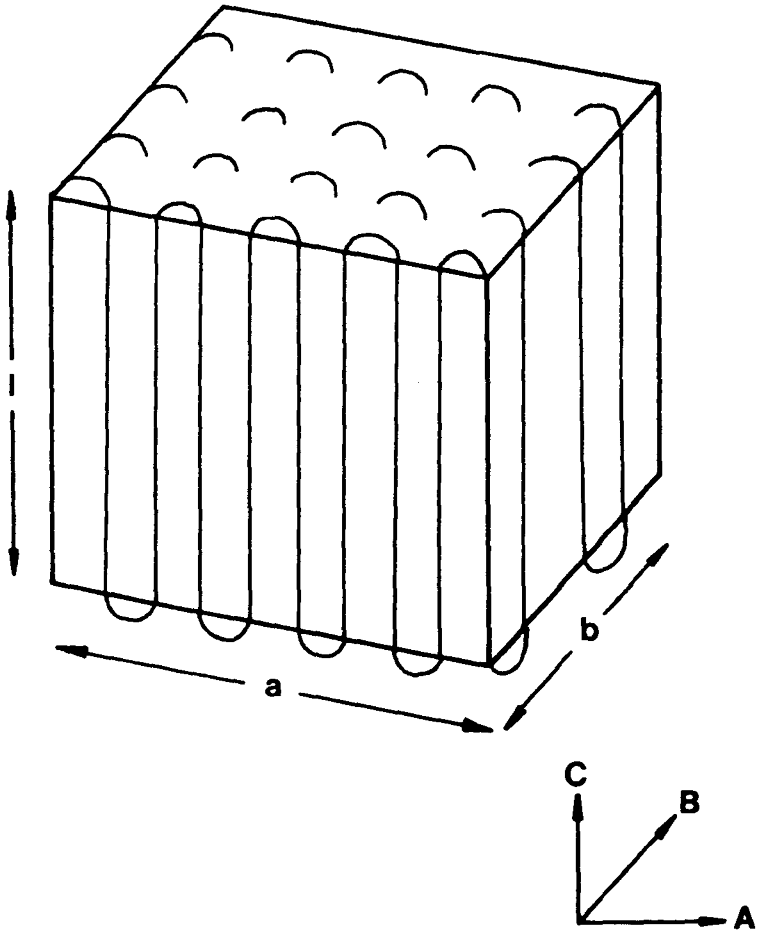


Fig 1.2. Schematic diagram of a chain-folded polymer nucleus.

The temperature effect of $\Delta G^*_{HOM}$ may be computed using the relationship

$$\Delta G_v = \Delta H_v - T\ \Delta S_v \qquad (1.7)$$

where $\Delta H_v$ and $\Delta S_v$ are the enthalpy and enthropy of fusion respectively. $\Delta S_v$ can be taken to be temperature independent as long as the degree of supercooling is not large. At the equilibrium melting point $T^om$ where $\Delta G_v = 0$

$$\Delta S_v = \frac{\Delta H_v}{T^om} \qquad (1.8)$$

Substituting Equation (1.8) into Equation (1.7) gives

$$\Delta G_v = \Delta H_v \left[ \frac{T^om - T}{T^om} \right] \qquad (1.9)$$

where $T^om$-T is the supercooling $\Delta T$ and T is the crystallization temperature. Using this approximation in Equation (1.6), the critical free energy of crystallization becomes

$$\Delta G^*_{HOM} = \frac{32\ \sigma^2\ \sigma_e\ (T^om)^2}{(\Delta H_v)^2\ (\Delta T)^2} \qquad (1.10)$$

$\Delta G^*$ is proportional to $1/(\Delta T)^2$, the inverse square of the supercooling.

The treatment of nucleation presented contains a number of limitations; the first is reached for large supercoolings. The second limitation is the assumption of strictly crystallographic growth. The initially crystallized material does not have the initial perfection permitting the use of $\Delta H_v$ and $\Delta S_v$ as measured from macroscopic melting experiments. Finally, the limitation of the nucleus to the equilibrium shape neglects other possible nucleation paths.

Binsbergen[13] made an attempt to describe the nucleation process taking into account all possible paths. The deviation found from the classical theory has been smaller than one would expect.

### 1.1.B HOMOGENEOUS NUCLEATION RATE

Turnbull and Fisher[14] have derived an expression for the rate of nucleation I based on the Boltzman's law. Considering that the probability for the presence of a nucleus of a given size is proprotional to exp(- $\Delta G/kT$), and using reaction rate theory[15], the rate of nucleation turns to be

$$I = I_o \exp\left[- (E_D + \Delta G^*_{HOM})/kT\right] \tag{1.11}$$

where $I_o = \frac{N\,k\,T}{h}$

The rate of nucleation refers to the number of uncrystallized elements N able to participate in nucleation by a single step. $E_D$ stands for the free energy of activation which governs the short distance diffusion of the crystallizing elements across the phase boundary. $\Delta G^*_{HOM}$ is the free energy of crystallization of a nucleus of critical size, and k, T and h are Boltzman's constant, temperature and Planck's constant, respectively.

By combining Equations (1.10) and (1.11), the homogeneous rate of formation of a chain-folded nucleus becomes

$$I = I_o \exp\left\{-\left[\frac{E_D}{kT} + \frac{32\sigma^2\sigma_e\,(T^o m)^2}{(\Delta T)^2(\Delta H_v)\,2kT}\right]\right\} \tag{1.12}$$

The nucleation rate equals zero at absolute zero and when

$T = T^o m$, because $\Delta G^*_{HOM}$ is proportional to $1 / (\Delta T)^2$. It attains a maximum value at some intermediate temperature. At temperatures just below Tm, the nucleation rate has a very large negative temperature coefficient. As the temperature is decreased further the nucleation rate increases. The transport term, $\exp(-E_D/kT)$ becomes the rate controlling term. As discussed by Wunderlich[16], this region of fast primary nucleation begins typically at a supercooling of 30-100°C.

Practically all experiments yielding direct information on homogeneous nucleation from polymer-melts or solution have been performed under conditions of high chain mobility and/or dilution. This is due to the fact that the presence of impurities allows heterogeneous nucleation to take place at smaller supercoolings before a sufficient low temperature is obtained for homogeneous nucleation to be significant.

Early experiments to gain information on the homogeneous nucleation process were divised by Vonnegut[1]. The melt was divided into small droplets that, because of their number, could not contain heterogeneous nuclei. Homogeneous nucleation was then followed by observation of the crystallization of the droplets under the optical microscope.

More recently homogeneous nucleation from dilute solution of PE (0.05% by weight) in toluene and xylene has been found by Wunderlich and Mehta[17] to occur at about 32°C supercooling. This conclusion has been achieved by the study of the morphology and the resulting crystals. These results together with those of Gornick[18] and Koutsky[19] showed the strong temperature dependance found in systems which are nucleation rate controlled.

## 1.2 HETEROGENEOUS NUCLEATION

### 1.2.A HETEROGENEOUS NUCLEATION CONCEPT

Crystallization is, in most bulk systems, initiated by heterogeneous nucleation. It makes use of foreign preexisting surfaces to reduce the free energy opposing primary nucleation. In practice it is impossible to purify a solution or melt to such an extent that nucleating impurities are absent[20].

As in the case of homogeneous nucleation, the free energy of formation of a nucleus is considered to be the sum of the bulk free energy and the interfacial free energy.

The same parallelepiped model used by Price[12] to describe a chain-folded polymer nucleus may be adopted to give a model for heterogeneous nucleation. The nucleus is placed in contact with a flat surface in such a way that the AC face (Fig. 1.2) of the crystal forms the interface with the substrate. Let $\sigma_{sc}$ be the interfacial energy between the substrate surface and the crystal face AB, and $\sigma_{sm}$ be the interfacial energy between the substrate surface and the melt. Then the free energy of formation of the crystal is:

$$\Delta G_{HET} = - ab\ell \ \Delta G_v + 2ab \ \sigma_e + 2b\ell\sigma + a\ell\Delta\sigma \qquad (1.13)$$

where $\Delta\sigma = \sigma + (\sigma_{sc} - \sigma_{sm})$ represents the specific interfacial free energy difference parameter accounting for one surface contacting the melt (surface free energy $a\ell\sigma$ ) and one surface contacting the heterogeneous nucleant. The other quantities are defined as in Equation (1.4).

When the substrate is absent, $\sigma_{sm}$ equals zero and $\sigma_{sc} = \sigma$. Hence, $\Delta\sigma = 2\sigma$ and Equation (1.13) is reduced to the homogeneous case of Equation (1.4). Thus at a given temperature, heterogeneous nucleation is facilitated as long as $\Delta\sigma$ is less than $2\sigma$. This implies that the energy required to construct the crystal surface in contact with the melt has to exceed the energy required for construction of a crystal surface in contact with the heterogeneous nucleant. When a polymer crystal and the heterogeneous nucleant interact strongly, the wetting of the latter by the former is good and this is reflected by a low value of $\sigma_{sc}$. For this event the nucleant strongly affects the rate of nucleation of new crystals. When the polymer crystal-nucleant interaction is weak, $\sigma_{sc}$ is large and $\Delta\sigma$ may approach $2\sigma$. In this case the rate of nucleation is low and crystals may appear sporadically with time.

The dimensions of the critical nucleus can be derived by equating the partial derivative of $\Delta G_{HET}$ to zero. The dimension for a* and $\ell$* are again as given in Equations (1.5a) and (1.5b) respectively while

$$b^* = \frac{2\Delta\sigma}{\Delta G_v} \qquad (1.14)$$

The free energy of formation of the heterogeneous nucleus should be accordingly:

$$\Delta G^*_{HET} = \frac{16\sigma\,\sigma_e\,\Delta\sigma}{\Delta G_v^{\,2}}$$

Substituting Equation (1.9)

$$\Delta G^*_{HET} = \frac{16\sigma\,\sigma_e\,\Delta\sigma\,T^{o}{}_{m}^{2}}{(\Delta H_v)^2\,(\Delta T)^2} \qquad (1.15)$$

$\Delta G^*_{HET}$ remains proportional to $1/(\Delta T)^2$, the inverse square of the supercooling as in the case of homogeneous nucleation, represented by Equation (1.10).

Heterogeneous nucleation on surface irregularities like steps, cracks or holes would be more advantageous than heterogeneous nucleation on flat surfaces. On such a rough surface the crystal nucleus could make use of a larger portion of the surface. Binsbergen[21] found that heterogeneous nucleation is enhanced by a high degree of accommodation of polymer molecules at the substrate by the presence of ditches in the latter which favour alignment of the polymer chains, thus facilitating crystallization.

### 1.2.B HETEROGENEOUS NUCLEATION RATE

Turnbull[22], using arguments similar to those used for homogeneous nucleation, obtained an expression for the nucleation rate per unit area of a nucleant in condensed phase

$$I_{HET} = I_o \exp\left[- (E_D + \Delta G^*_{HET}) /kT\right] \qquad (1.16)$$

where $I_o = NkT/h$ and N is the number of uncrystallized elements able to participate in nucleation by a single step. The other terms having been defined earlier.

Substituting $\Delta G^*_{HET}$ according to Equation (1.15) then

$$I_{HET} = I_o \exp\left\{-\left[\frac{E_D}{kT} + \frac{16\sigma\ \sigma_e \Delta\sigma (T^o m)^2}{kT\ (\Delta T)^2\ (\Delta H_v)^2}\right]\right\} \qquad (1.17)$$

When the nucleation process is assisted by the presence of surface heterogeneities, its temperature dependence is the same as in the homogeneous case although the numerical factor differs. As a consequence, heterogeneous nucleation will become significant at smaller supercoolings than will homogeneous nucleation.

### 1.2.C EXPERIMENTAL OBSERVATIONS OF HETEROGENEOUS NUCLEATION

The control of primary nucleation in the crystallization of polymeric materials is of scientific and technological importance[23]. Numerous reports have appeared in the literature that show the effectiveness of certain substances to promote nucleation when incorporated into a polymer matrix. However, although there have been many attempts to control the nucleation process, the present knowledge is mainly empirical, and an unambiguos correlation between chemical composition, crystal structure and physical properties of the nucleator additive and polymer has not been well established.

Beck's[24] study on heterogeneous nucleating agents for polypropylene crystallization presented a model nucleating agent consisting essentially of two parts. One part should be capable of reducing the interfacial surface free energies involved, then it should be wet by the polymer. An organic group would play this role. The other part would require that the nucleating agent contains a polar group capable of rendering the nucleating agent insoluble in the polymer. Such a model may be represented by an organocarboxylic acid salts. From a wide selection of different compounds in which the effects of metal cations, substituent groups and length of aliphatic groups were studied; sodium benzoate and basic aluminium di-benzoate were among the most ideal representatives of the model nucleating agent found so far for polypropylene.

Following the same paths, Binsbergen[25] tested a wide range of substances for their possible nucleating effect on the crystallization of polyolefins. He suggested that most of the active compounds had crystal structures with alternating rows of polar and non polar groups at the seed crystal surface. The polar groups pointed towards the center of the crystal, while the apolar groups were exposed to the polymer melt. As a result, the orientation of the nucleating particles in the polymer melt causes oriented crystallization of the polymer. He also concluded that the activity of the agents is strongly dependant on the degree, and sometimes on the method of dispersion.

Yim and St. Pierre[26] showed quantitatively that the nucleating ability was directly related to the interfacial energy between the polymer and the nucleating agent. They observed that silicas could nucleate the crystallization of polydimethylsiloxane (PDMS) but more significantly they showed that by modifying the surface of the silica, its nucleating ability could be altered. Coating the silica surface with alcohols of alkylchlorosilane[27] could alter the number of hydroxyl groups on the surface. It was found that the interaction between the surfaces of the silica and PDMS was related to the heat of adsorption on silica by a low molecular weight model compound. The lower the number of hydroxyl groups on the surface, hence the more extensive the silica surface modification, the lower the heat of absorption. They also found that for the same filler content, the silica of lower surface energy, required the largest undercooling to nucleate the PDMS crystallization.

A linear relationship was obtained between the logarithm of the nucleation rate and the adsorption energy per segment of polymer.

$$\ell n\ I = (\ell n\ I_o - E_D/RT - J/RT) + L\ \Delta H_{ads}/RT \qquad (1.18)$$

where J and L are constants and $\Delta H_{ads}$ is the net heat of adsorption per segment of nucleant. The other terms having been defined earlier.

Further results by Cole and St. Pierre[28] support the premise that the effectiveness of a nucleating particle is directly related to the surface energy. They found from photomicrography that the addition of silica filler, produced more nuclei in the crystallization of isotactic polypropylene oxide (i-PPO) and polyethyleneoxide (PEO) as compared to the un-nucleated polymer films. The modified silica was found to be a less effective nucleant in both i-PPO and PEO crystallization, the number of nuclei was less for a treated silica composite than for the untreated silica composite containing the same quantity of silica. It was concluded that the difference in nucleating ability of the silicas was caused by a change in the chemical nature of the surface through modification of the acidic silanols on the untreated silica surface.

Other experiments to gain information on the heterogeneous nucleation process were divised by Groeninckz et al[29]. The nucleation of polyethylene terephthalate (PET) melts by in organic compounds like talc, kaolin, silicon dioxide and titanium dioxide was investigated. It was found that crystallization of the supercooled polymer varied with concentration, size distribution and nucleating ability of the solids. Talc and titanium dioxide were most effective. It was suggested that the crystallization initiated by the fillers had a different time dependance for each filler.

It was also found by Van Antwerpen and Van Krevelin[30] that PET could be effectively nucleated by magnesium silicate and silica. It was also found that calcium carbonate particles which were coated with either benzoate or stearate were more effective nucleants than the uncoated particles. Because the coated filler caused no modification in shape or particle size, the change in nucleating ability was attributed to the chemical nature of the filler particle.

In a more recent work, Turturro et al[31] demonstrated that silica particles can nucleate the crystallization of PET and isotactic polystyrene (i-PS). However further increase in the nucleant concentration resulted in a lower temperature of crystallization as compared to the un-nucleated polymers. It has been concluded that this retardation effect is a result of the nucleant inhibiting the transport of the polymer segments to the crystallizing site.

Several less detailed studies of other polymer melts nucleated by the addition of foreign materials have been reported. Kargin et al[32] found that the addition of indigo (1% by weight) sharply increased the crystallization process of i-PS. Wlochowicz[33] studied the influence of pigments with various chemical structures on the crystallization process of polypropylene.

To locate the nucleation sites, and to evaluate the nucleation density, it is convenient to use a well defined interface between the polymer and the substrate.

When heterogeneous nucleation occurs with sufficiently high density at the surface of substrates, the resulting radial growth produces a type of columnar growth in contact with the substrates. This phenomenon is called transcrystallinity. Because of the crowding of nuclei, lateral growth is restricted due to impingment while growth continues in the direction normal to the plane of the substrate[34].

Transcrystalline growth has been reported to occur for example for polypropylene crystallized in contact with various polymers and metal oxides[35,36,37], graphite fibers[38] and some thermoplastic fibers[39,40,41].

Fitchmun and Newman[35] showed that transcrystallinity occurred when polypropylene and polyethylene were in contact with mylar and teflon, while aluminium and copper oxides showed little influence on the surface morphology of crystallizing polymers. It was also found that transcrystallinity was dependent on the experimental conditions. Crystallization at low temperatures (large supercoolings) increases the nucleation rate in the bulk and diminishes the activity difference between different types of heterogeneities.

Chatterjee and Price[36] studied the nucleating abilities of various substrates, mostly polymeric by examining the substrate induced morphologies of the crystalline polymer. These morphologies have been classified into three groups, depending on whether the substrate is very active (transcrystallinity), moderately active or inactive as a nucleating agent. The morphologies observed are temperature dependant, changing from transcrystalline to spherulitic upon increase of the crystallization temperature. At intermediate temperatures, mixed surface morphologies (transcrystalline plus spherulitic) were observed. From a survey of 43 substrate-crystallizing polymer pairs, they concluded that none of the following three is a necessary condition for strong nucleating action (transcrystallinity) in polymer melt crystallization: a) similarity of chemical structure of substrate and crystallizing polymer b)similarity of crystallographic unit cell type of the chosen pair and c) close match of crystal lattice parameters of the chosen pair.

Further more they concluded that the surface energy of a substrate does not indicate its nucleating ability. Low energy surface polymers are capable of inducing transcrystallinity; and crystallinity is a necessary but not sufficient condition for a substrate to be a strong nucleating agent.

The use of graphite fibers as a nucleating agent for polypropylene was investigated by Hobbs[38]. Crystallization from the melt showed that only graphite fibers with crystals of the size of the fold length of the polypropylene lamellae were active nuclei and produced transcrystallinity. A match of the helical period of the polymer with the H-adsorption sites of graphite was suggested to enhance nucleation.

Other workers[39] attempted to obtain a correlation between the chemical nature of thermoplastic fibers and their ability to nucleate. Specifically nylon 6, nylon 66 and nylon 11 were tested as nucleating agents for polybutene and polypropylene. Although a transcrystalline region was obtained a clear effect of the chemical nature upon their ability to nucleate was not established.

Recently it has been reported by Legras et al [42] that significant differences appear in the kinetics of crystallization of PET mixed with alkali metal salts of the family of aromatic carboxylic acids, as a function of different mixing conditions. According to their results a chemical reaction occurs during the mixing process between the salt and the ester links of the macromolecules. This reaction produces ionic end groups which are responsible for the acceleration of the crystallization rate. This phenomenon is called "chemical nucleation".

Another factor that has been proposed in the crystallization process governing the nucleating capacity of polymeric substances is epitaxy.

Although Binsbergen[21] has excluded lattice matching type epitaxy as the major mechanism for heterogeneous nucleation, Wittman and Lotz[43] in a recent work suggested that structural similarities between some of the apolar parts of the well known nucleating agents and polyethylene are stricking and indicates a need for a re-examination of the experimental evidence on which the up-to-date conclusions rest.

Further reports[44] on several different inorganic materials, among them mica and alkali halides, have shown fold plane and rod-like epitaxy on polyoxymethylene.

## 1.3 SELF NUCLEATION

The term self-nucleation or self-seeding has been introduced by Blundell, Keller and Kovacs[45] to describe nucleation of chain-folded crystals grown from solution on high molecular weight remnants of its own crystals which remained through the dissolution step. In a more general way the concept would be used here to describe nucleation of macromolecular melt or solution by its own crystal grown previously. Macromolecules are particularly well suited for self-nucleation because of a large temperature range in which crystals do not melt or crystallize even when nucleated.

Early evidence presented by Turnbull[46] proposed that crystal fragments, grown on small cracks of a foreing surface may have an elevated melting point and thus survive the initial dissolution or melting of the bulk of the material and serve as nuclei on subsequent cooling.

In all cases of self-nucleation it is found experimentally that, over a certain temperature range and a given time, the supercooling required for a crystallization process is critically dependent on the degree of heating above the melting or dissolution temperature of the polymer.

For self-nucleation from dilute solution, the factors influencing it were according to Blundell and Keller[47]: First the number of nuclei formed is determined mainly by the dissolution temperature. Second, the final crystallization temperature has little effect on the number of active nuclei, in contrast to heterogeneous nucleation on foreign surface where the number of nuclei was strongly dependant on the crystallization temperature. Third, the high molecular weight fraction of the sample is particularly active in self-nucleation. Fourth, the rate of heating to the dissolution temperature, the concentration and temperature of initial crystallization are of some importance and finally, the concentration of the final crystallization had little effect (a range of 0.01 - 1.00% by weight of polymer) on the number of nuclei per gram of polymer.

Quite similar to self-nucleation from solution is self-nucleation from the melt. Vidotto et al [48] have studied the self nucleation effect on polyethylene, polyethylene oxide and polybutene. They found that for polyethylene the number of nuclei capable of self-nucleation decreases rapidly as a function of the melting temperature, then a certain limit is reached. These remaining permanent nuclei seem to be foreing heterogeneous nuclei. The explanation given for the narrower region of self-nucleation was found in the larger fold length and perhaps faster annealing of the whole sample when crystallized from the melt.

For polybutene the behaviour was different due to the fact that this polymer crystallizes in two crystal forms, trigonal (I) and tetragonal (II). The second form crystallizes from the melt at a higher temperature. The conversion of form II to form I could be possible. The limit of self-nucleation of form II on seeds of form I is reached at a higher temperature in contrast to form II nuclei which reach their limit at about 10°C below form II.

Data on polyethylene oxide give also a somewhat different behaviour to that of polyethylene. The number of nuclei capable of self-nucleation decreases rapidly to the first critical temperature, then it changes to a much slower process reaching the second critical temperature; after this temperature, the number of nuclei capable of self-nucleation remains constant.

The effect of heating above the melting temperature on nucleation in polyethylene (PE) was studied by Schultz[49]. Samples of PE melt were cooled from 150°C and 180°C under similar conditions. The sample cooled from 150°C at 30°/minute crystallized about 2°C earlier. On isothermal crystallization, quenching from the lower melt temperature gave rise to larger spherulites and a higher degree of crystallinity with no change in fold period. Schultz found it difficult to explain that on cooling, the large number of embryos could start crystallization at 150°C but on isothermal crystallization this should lead to more and not less spherulites. He suggested that perhaps the overall molecular order in the melt was affected but admitted that this will need further study.

## 1.4 THE GROWTH OF THE CRYSTALLINE PHASE

The problem to be discussed in this section is the growth of polymer crystals once they have been nucleated through homogeneous, heterogeneous or self-nucleation processes.

In general, the growth of a crystal is based on the surface nucleation of a new layer of crystallizing material after the initial crystal nucleus is established. Once the primary nucleation has occurred and the crystal commences to grow radially, the process still has an additional energetic barrier to overcome. This energetic barrier which retards the addition of each new molecule to the growing crystal is called secondary nucleation.

As an extension of the Turnbull-Fisher equation for nucleation[14], the growth rate of polymer can be represented by:

$$v = v_o \exp(-E_D/kT) \exp(-\Delta G^*/kT) \qquad (1.19)$$

where v represents the linear crystal growth expressed in nm/sec. The last two terms represent the activation energy for the transport of the crystallizing unit across the phase boundary and the formation of a nucleus of a critical size respectively.

As in the case of general nucleation, the growth of macromolecular crystals from the melt is temperature dependant with an optimum temperature for crystal growth. At lower temperatures the radial growth rate will have a positive activation energy, and is related to the transport of the crystallizing element in the same way as the primary nucleation process. However, above this optimum temperature there is a negative activation energy region which corresponds to the stability of the crystallizing element deposited on the growing crystal face. An important question is whether the energy exchange between the crystallizing element and the surrounding polymer melt would be such that the crystallizable part of the polymer adhere to the crystal face without moving away. At very high temperatures it would be more difficult for the crystallizing element to stay at the crystal-melt interface. It has been observed experimentally that the growth rate drops more rapidly to zero when approaching the melting temperature. The elementary growth steps of a crystal must be the addition of one crystallizing unit after the other on to a location where addition of polymer causes no increase in surface free energy. Additional growth to the corner of a crystal can fulfil this requirement. Thus it can be concluded that the initial irregular surfaces of the nucleus grow faster than those which are smooth on a molecular level. However, a molecularly smooth surface can support growth only after secondary nucleation and this is a slow process. This would be the controlling step that governs the crystal growth.

If it is assumed that secondary nucleation of a new layer of crystallizing material on a molecularly smooth surface is related to the heterogeneous nucleation as described by Equation (1.13) with the condition that $\Delta\sigma$ is zero; and that the thickness b is a constant $b_o$[50], then $\Delta G^*$ can be expressed by

$$\Delta G^* = \frac{4\,\sigma\,\sigma_e\,b_o}{\Delta G_v} \tag{1.20}$$

Substituting $\Delta G_v$ with Equation (1.9), then

$$\Delta G^* = \frac{4\sigma\,\sigma_e\,b_o\,T^o m}{\Delta H_v\,\Delta T} \tag{1.21}$$

where $\sigma$ and $\sigma_e$ are interfacial free energies per unit area parallel and perpendicular, respectively, to the molecular chain direction. $\Delta T$ is the supercooling, $T^om$ is the equilibrium melting temperature and $\Delta H_v$ is the enthalpy of fusion.

The transport term as expressed in Equation 1.11 involves the simplest approximation that the activation energy, $E_D$, is temperature independent. However, this is not the case in polymer crystallization. Its temperature dependence is expected to be similar to the temperature dependence of viscosity. At high temperature $E_D$ is almost constant, at lower temperatures it increases rapidly as the glass transition temperature is approached. If the transport term is replaced by the expression derived by Williams, Landel and Ferry[51] for viscous flow it leads to the accurate fit for the temperature dependence of the viscoelastic parameters above the glass transition temperature.

The expression for the transport term using the expression from 51 becomes then

$$E_D/kT = C_1/(C_2 + T - Tg)\ k \qquad (1.22)$$

where $C_1$ and $C_2$ are constants, T is the crystallization temperature and Tg is the glass transition temperature where no further transport across the phase boundary can take place. Williams et al[51] had found constant values for $C_1$ and $C_2$, but for macromolecules the variation from one polymer to another was too great to allow the use of the universal values. Hoffman et al[52] have related $C_1$ and $C_2$ in the case of polymer crystallization to motion in a physically absorbed yet mobile surface layer of molecules in the crystal. Taking into account the correction made for the transport term (Eq. 1.22) and Equation (1.19), the expression for polymer crystal growth with chain folds can be

$$V = V_o \exp\left( - \frac{C_1}{(C_2 + T - Tg)k} \right) \exp\left( - \frac{4\sigma\, \sigma_e\, b_o\, T^o m}{\Delta H_v \;\; \Delta T \; kT} \right) \quad (1.23)$$

Boon et al[53] suggested that $v_o$ is largely determined by the mobility of the molecules, as an example they found that the presence of a bulky group like the phenyl group in polystyrene will lowever $v_o$, compared to that of polyethylene.

## 1.5 PRESENT INVESTIGATION

It follows from the above review that the nucleation is a complex process dependent on numerous factors. These factors include, among others, crystalline morphology of the substrate[36,38], chemical composition of the surface[62], temperature gradient at the surface[54,55], wettability and surface energies of the substrates[19,26], and epitaxial growth on to the substrate surface[43,44].

It has been suggested[24] that the nucleating ability of a particular compound appears not to be an exclusive function of any one property or variable, but is probably the effective summation of many properties, all operating at the same time. However, the present knowledge is based mainly on empirical and not systematic results, and for this reason an unambiguous correlation between chemical composition, crystal structure or physical properties of the polymer and of the nucleating agent has not been well established. Some results are still controversial, e.g. the relationship between surface energy and nucleating ability, or the occurance of an epitaxial growth. Most of the studies mentioned above are dealing with one or two polymers and their interaction with one or two nucleating agents. As a consequence, it is difficult to establish the general requirements which cause a nucleating agent to be effective and to propose a mechanism of nucleation.

In this work the nucleation mechanism has been studied more systematically, i.e. the nucleation behaviour of more than fifty polymer/nucleator systems have been investigated under similar conditions and using the same experimental techniques. This has enabled us to establish firstly, if the nucleating agents of different geometry and chemical composition (organic or inorganic) are able to nucleate one specific polymer to the same extent and secondly, if polymer of different morphology and chemical structure would be nucleated by one specific nucleating agent. An attempt has been made to explain the cause of the shift in the crystallization temperature, promoted by the nucleating agents and also to establish, if the nucleating agents used in the present investigation are causing the maximum shift in the crystallization temperature or if a better nucleator can be found for each polymer. For this reason the self-nucleation behaviour of various polymers was investigated and the temperature shift obtain compared with heterogeneously nucleated samples.

Different techniques, some of them specially developed, have been used to obtain the required information for the nucleation behaviour of talc, sodium benzoate, boron nitride, saccharin and sorbitol on the crystallization of polypropylene, polyethylene, polybutene, polyoxymethylene, polyethyleneterephthalate, polyhydroxybutyrate and nylon 6.6. Several polymer fillers, like calcium carbonate, silica, molybdenum disulphide and others, were also tested, but as they do not show any nucleation, they are not reported in this work.

Differential scanning calorimetry (DSC) has been the major technique used in this work as it provided a very reliable information about the crystallization processes of various polymers. this technique has been successfully combined with light microscopy which enabled us to assess morphological changes occurring under different conditions of crystallization. Some important information has been obtained from the specimens crystallized on a substrate and in a temperature gradient.

Finally, the nature of the interaction between the polymer and the nucleating particles has been elucidated by studying the polymer-nucleant interface. The crystallographic requirements and the active sites which make a certain particle a nucleating agent have been obtained with electron diffraction techniques.

# CHAPTER 2

# 2. EXPERIMENTAL PART

In this chapter the materials and techniques used in the present investigation will be described, including details of the apparatus used. The main areas of interest consist of crystallization measurements and morphology studies using light and electron microscopy. Differential scanning calorimetry (D.S.C.) was used to obtain information about the crystallization process of various polymers. The effects of melting temperature, melting time, rate of cooling, nucleating agents and self-nucleation on the crystallization temperature of polymers were obtained with D.S.C. Light microscopy was used to assess morphological changes under different conditions of crystallization and electron microscopy to obtain crystallographic information on the polymer-nucleant interaction.

## 2.1 MATERIALS

### 2.1.A POLYMERS

Different polymers of commercial grade were used to study the effect of a nucleating agent on their crystallization process. The polymers are listed in Table 2.1 with details of their origin and melting properties.

### 2.1.B NUCLEATING AGENTS

The substances to be tested for their nucleating ability were of commercial type. Talc, sodium benzoate, boron nitride and saccharin were used as received. Millad 3905, a substituted sorbitol, was kindly supplied by Northern Petrochemical company and produced by Milliken Chemical U.S.A.

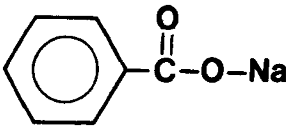
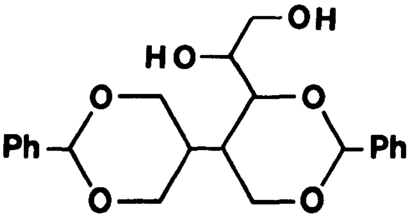
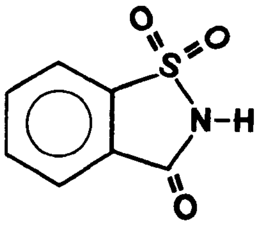
TABLE 2.1. List of polymers used in the present investigation with details of their origin and physical properties.

| POLYMER | ORIGIN | MELTING POINT (K)* |
|---|---|---|
| HIGH DENSITY POLYETHYLENE (HDPE) | PHILLIPS PETROCHEMICALS (MARLEX TR-885) | 408.0 |
| LOW DENSITY POLYETHYLENE (LDPE) | I.C.I. (46/63) | 386.3 |
| POLYPROPYLENE (i-PP) | I.C.I. (PROPATHENE GXM 43) | 439.5 |
| POLYBUTENE 1 (PB-1) | I.C.I. | 404 .9 |
| POLYOXYMETHYLENE (POM) | HOECHST (HOSTAFORM) | 439.6 |
| POLY-3-HYDROXY BUTYRATE (PHB) | I.C.I. (BX IRD 2) | 447.4 |
| POLYETHYLENE-TEREPHTHALATE (PET) | I.C.I. | 531.1 |
| NYLON 6.6. | I.C.I. | 537.5 |
| ISOTACTIC POLYSTYRENE (i-PS) | YARSLEY RESEARCH LABORATORIES | 523.7 |

* determined from DSC measurements at a heating rate of 5 degrees per minute.

It is of importance that the nucleating agent must present a solid surface to the polymer in the temperature range of crystallization, so it should melt above the polymer melting point. The melting temperatures for sodium benzoate, Millad 3905 and saccharin were obtained from the DSC curves and that for talc and boron nitride from the literature. Table 2 summarizes these results.

**TABLE 2.2. Nucleating agents used with details of their physical properties.**

| NUCLEATING AGENT | MELTING TEMPERATURE (K) | CRYSTALLIZATION TEMP (K) |
|---|---|---|
| TALC<br>$Mg_3Si_4O_{10}(OH)_2$ | 1223 | DECOMPOSES |
| SODIUM BENZOATE<br> | 573 | DECOMPOSES |
| BORON NITRIDE<br>BN | 3273 | - |
| Millad 3905<br> | 499 | 463 |
| SACCHARIN<br> | 501 | DECOMPOSES |

## 2.2 DISPERSIONS

Polymer-nucleant compounds were prepared by mechanically mixing certain amounts of nucleating agent into the polymer, at temperatures approximately 20°C above its melting point. A simple procedure was used, the polymer granules were placed on a preheated glass slide and the nucleating agent added to the molten polymer. In order to produce the required shear forces that would ensure a good dispersion, a glass rod was rolled onto the polymer-nucleant mixture until the mixing was complete. The homogeneity of the compounds was studied by light microscopy and found to be comparable to that obtained with a mini two roll mill or a Brabender mixer.

Compounds of 0.5, 1, 5, and 10% (w/w) of the nucleant in polypropylene, high density PE and low density PE were prepared; for the remaining polymers under study, only composites of 1 and 10% (w/w) of the nucleant were prepared.

## 2.3 DIFFERENTIAL SCANNING CALORIMETER TECHNIQUE

A Perkin-Elmer Differential Scanning Calorimeter (model D.S.C. 2) was used to study the crystallization behaviour of the polymers and their composites. The operation of the calorimeter is based on the temperature control of two similar sample holders. The system consists of two separate control loops, one for an average temperature control, the other for differential temperature control. In the average temperature control loop, the operator will select the desired temperature of the sample and reference holders. If the average temperature of the sample and reference holders is higher than that demanded by the operator, the power to both heaters will be decreased.

But if the average temperature is lower then more power will be fed to the heaters of both holders.

In the differential temperature control loop, signals representing the sample and reference temperature are fed to a circuit which determines which temperature is greater. The differential temperature amplifier output will then proportion a small increment of power between the reference and sample heaters in such a way as to correct any temperature difference between them. This is done by increasing the power to one while decreasing the power to the other. A signal is also transmitted to a recording system. The direction of the signal will depend upon whether more power is required in the sample or reference heater. When a transition such as crystallization or melting occurs an exothermic or endothermic process is evidenced. The change in power required to maintain the sample holder at the same temperature as the reference holder (its programmed temperature) during the transition, is the differential power and is recorded as a peak.

A typical D.S.C. thermogram is shown in Fig. 2.1. The ordinates provide a direct measurement of enthalpies of any transition by giving the differential heat flux, dQ/dt (expressed in mcal/sec) between the sample and an inert reference. The abscissa represents temperature in degrees K. The enthalpy of any transition considered is directly proportional to the area under the peak.

During crystallization, heat is released, and the effect is observed as an exothermic peak. The initial crystallization

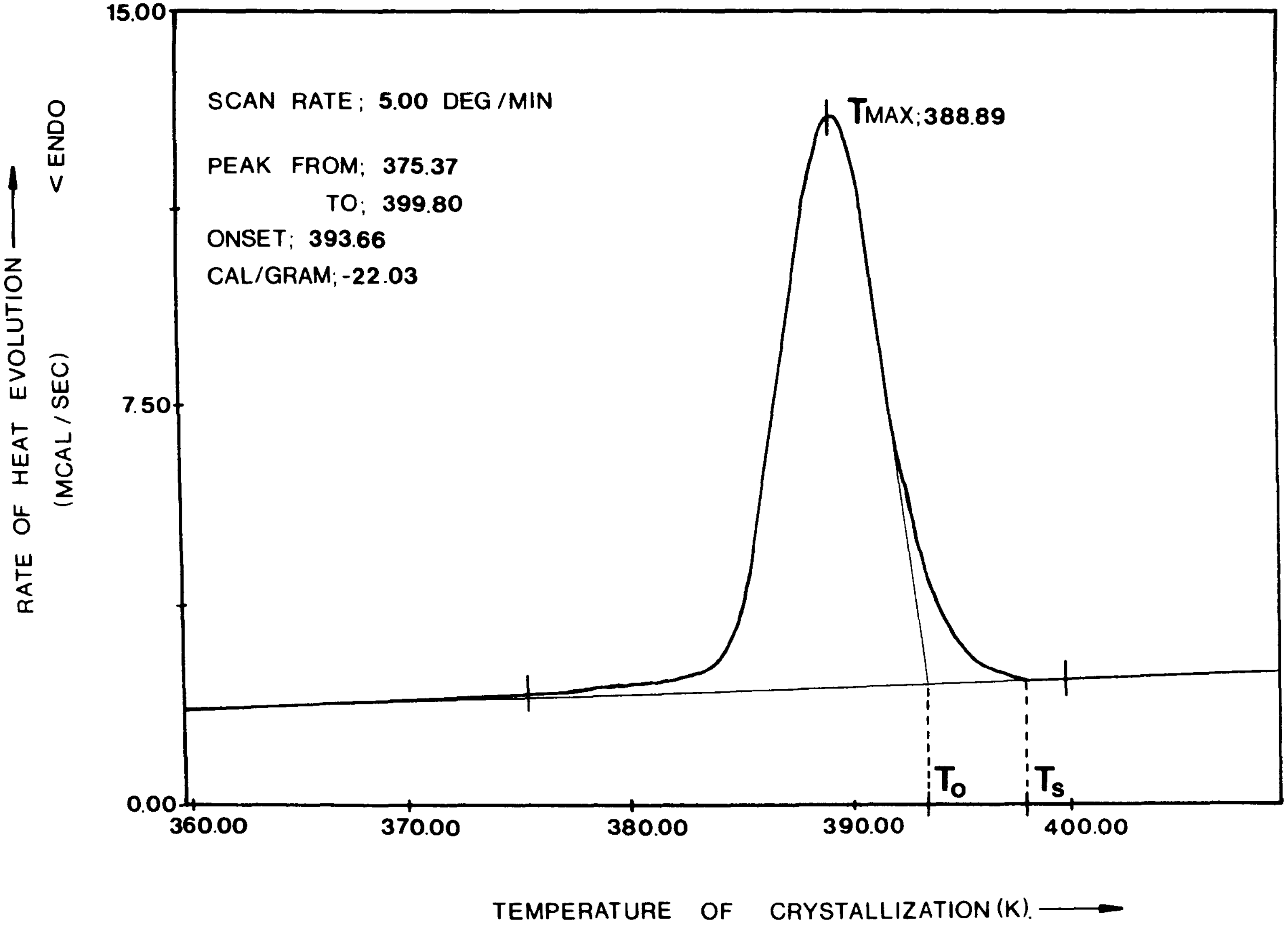


Fig. 2.1. DSC crystallization thermogram of a polymer (PP) showing transition temperatures.

temperature would be the point of first observable deflection from the base line and corresponds to $T_s$ in Fig 2.1. This temperature, however, cannot be measured accurately and a more convenient method to obtain this would be to extrapolate the base line until it meets the tangent drawn from the side of the peak, which gives a temperature $T_o$ as shown in Fig. 2.1. This temperature is known as the "onset" temperature. The temperature at which the bulk of the polymer has crystallized at a maximum rate is called $T_{max}$ and corresponds to the maximum of the peak.

The temperature readout from the calorimeter was calibrated using the melting points of pure substances such as indium (156.6°C), benzoic acid (122.5°C) and naphthalene (80.2°C), and showed that the indicated temperature was accurate within 0.5°C. Nitrogen dried over silica gel was used as the sweeping gas in all the experiments. Standard aluminium pans were used rather than hermetically sealed volatile pans because they have a wider and flatter base and so provide better thermal contact between the pan, sample and sample holder. Usually samples of 10-30mg weighed to an accuracy of ± 0.02mg were used.

The D.S.C. 2 Perkin-Elmer used to study the crystallization behaviour of polymers was interfaced with a thermal analysis data system (TADS). This system enabled us to store energy flow data at present time intervals directly into the memory of the data system. This improves the accuracy of the measurement of time and enables the evaluation of the "onset" temperature of crystallization. The system can also store the calorimeter base line without a sample, as a function of temperature, and subsequently subtract it from subsequent measurements with samples. This has substantially improved the linearity of the corrected baseline of the calorimeter over a wide temperature range. Also the enthalpy of crystallization can be calculated with the TADS system.

The crystallization experiments were performed at a cooling rate of 5 degrees per minute in the temperature range of 550 - 320 K. The upper limit at which the polymer sample was molten prior to crystallization was chosen according to its melting point. Usually the polymer was heated up to 30 degrees above its melting point and kept at this temperature for about 10 minutes. This procedure was adopted to wipe out, as much as possible, any previous morphological history in the sample. The polymer was then cooled at the selected rate (usually 5 degrees per minute) until the crystallization process was completed.

The various compositions prepared by thoroughly mixing a given amount of nucleating agent into the polymer matrix, were submitted to the previously described crystallization procedure. The effect of the nucleant content on the crystallization temperature of a polymer was then evaluated as the shift caused in its crystallization temperature compared to that of the pure material.

In order to characterize quantitatively the nucleating ability of talc, sodium benzoate, boron nitride, sorbitol and saccharin and the nature of the nuclei formed, an experimental technique based on the method of crystallizing polymers in contact with a continuous substrate of nucleating agent has been used. This technique has also enabled us study the substrate-induced morphology raised from the presence of the nucleating agent.

To obtain a continuous layer of substrate, a very fine dispersion of nucleant in acetone, was deposited at the bottom of the standard aluminium pan for DSC, and acetone was allowed to evaporate slowly.

The polymer sample to be crystallized on the substrate was moulded into the shape that would fit the aluminium pan as shown in Fig. 2.2. By means of this technique not only the nucleating ability of different compounds was characterized but the effect of different thermal histories applied to the polymer melt on the nucleating ability of the compounds was assessed.

Specifically polypropylene samples on different substrates were molten at 450 K and 470 K for 2 and 20 minutes respectively. The samples were then cooled at a constant scan speed until the resulting exotherm had been obtained. Reference samples without the presence of substrate were submitted to the same procedure.

Also observations concerning the effect of different cooling rates upon the crystallization of polymers were made. Samples of polypropylene on talc substrate were cooled at speeds of 1.25, 5, 10 and 20 degrees per minute.

In order to make sure that the effect of different cooling rates on the crystallization process was characteristic of polymeric materials and not due to insufficiently fast response of the

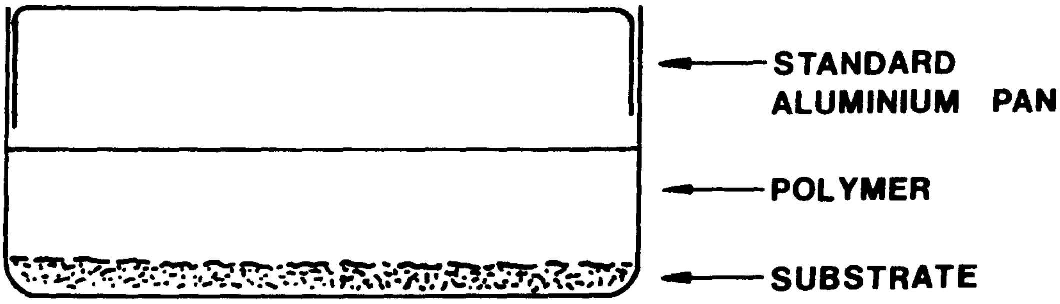


Fig. 2.2. Schematic representation of the polymer sample crystallized in the DSC.

calorimeter, pure indium was cooled down from the melt at different scanning speeds. It was found that varying the cooling rate from 1.25 degrees/minute to 10 degrees/minute, the onset temperature was shifted one degree, assuring a fast and accurate response of the calorimeter. With different cooling rates the shape of the curves and the maximum peak temperature varied as shown in figure 2.3 but the enthalpy of crystallization remained constant. In all these cases the initial parts of the crystallization curves are similar and not dependent on the rate of cooling. This again asures of an accurate response of the calorimeter.

The possible "insulating" effect of the substrate layer coating the aluminium pan was studied by placing a sample of indium on a talc coated pan, melted and cooled down at 5 degrees/minute. It was found that the onset temperature was unchanged compared to that of indium without a substrate, cooled at the same speed; only the shape of the curve was modified (see Figure 2.4 a,b).

To study the effect of isothermal crystallization on the nucleation process, samples of polypropylene, prepared under the same technique of substrate induced morphology, were crystallized at constant temperatures of 414 K, 407 K, 403 and 400 K. These temperatures were chosen according to the effect observed of the cooling rate on the speed of crystallization of polypropylene.

The thermal history of the polypropylene samples for isothermal crystallization was the same as described for non-isothermal conditions, except that the samples were cooled rapidly from the

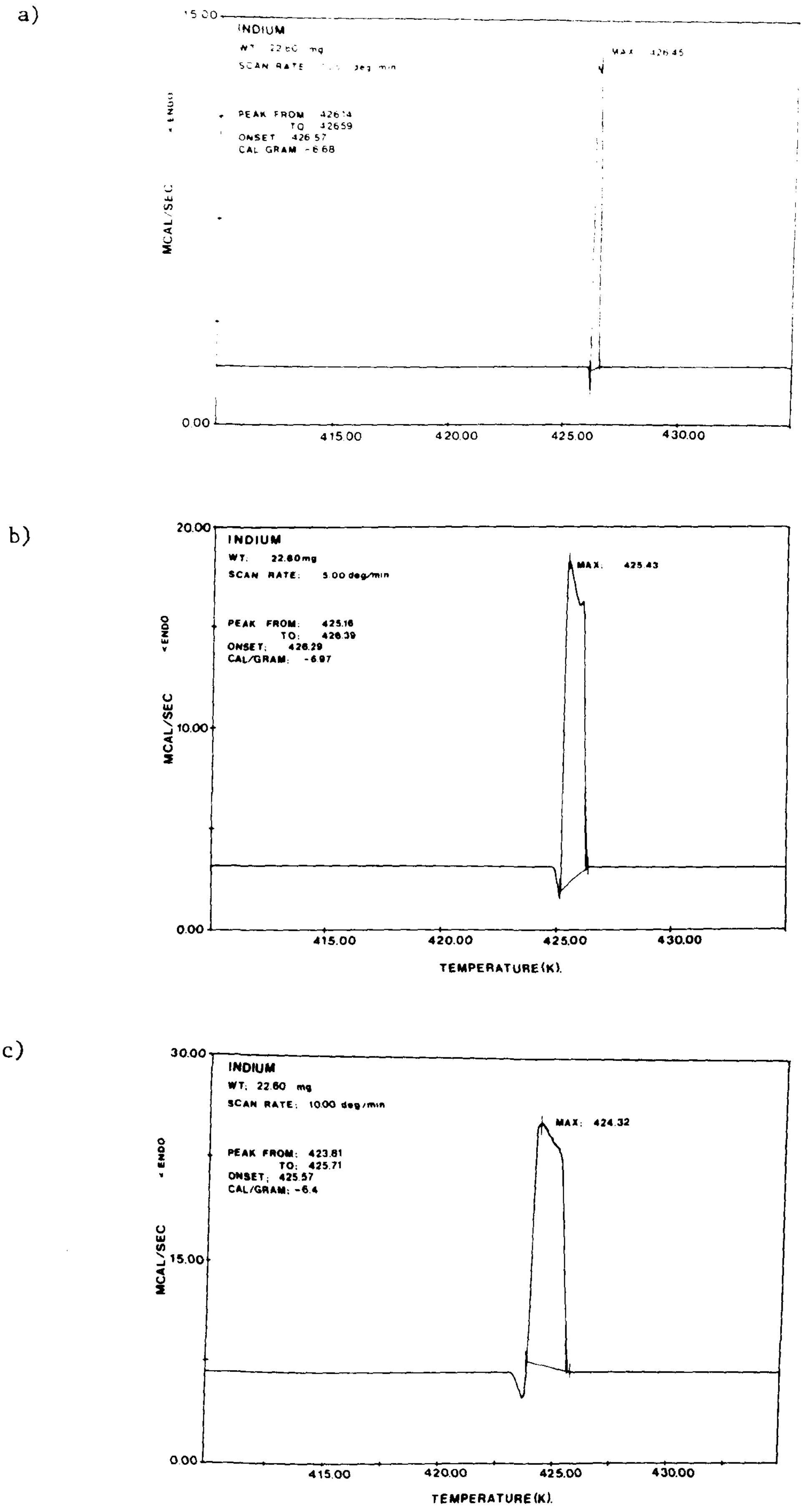


Fig. 2.3. Crystallization exotherms of indium at different cooling rates a) 1.25 degrees/min b) 5 degrees/min and c) 10 degrees/min.

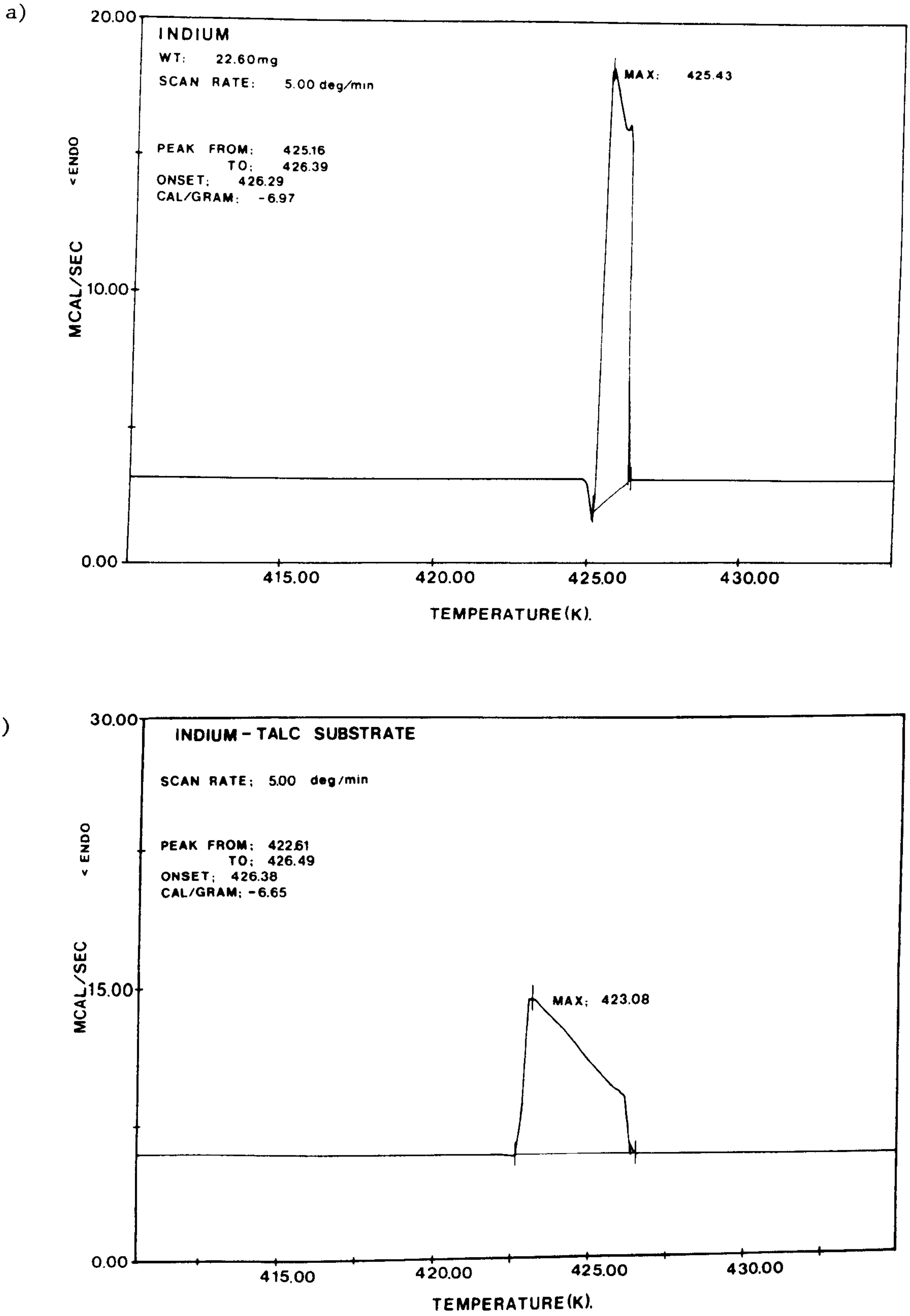


Fig. 2.4. Crystallization exotherms of indium
a) in contact with the aluminium pan
and
b) in contact with talc substrate.

molten temperature to the selected crystallization temperature (40 degrees per minute) and kept at this temperature until the process was over.

A different approach to the effect of the melting temperature on the crystallization process was developed when pure samples, samples with the substrate induced morphology and samples mixed with the nucleant were melted close to and above their melting temperature.

Samples of polypropylene and polypropylene loaded with 10% Talc were investigated over a range of melting temperatures from 435 K to 475 K. In order to obtain consistent results all the samples to be tested were previously crystallized under the same conditions so as to obtain a constant spherulitic size.

Samples of polyhydroxybutyrate on boron nitride, talc and saccharin substrates, mixed with the nucleators and pure, followed the same procedure described above but the melting temperatures varied from 440 K to 480 K.

## 2.4 PHOTOMICROGRAPHY

In order to assess changes in morphology resulting from the presence of the nucleating agent, light micrographs of microtomed sections of the various crystallized composites and pure materials were obtained. Also the transcrystalline morphology resulting in the substrate-induced samples, prepared as described above, was analyzed.

After the DSC measurements were performed and the specimens were removed from the aluminium pans, thin sections between 4-6μm thick were cut with a metal knife microtome. These microtomed sections were examined using a Reichert Zetopan Microscope with polarized light. Optical micrographs were taken with a 35mm camera using Kodak Plus X pan black and white film. The magnification was calibrated by photographing a 1mm scale with divisions of 0.01mm.

## 2.5 SELFNUCLEATION MEASUREMENTS

Polymer melts can cool and crystallize under isothermal or nonisothermal conditions. In the case of a nonisothermal crystallization, the temperature gradient throughout the polymer cross-section will influence the course of the crystallization and thus the morphology and properties of the product[54,55].

A simple apparatus with an accurate control of the temperature gradient was conceived for studying the influence of such a gradient on the crystallization process of various polymers.

The apparatus shown in Figure 2.5 consists of a copper bar with an electrical resistance heater at the top and a cooling coil with circulating water at the bottom of it. Setting the heater to a required value and allowing the system to reach a steady state, a temperature gradient is obtained along the bar. A polymer film prepared by solvent casting onto a cover slip can then be placed on the copper bar and the effects of the temperature gradient recorded. An asbestos-cement holder, cut to the size of the cover slip was attached to the copper bar. The holder also provided an accurate spacing for 6 thermocouples.

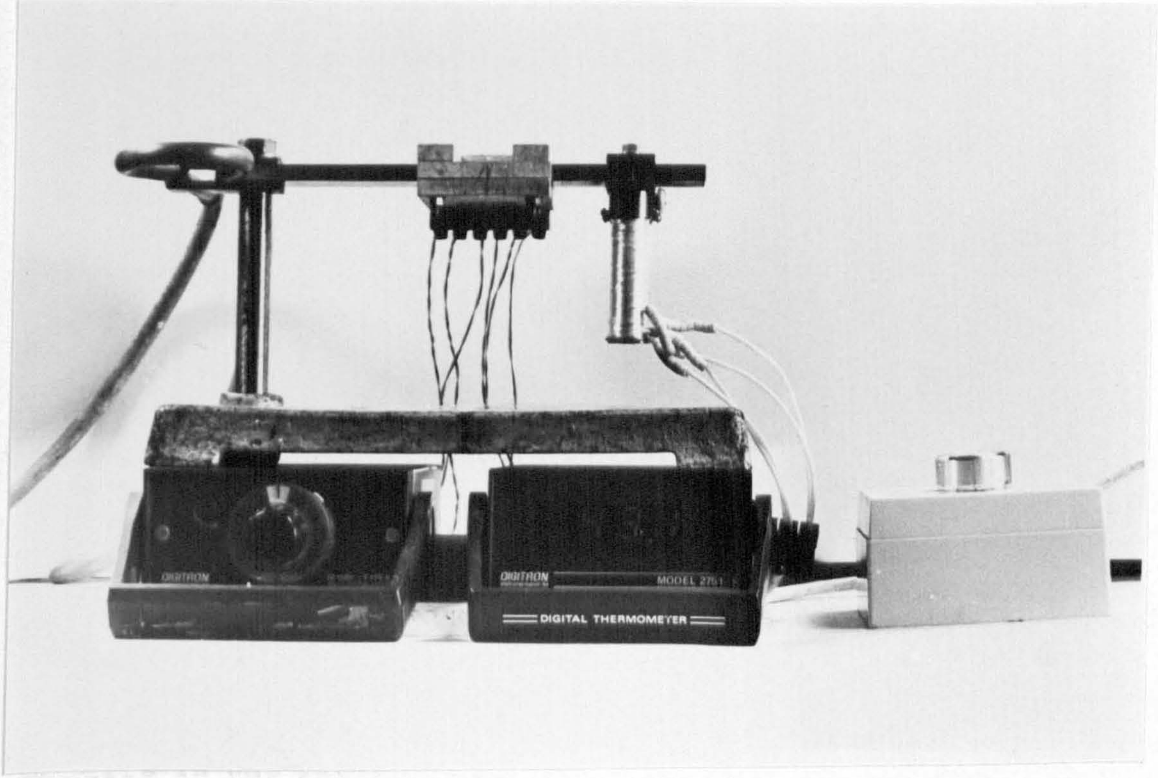


Figure 2.5. Apparatus constructed to obtain an accurate temperature gradient.

The length of the bar was adjusted in such a way as to ensure that the steepness of the gradient that can be established on the specimen was within the range of its melting temperature.

The temperature readout from the apparatus was calibrated with the melting point of a pure substance such as benzoic acid (122.5°C) and found to be 124.0°C. This 1.5°C of discrepancy is due to slightly different calibration curves for chromel/alumel thermocouples made for the stage, to those provided by the manufacturer of the digital thermometer (Digitron).

A crystallization experiment is conducted by placing a polymer specimen onto the sample holder that has been previously heated so that the melting temperature of the polymer is reached at the mid point of the sample holder (see Fig 2.6). sufficient time is allowed to establish the steady-state linear temperature profile in the polymer then the gradient temperatures along the sample holder read and the sample quickly withdrawn and allowed to cool in air to room temperature. A plot of temperature of the bar versus distance is obtained.

Polymer specimens of even thickness and with a well developed spherulitic structure have shown, after the experiment was performed, a transition band that has begun at the cooler face and proceeded outward into the melt, establishing a crystal-melt interface which corresponded to a certain temperature gradient. This gradient could be calculated by simply measuring the width of the transition band and compare it with the corresponding temperature gradient graph.

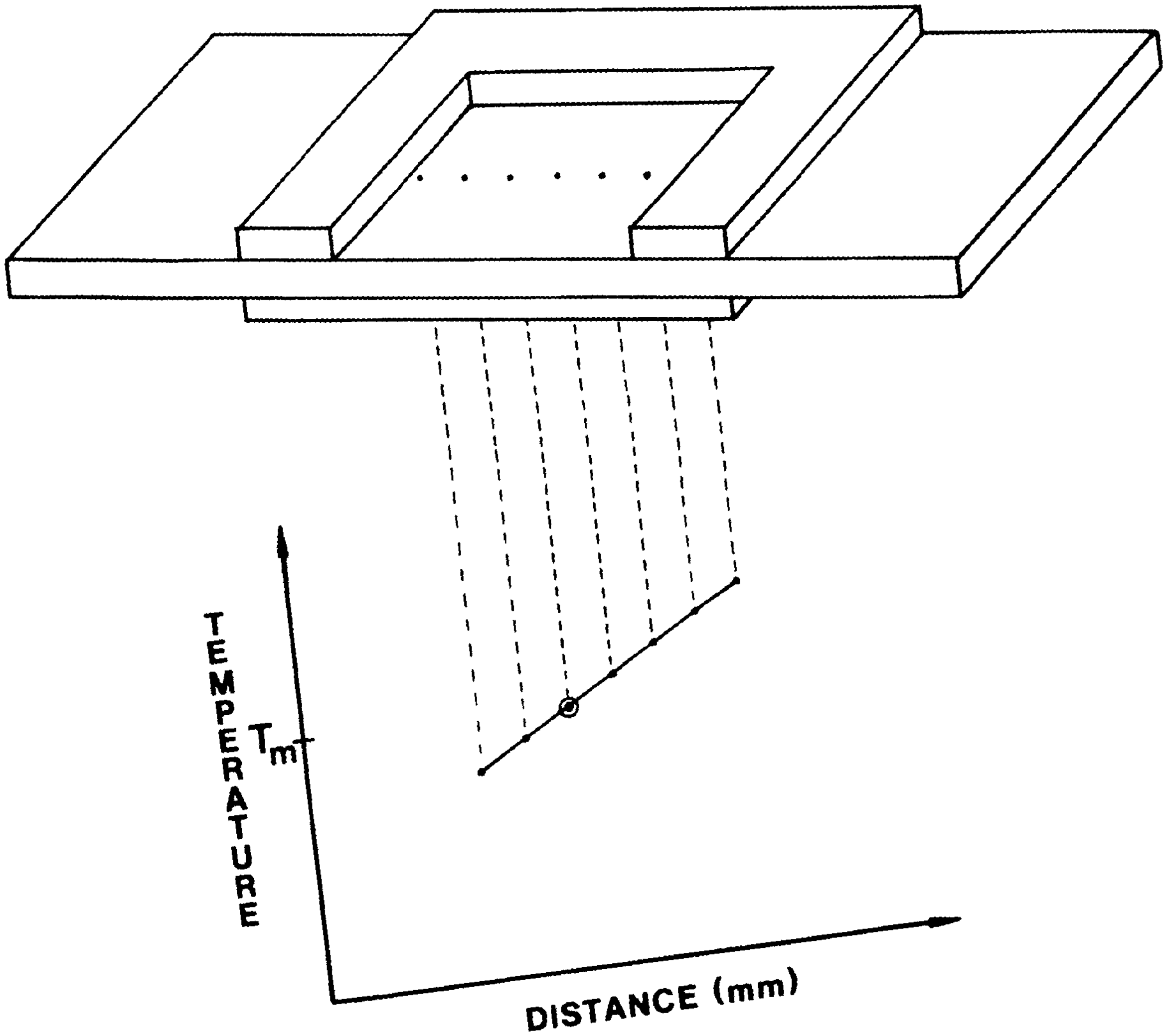


Fig. 2.6. Schematic representation of the spacing of thermocouples along the copper bar and plotting of the temperature gradient.

The transition bands, and thus the temperature ranges for the selfnucleation, were established for the following polymers: polyethylene, polypropylene, polybutene, polyoxymethylene, polyhydroxybutyrate, polyethyleneterephthalate and Nylon.

## 2.6 ELECTRON MICROSCOPY

In order to reveal the structure of the nuclei formed and to establish a possible crystallographic correlation between the polymer matrix and the nucleant, electron diffraction studies have been undertaken.

A Hitachi HT700 electron microscope that can be operated within a range of 75 to 200 KeV has been used. The electron beam from the electron gun is focussed via a double condenser lens system with field-limiting apertures onto the specimen. The imaging system that is placed below the specimen comprises of four lenses: objective, intermediate and projector lenses. With the condenser lens system, and particularly with the condensor/objective lens (STEM system), the size and angle of the incident electron probe can be controlled. The image of the specimen is focussed with the second condensor and condensor/objective lens and the required magnification in the STEM mode is obtained by controlling the scan raster. The image contrast is enhanced by the use of an intermediate lens aperture. When the condensor objective is adjusted to focus its back focal plane on the screen, the diffraction pattern is formed. The dispersion of the diffraction patterns is controlled by the intermediate and projector lens. At any time during operation of an electron microscope both image and diffraction patterns are produced, the setting of the condensor and objective lenses determines the focus of the image or the diffraction pattern. This image is observed on a cathode ray tube and recorded by the camera system. The diffraction pattern is observed on the fluorescent screen and recorded by another camera system.

Most synthetic polymers are very sensitive to the electron beam[56] and it is difficult to obtain reliable information from undamaged specimens. To overcome this difficulty Vesely[57] adapted the scanning transmission electron microscopy (STEM) technique, which consists of using the strongly excited objective lens to focus a fine electron probe on the sample, and modified the operating conditions to obtain large spot size (1-3μm) and simultaneously sharp diffraction patterns with minimum beam damage.

The same technique has been used in the present investigation and the spot size of the scanning microdiffraction mode was adjusted to approximately 3.0μ and measured by contamination marks on a carbon film.

The extent of rotation of the diffraction pattern with respect to the image was determined using molybdenum trioxide crystals, and found to be 15° for magnification of 5 K and the diffraction conditions used. The camera length was determined using thallous chloride, and found to be 800mm.

Samples suitable for electron microscopy were prepared on glass slides by solvent casting a dilute solution (c.a. 0.1% w/w) of polymer in an appropriate solvent to which it has been added a small amount of the nucleating agent (0.01% w/w). For most of the polymers under study, p-xylene was a good solvent but for polyhydroxybutyrate, ethylene chloride was used as a better solvent. For polyoxymethylene, the selected solvent was dimethylformamide.

Once dried, the films with nucleating agent were melted in a vaccum oven for one hour, and subsequently recrystallized. After carbon coating, suitable areas for electron diffraction were selected under the optical microscope. A polyacrylic acid backing had to be used to detach the film from its supporting glass slide, then floated off on water and mounted on copper grids.

Reference samples without the presence of the nucleating agent were prepared in the same way as described previously. Diffraction patterns at the polymer-nucleant interface were taken in the following way. The microscope was set up to operate in the scanning transmission mode. A specimen was scanned until a suitable particle nucleating a spherulite was found. The position of the particle was marked on the screen and the diffraction spot was then focussed on one side of the area investigated. Once the beam current was lowered, the diffraction spot was accurately placed at the marked area on the screen. Then the shutter of the TEM camera opened and the beam current increased. The specimen was exposed for about 3 seconds to the electron beam, during which time the diffraction pattern was recorded. The corresponding image was recorded with the STEM camera. Kodak FP-4 film was used for image recording and Kodak non-screen NS-2T film for diffraction patterns.

# CHAPTER 3

# 3. SURFACE CRYSTALLIZATION OF POLYMERS ON SUBSTRATES

Certain substances when dispersed in a polymer melt promote crystallization and are referred to as nucleating agents. The addition of such heterogeneities appears to control nucleation density and brings about homogeneity in nuclei distribution[58,59]. This control can improve a number of physical properties of a manufactured polymer as well as an increase in the crystallization temperature leading to shorter processing cycles.

A large number of nucleating agents have been studied for various polymers[60,61]. In most cases however, little could be concluded about the properties which cause a nucleating agent to be effective. As reviewed in the introductory section, several factors have been suggested; Beck[62] considered that the chemical structure of the nucleator is the most important factor; other authors[36,38] considered the crystalline morphology of the substrate to be more important. Controversial results were obtained when a relationship between surface energy and nucleating ability was considered. Koutsky[19] found that changing the surface energy of the alkali halide substrate by a factor of 4 did not result in any significant change in their nucleating ability towards polyethylene. Yim and St. Pierre[26] on the other hand showed that modified silicas could nucleate polydimethylsiloxane. Rybnikar[63] proposed that the evolution of volatile products from the nucleant was an important factor in nucleation.

Still an unambiguous correlation between these several factors has not been well established. In the present investigation, in order to clarify the nucleation process further, it is important to establish the nature and extent of the interfacial layer formed between the polymer and the nucleating agent. An experimental technique based on the method of crystallizing polymers on different substrates of densely packed particles is used. The formation of a transcrystalline region above the substrate is considered as an indication of nucleating ability of the various substrates used. To establish if the substrate activity in nucleating crystallization is temperature-dependant, the influence of melting temperature, melting time, cooling rate and crystallization temperature on the crystallization process and specifically on the transcrystalline region was investigated.

## 3.1 RESULTS AND DISCUSSION

The crystallization behaviour of polyethylene, polypropylene, polybutene, polyoxymethylene, polyethyleneterephthalate, polyhydroxybutyrate and nylon 6.6 nucleated on various substrates has been examined by DSC. The effect on the morphology of the nucleated polymers was investigated with light microscopy. Most of the work initially done in order to develop a framework for studying the crystallization behaviour of polymer (e.g. rate of cooling, melting temperature and time) was carried out with polypropylene. Once these conditions had been established, they were then used to test other polymers.

### 3.1.A POLYPROPYLENE

When PP is cooled from the melt on a D.S.C., it exhibits an exotherm as shown in Fig. 3.1a. It reveals that the polymer crystallizes at a maximum temperature of 388.9K when a constant

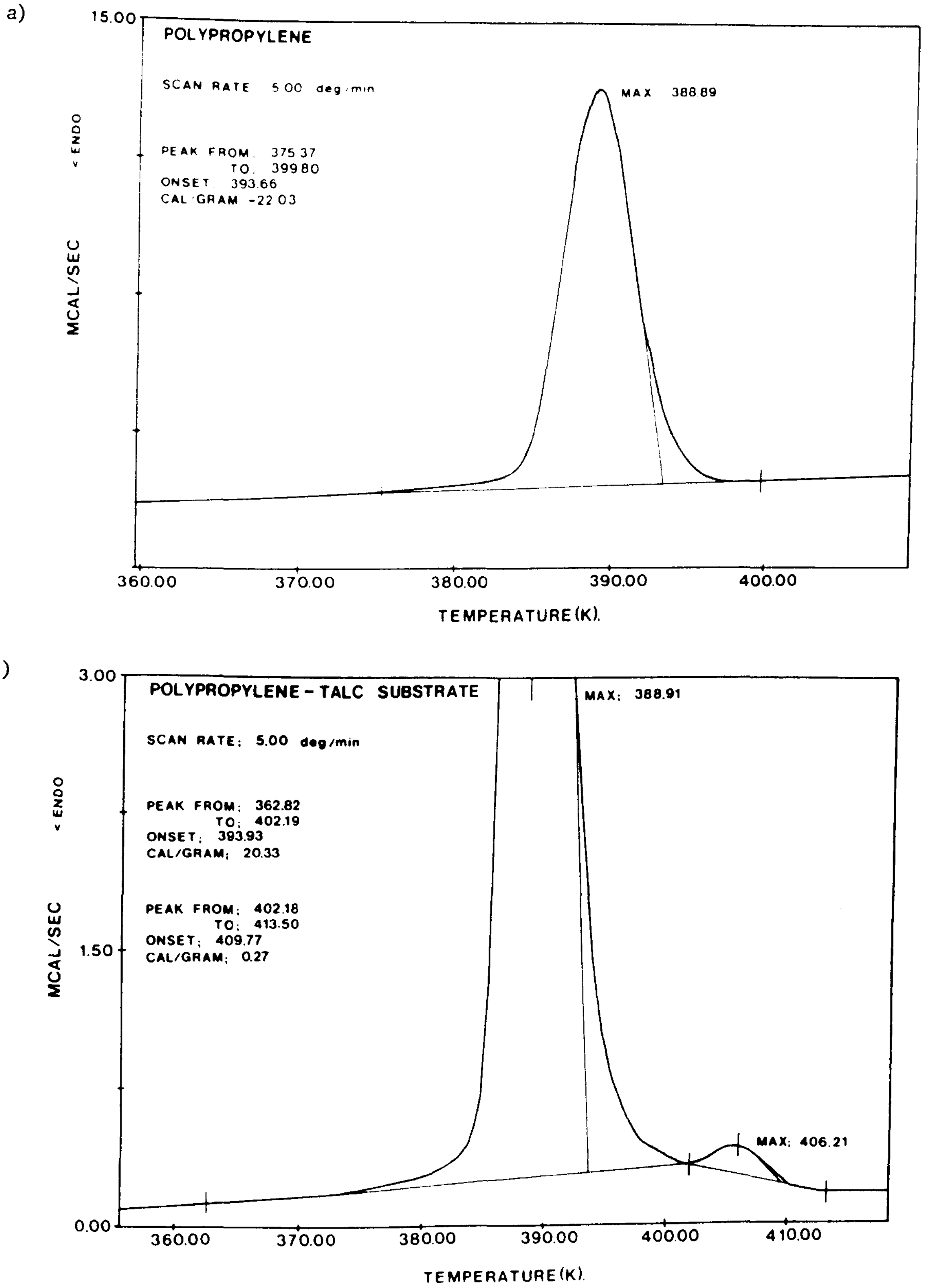


Fig. 3.1. Crystallization exotherms of a) pure polypropylene and b) polypropylene - talc substrate, melted at 470K and crystallized at $5^0$/min.

cooling rate of 5 degrees/min is used. But when PP is crystallized onto a talc substrate, the exotherm obtained (Fig. 3.1b) has indicated the presence of two distinct processes. One occurs at a higher range of temperatures with a maximum at 406K and another at a lower range with a distinct maximum at 389K. By comparing both crystallization exotherms in Fig. 3.1, it can be seen that the presence of the nucleating agent in a substrate form, had induced some changes in the crystallization process of polypropylene with the appearance of a new small peak. In order to make the small peak clearly visible, the vertical scale of the crystallization exotherm in Fig. 3.1b has been expanded to three times its original size.

The samples were microtomed at different levels throughout their structure. All of them have shown clearly that there has also been a change in morphology. In polypropylene-talc substrate samples (Fig. 3.2b) the effect of the substrate has been such that the nucleation density will prevent lateral growth of the spherulites in contact with it, and allow them to grow in a direction normal to the substrate. The resultant columnar morphology is known as transcrystallinity[34,35,36]. At a depth of 50-80μ the morphology reverts and the polymer has crystallized without restriction, giving rise to fully developed spherulites. The depth attained by this region is determined by the point of impingement with spherulites nucleated and growing symmetrically in the bulk. The thickness of the layer is similar to the radius of an average spherulite indicating that the spherulites in the bulk were born more or less at the same time as those in the transcrystalline region.

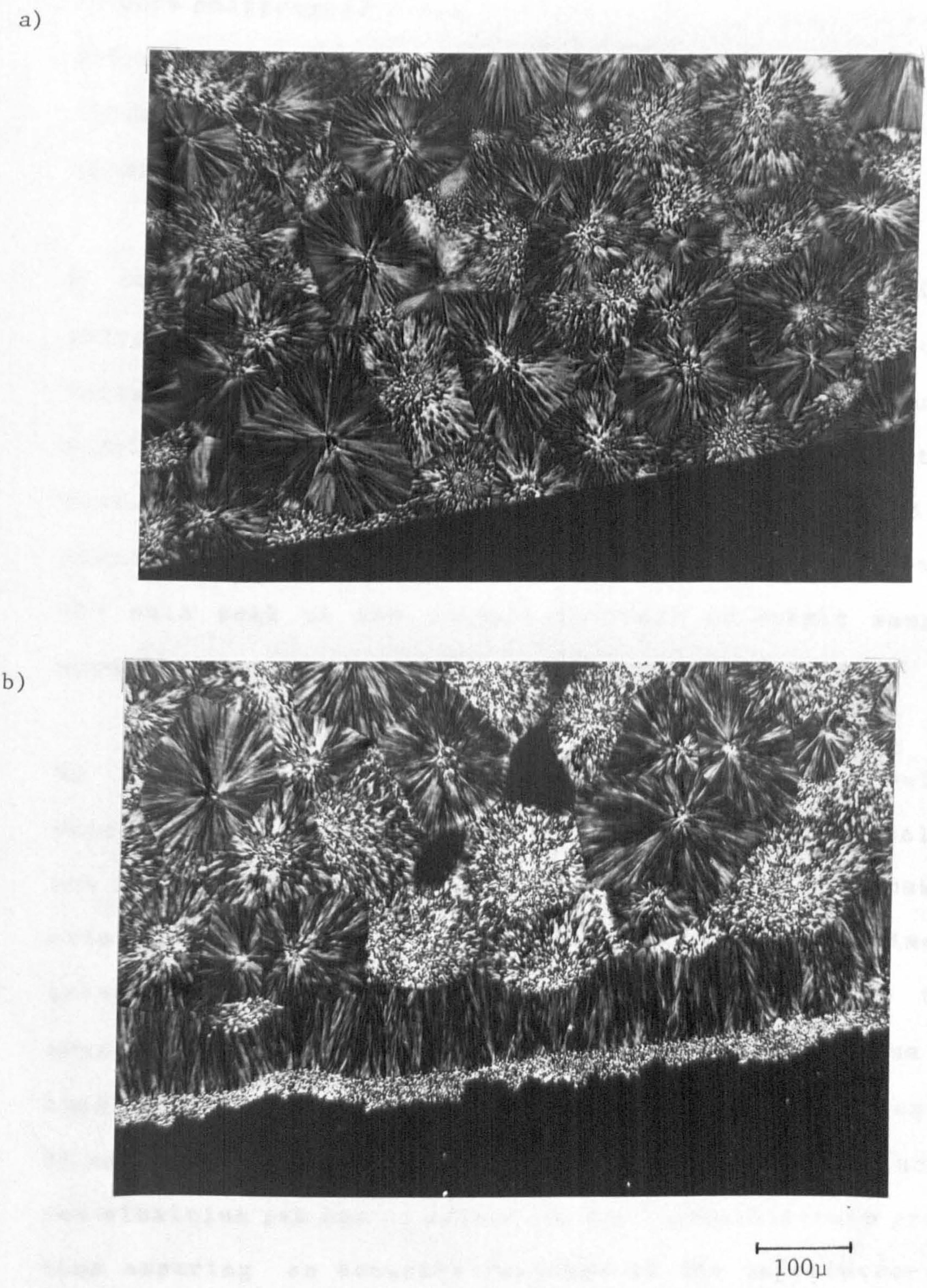


Fig. 3.2. Microtomed samples of a) pure polypropylene and b) polypropylene - talc substrate. Samples melted at 470K and crystallized at 5 degrees/min.

In pure polypropylene sample (Fig. 3.2a), spherulites have grown without restriction. Even the spherulites close to the surface, which are in contact with the aluminium pan, have a spherical symmetry.

A comparison between the spherulites obtained in pure polypropylene and those in the bulk material above the transcrystalline region in polypropylene-talc substrate samples has shown that they are similar in size and of the same type. The temperature at which the pure material has crystallized (Fig. 3.1a) is the same as the temperature at which the main peak in the polymer-nucleant substrate sample has appeared.

To prove the reproducibility of the above results, a polypropylene-talc substrate sample previously crystallized, was placed up side down in the aluminium pan. Both peaks were obtained at the same temperature as before. This experiment has proved that the origin of the small peak is due to the crystallization process of the polymer itself and not due to any insulating effect caused by the presence of the talc substrate. It has also proved that the way in which the heat is extracted in the aluminium pan has no effect on the crystallization process, thus assuring an accurate response of the calorimeter.

A major characteristic of the crystallization of polymers is the strong dependence of the rate of cooling on the crystallization temperature. The nucleation density of a pure polymer is affected by cooling rate, slow cooling producing a lower nucleation density than quenching. Beck[62] report a 16oC difference in crystallization temperature between cooling rates of 1°C/min and 20°/min for polypropylene. Figure 3.3 shows the relative decrease in maximum crystallization temperature obtained for talc substrate samples with increasing cooling rates. For the main peak, 18° difference in crystallization temperature between cooling rates of 1 and 20 degrees/min was obtained. These observations are in agreement with the results of Beck. The same behaviour was observed for the secondary peak and both are shifted in a parallel way, and indicates a finite rate for the crystallization process. Obviously, close control of the cooling rate is essential for reproducible results. Crystallization measurements were performed at a convenient rate of cooling of 5 degrees per minute.

It has been shown that the rate of polymer crystallization can be dependent on the thermal history of the melt[19]. Turska and Gogolewski[64] studied the crystallization of nylon 6 and found it to be dependent on the thermal history of the melt. Similar results were obtained for i-PS by Boon et al[65]. In all such cases, as the time the polymer is kept at the melt temperature is increased, the crystallization rate is lowered. Also the temperature at which the polymer is melted is of importance. This behaviour is generally attributed either to incomplete melting of highly crystalline fragments, i.e., the centers of spherulites, or to the persistance of small crystalline regions trapped in cavities of solid impurities. On the other hand, Chatterjee and Price[36] observed that the columnar region obtained for various polymeric substrates is temperature-dependent, changing from transcrystalline to spherulitic upon increase of the crystallization temperature. For this reason

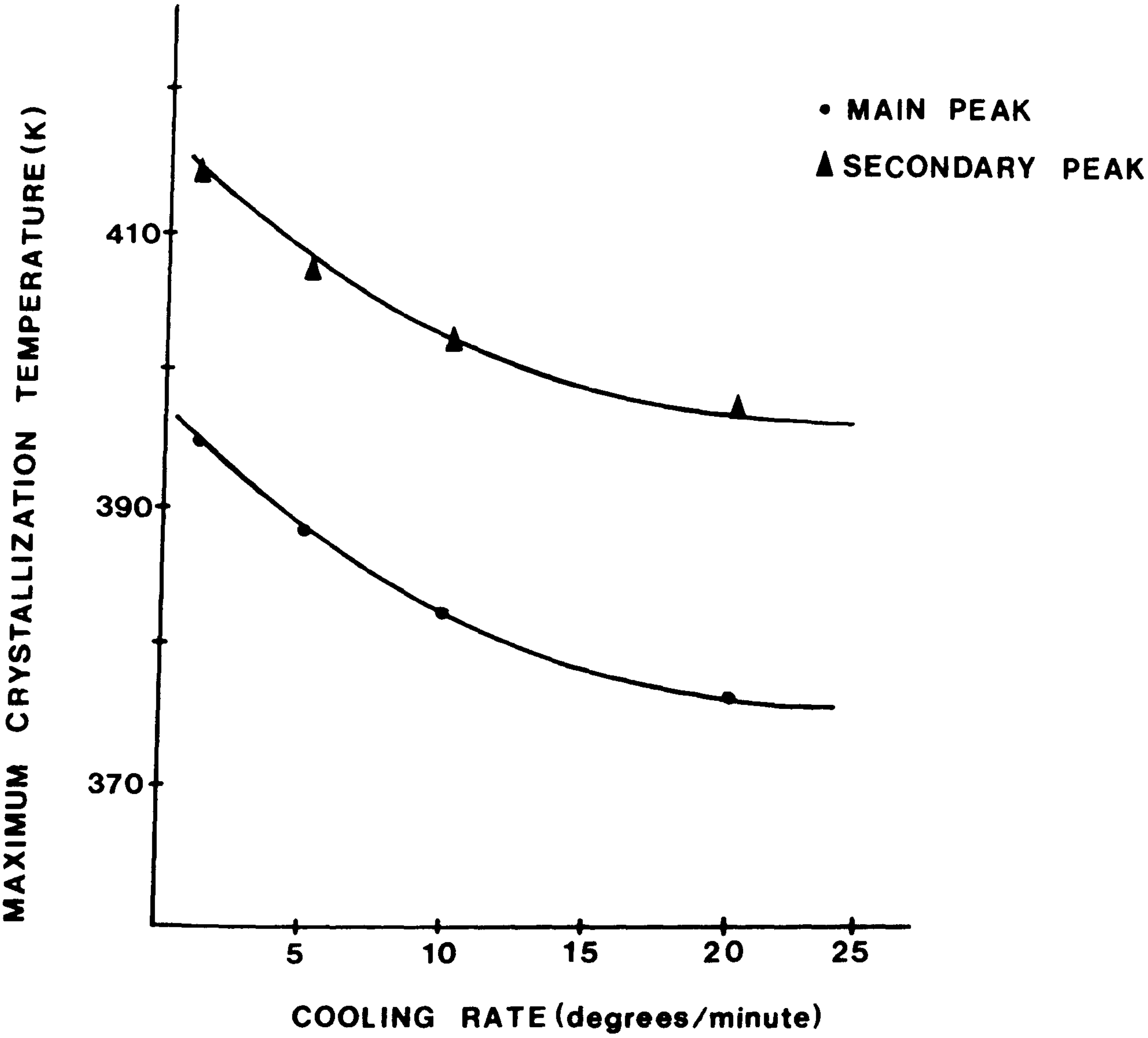


Fig. 3.3. Variation of crystallization temperature with cooling rate for polypropylene - talc substrate sample.

the effect of different thermal history above the melting point upon the crystallization of substrate samples was investigated.

The samples were melted 30 and 10 degrees above their melting point for 2 and 20 minutes before the crystallization commenced. There has been no change observed in the crystallization exotherms. Both peaks in all cases were obtained at the same temperatures as in Fig. 3.1b. The nucleating ability of talc substrate has shown no significant changes in the transcrystalline region. The morphology was similar in all the samples and the height of the columnar region was not affected either. The spherulites obtained in the bulk material were not influenced in their size or type with different thermal treatments.

To explore the effects of crystallization temperature on surface morphology of substrate-polymer samples, PP specimens were crystallized isothermally in contact with talc. Different temperatures were chosen according to the temperature at which the small peak appeared in the non-isothermal experiments performed at various scan speeds. The isothermal crystallizations were carried out at 414K, 407K, 403 and 400K. Figures 3.4 and 3.5 show the maximum height attained for the transcrystalline region where samples were crystallized at 414K, 407K and 400K. No significant difference in transcrystalline height compared with the non-isothermal samples could be obtained. The size of the spherulites in the bulk material were observed to be increased in the same proportion as the transcrystalline region.

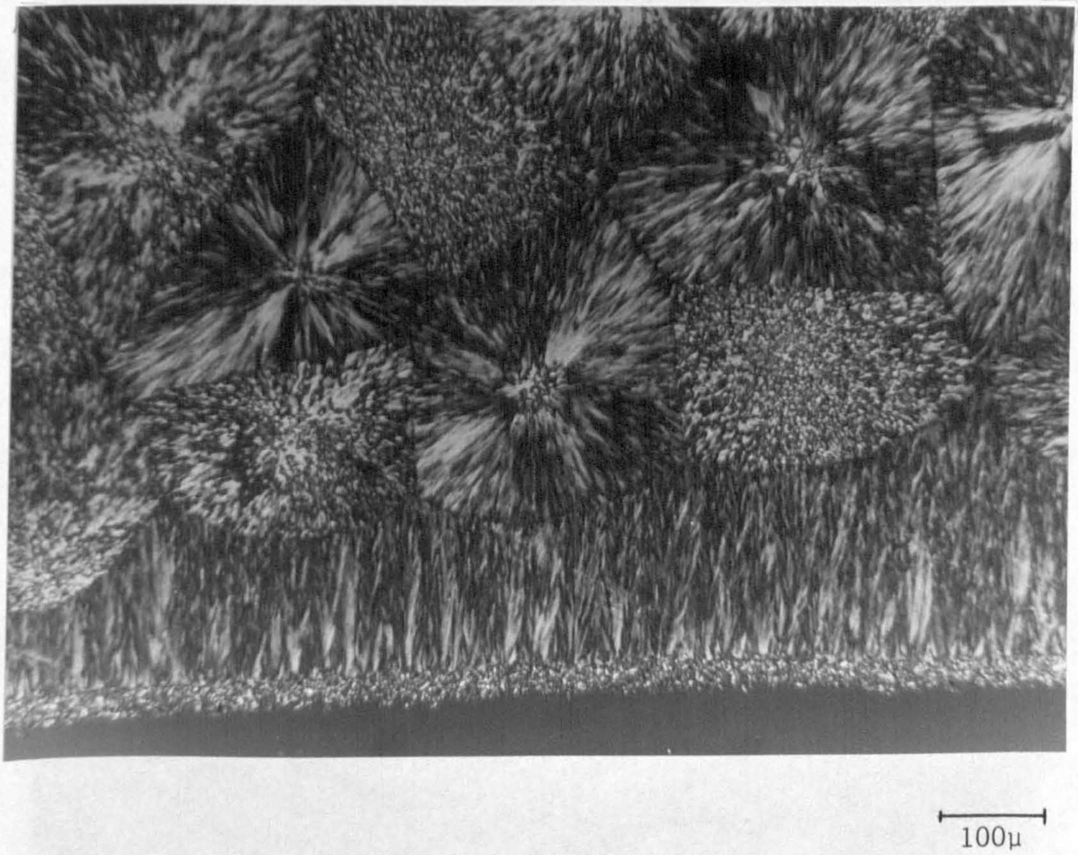


Fig. 3.4. Microtomed sample of polypropylene - talc substrate isothermally crystallized at 414K.

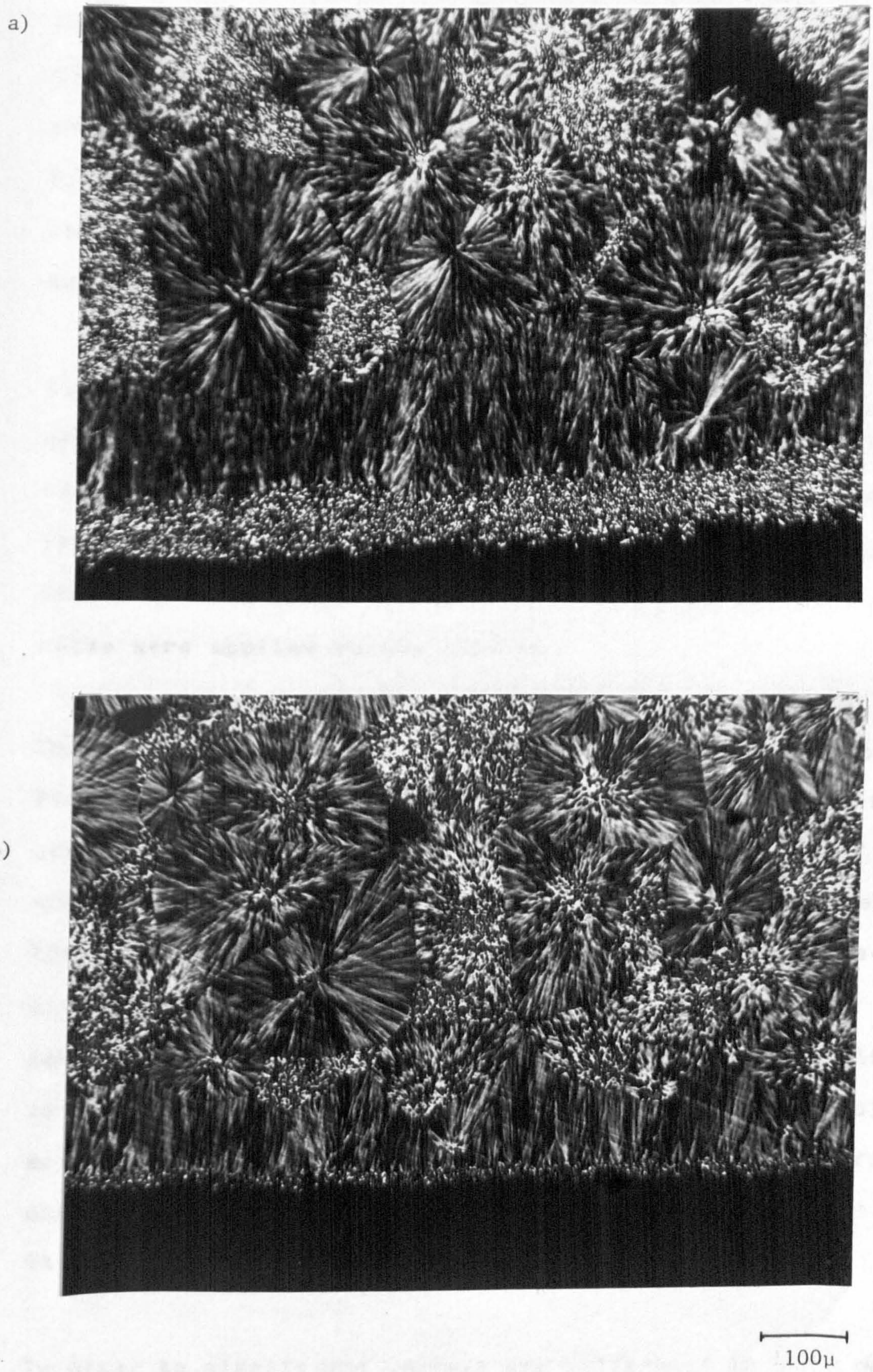


Fig. 3.5. Microtomed sample of polypropylene - talc substrate isothermally crystallized at a) 407K and b) 400K.

The above results clearly demonstrate that conditions which ensure complete melting of the polymer have no effect on the crystallization rate for polypropylene-talc substrate samples. For isothermally or non-isothermally crystallized samples, no change in morphology either in the transcrystalline region or in bulk material was noted.

Fitchmun and Newman[35] reported different results, where PP was crystallized on Teflon or Mylar at different crystallization temperatures. According to those authors, a transition from transcrystalline to a normal spherulitic morphology was observed. The same transition occurred when different cooling rates were applied to the samples.

Chatterjee and Price[36] reported similar results to those of Fitchmun and Newman[35]. They observed the effect of crystallization temperature on the surface morphology of PP in contact with isotatic polystyrene (i-PS). A transition between transcrystallinity and spherulitic morphology was detected at a crystallization temperature of 133°C (406K). Above that temperature the surface is insufficiently active to influence the transcrystalline region and the sample has a spherulitic morphology. In the present investigation, no significant changes were observed at that temperature, and over a range from 141°C to 127°C, as shown in figures 3.4 and 3.5.

In order to clarify and explain the difference in our results compared to those by Fitchmun and Newman[35] and Chatterjee and Price[36], the crystallization of PP on i-PS was performed in the DSC.

Figure 3.6a shows only one peak appearing at 387K, the usual crystallization temperature for PP. Microtomed sections (Fig. 3.6b) taken at different levels throughout the sample show that some spherulites appear to be nucleated on the surface and are somewhat elongated. This indicates that this partially transcrystalline region was not able to produce a secondary peak as was detected for PP-talc samples. The reason for this could be either that the density of nuclei in the transcrystalline region is very low and the calorimeter is not able to detect small changes, or that the rate of nucleation is similar in both regions giving rise to one peak only. Which ever case is considered, it is clearly demonstrated that the nature of the interaction of the polymer with the substrate is an important factor. To be effective, the surface must have a nucleating efficiency equal to or greater than that of the nuclei present in the polymer.

For the PP-talc sample the nucleating density of the substrate is very high and approximately constant for various crystallization temperatures (141°C to 127°C). In the bulk material, the nucleation density is reduced to approximately half at 141°C compared with that at 127°C as shown in Figures 3.4 and 3.5. This effect reveals a strong interaction of the nucleating particles with the polymer, and is independent of the thermal history. What still remains to be established is the nature of the interaction and the active sites in the substrate particles. This will be elucidated by electron miroscopy.

When the interaction between the nucleating substrate and the polymer is weak, the nucleation density and the morphologies

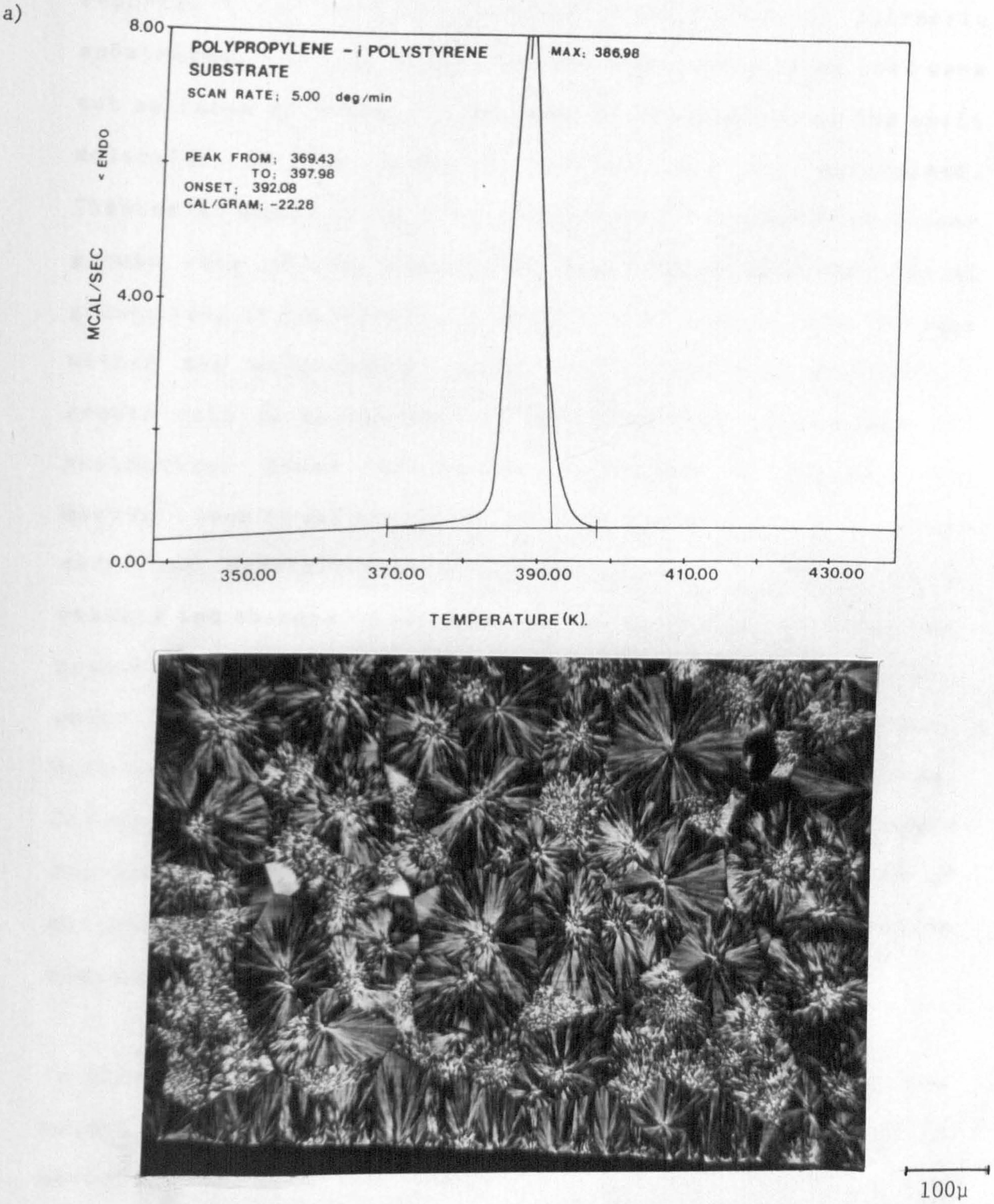


Fig. 3.6. a) crystallization exotherm of polypropylene - isotatic polystyrene substrate, melted at 470K for 20 minutes and crystallized at $5^o$/min. b) microtomed sample of polypropylene i-PS substrate.

obtained are temperature-dependent. This has been extensively reported[36] for various polymers crystallized on polymeric substrates. In that study, the polymeric substrates used were cut surfaces of pressed films, and the orientation of the chain molecules in the substrate surface was not determined. Chatterjee and Price in a following paper[66] compared the linear growth rate of the transcrystalline region with the radial growth rate of spherulites in the bulk and found it to be the same within the experimental error. Also, the transcrystalline growth rate is independent of the substrate responsible for nucleation. These results were confirmed by Campbell and Qayyum[41] when PP was crystallized on Terylene and nylon fibers at different crystallization temperatures. To explain these results and changes in nucleation density around the fiber they presupposed the existence of some type of attractive, possibly polar, forces between the surface of the fibers and the polymer. With decreasing temperature the melt viscosity would increase. Consequently, the mobility of the heterogeneities would decrease and this could also contribute to the build up of nucleating sites observed at lower isothermal crystallization temperatures.

In order to clarify the nucleation process further, mainly the nature of the transcrystalline region and the possibility to correlate it with the presence of the small peak in the crystallization exotherms, a multilayer sample has been prepared. It consisted of several alternating layers of substrate and polymer. Each polymer layer was prepared at a thickness of approximately 80μm. This would ensure that most of the volume of the polymer to be crystallized would be filled by the transcrystalline regions.

The crystallization exotherm of the multilayer sample in Fig. 3.6a shows the appearance of two peaks; one at 406K and another at 391K. Comparing the crystallization exotherms of a monolayer sample (Fig. 3.1b) and the multilayer sample (Fig. 3.6a), it can be seen that the maximum temperature at which the small peak appeared in both cases was the same, 406K. The maximum temperature of the main peak was slightly shifted to 391K in the multilayer sample compared to 389K for the monolayer sample. In Fig. 3.1b (monolayer sample) the two peaks were perfectly distinguishable but in Fig. 3.6a (multilayer sample) the small peak has become part of the main peak.

A careful analysis of microtomed specimens of multilayer samples shown in Fig. 3.6b has explained the nature of the columnar region. It could be observed that mainly transcrystalline regions were obtained and that they impinged one with the other, allowing just a few well developed spherulites to grow in between.

The significant increase in area of the small peak in the multilayer experiment, compared with the monolayer experiment, was due to the fact that the effective area of nucleation has been increased about 3 times because of the presence of multiple layers of substrate.

The presence of two crystallization peaks when the multilayer sample is filled mainly with transcrystalline regions allow us to conclude that two distinct processes are involved in that region. One is occurring at a higher rate as can be observed by the slope of the peak reaching its optimum temperature at 406K

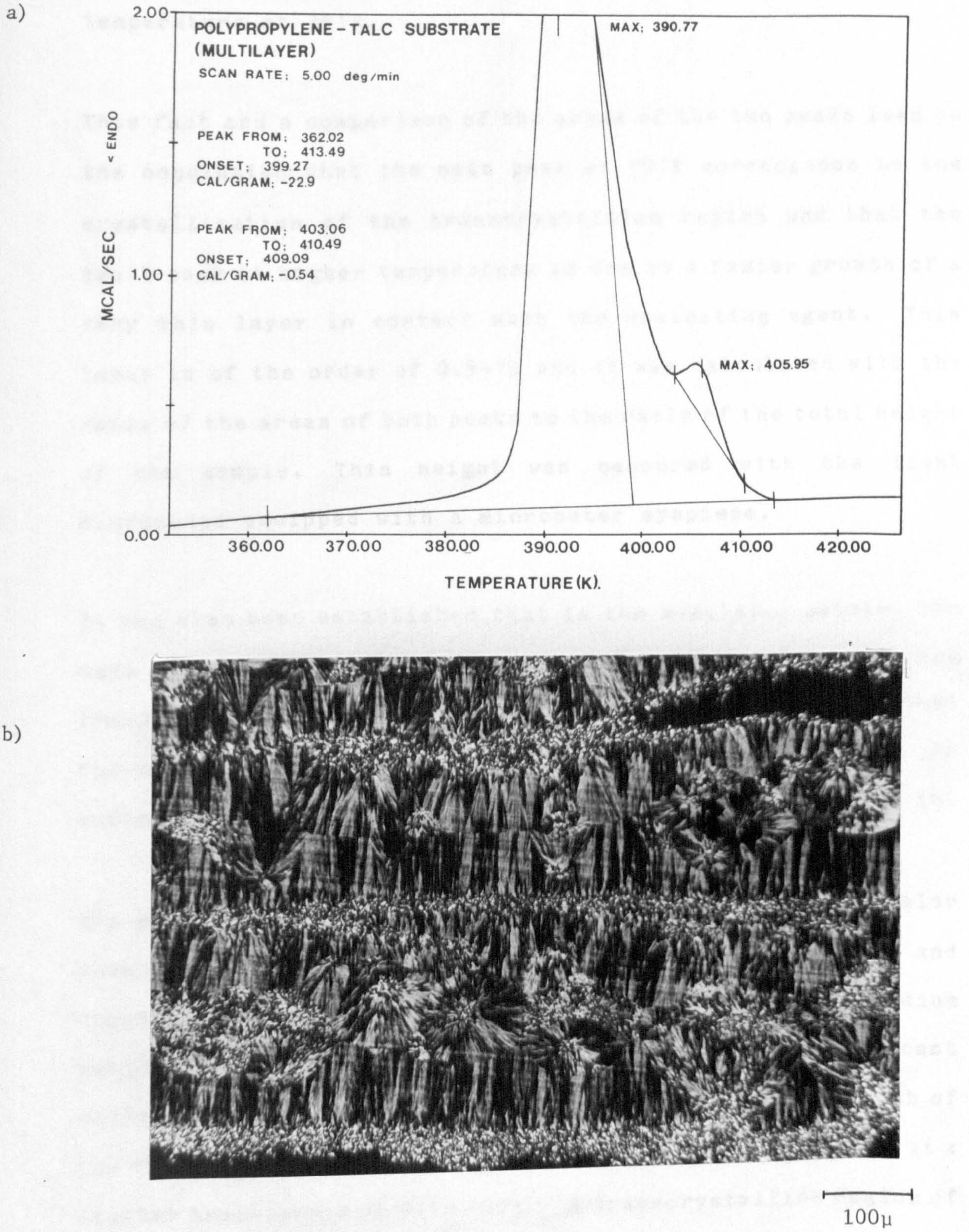


Fig. 3.6. a) Crystallization exotherm of polypropylene - talc substrate multilayer.

b) Microtomed sample of polypropylene - talc substrate multilayer.

(Fig. 3.6a). The other is occurring at a lower rate (observed by extrapolating the main peak), and reaching its optimum temperature at 391K.

This fact and a comparison of the areas of the two peaks lead to the conclusion that the main peak at 391K corresponds to the crystallization of the transcrystalline region and that the small peak at higher temperature is due to a faster growth of a very thin layer in contact with the nucleating agent. This layer is of the order of 0.5-1μ and it was calculated with the ratio of the areas of both peaks to the ratio of the total height of the sample. This height was measured with the light microscope equipped with a micrometer eyepiece.

It has also been established that in the monolayer sample, the main peak corresponds to the crystallization of the transcrystalline region and the bulk material above it, and that the small peak accounts for the strong interaction between the nucleating agent and the layer of polymer in contact with it.

The effects of the substrate induced morphology on PP was also investigated for sodium benzoate, boron nitride, sorbitol and saccharin. When the substrate was changed from talc to sodium benzoate or boron nitride, or sorbitol, no significant difference from the above results were observed. The growth of the thin layer in contact with the nucleating agent occurred at a similar temperature as with talc. A transcrystalline region of similar morphology and height was obtained as shown in Fig. 3.7. No effect on the crystallization rate was found by varying the melting temperature and melting time of the samples prior to

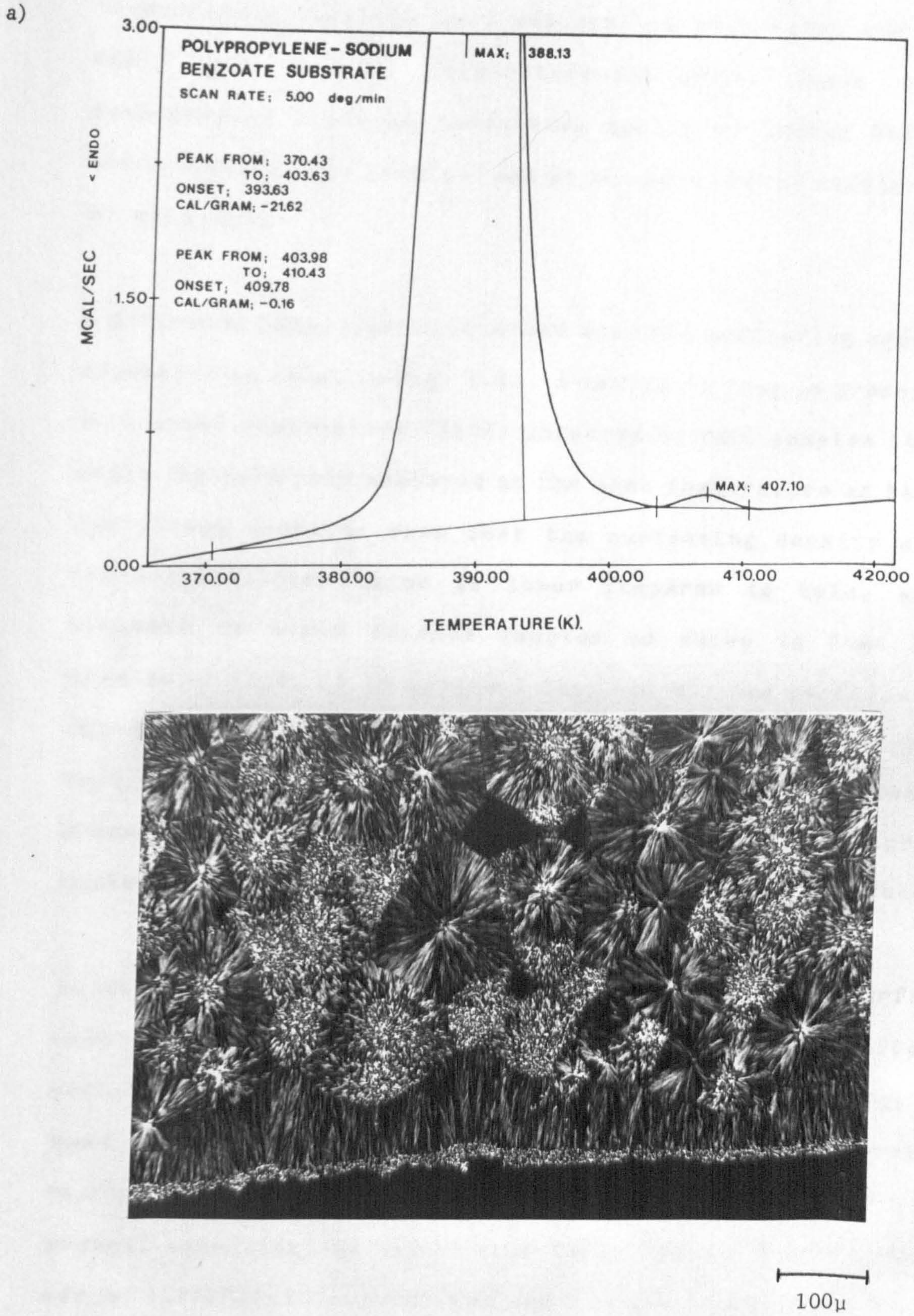


Fig. 3.7. a) crystallization exotherm of polypropylene sodium benzoate substrate, melted at 470K and crystallized at $5^{o}$/min. b) microtomed sample of polypropylene sodium benzoate substrate.

crystallization. The effects of crystallization temperature on surface morphology were the same as with talc; and proved again not to be temperature-dependant. These results demonstrated a strong nucleating action of sodium benzoate, boron nitride, and sorbitol and at the same time of similar order as with talc.

A different behaviour is observed when the nucleating agent was saccharin as shown in Fig. 3.8. A secondary peak is present but at a lower temperature (398K) compared to talc samples (406K), while the main peak appeared at the same temperature as before. Microtomed sections show that the nucleating density of the transcrystalline region is lower compared to talc, sodium benzoate or boron nitride samples as shown in Fig. 3.8b. Because of this, it is apparent that not all the particles are able to nucleate the polymer. Still, a good interaction between some of them is evident by the fact that the secondary peak is present. Perhaps other particles do not offer an appropriate active site hence the nucleating efficiency is diminished.

In determining the nucleating activity of a foreign surface, considerable attention has been devoted to the importance of wettability[67]. For polypropylene melt the surface energy has been found to be only about 21 dynes/cm around 190°C[68], partial or complete wetting of any of the substrate surfaces used in the present investigation may be expected. Then, the reason for a marked difference in activity of saccharin substrate compared to talc, sodium benzoate or boron nitride must rise from the specificity of the heterogeneity to the polymer and its activity relative to the nuclei present throughout the material.

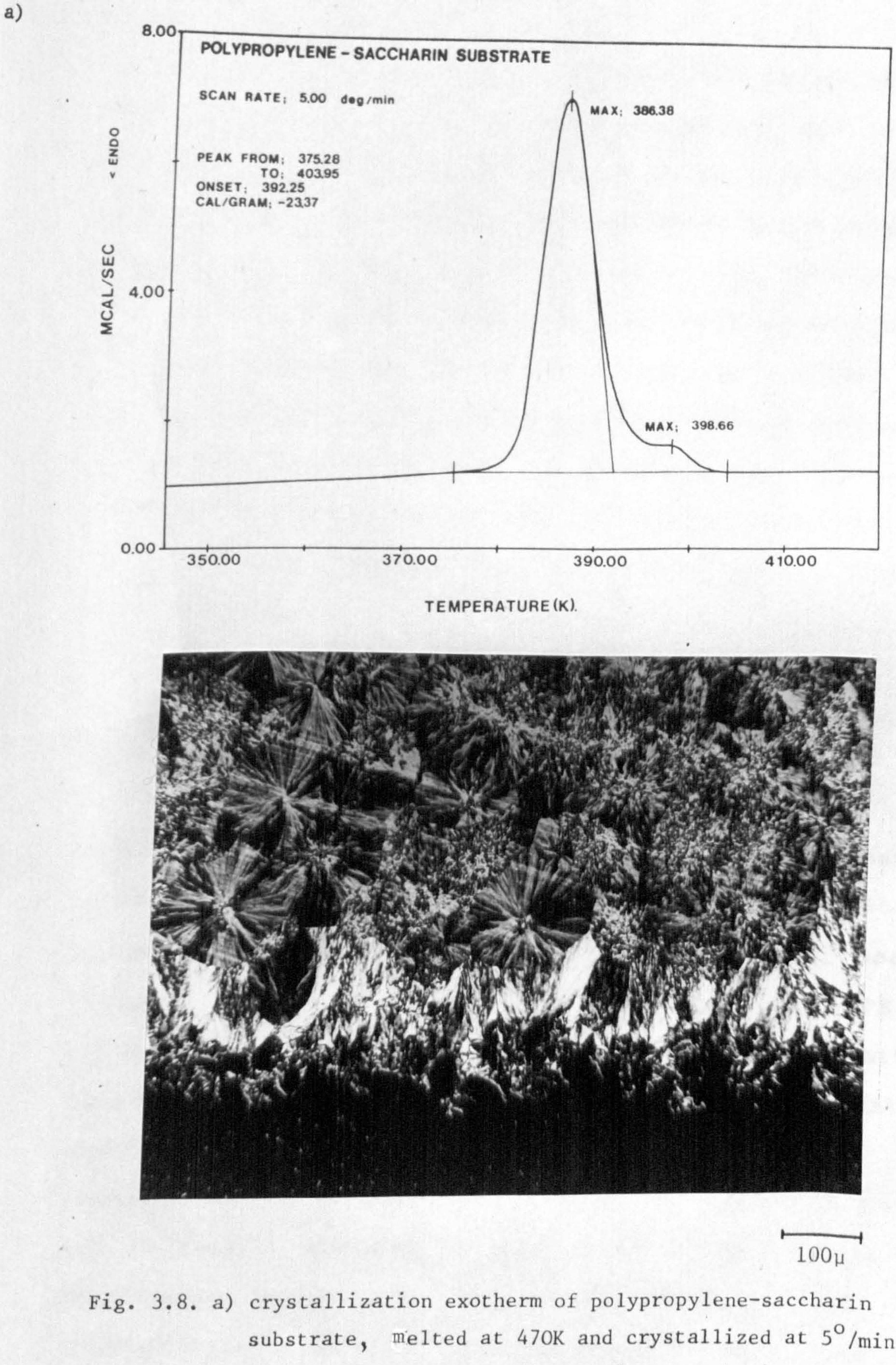


Fig. 3.8. a) crystallization exotherm of polypropylene-saccharin substrate, melted at 470K and crystallized at $5^o$/min
b) microtomed sample of polypropylene saccharin substrate.

### 3.1.B OTHER POLYMERS

The previous results demonstrate that PP can be nucleated by different substrates, of different geometry and chemical structure, to approximately the same extent. To clarify the nucleation process further, it is important to establish the role played by inherent characteristics of the polymer such as, chemical structure and morphology, on the substrate-induced crystallization. For this reason various polymers were crystallized in contact with the same substrates as used for PP. Polyethylene, polybutene, polyoxymethylene, polyethyleneterephthalate and nylon 6.6. were molten 30 degrees above their melting temperatures for 10 minutes prior to crystallization.

The results obtained, and summarized in Table 3.1, together with the corresponding microtomed samples revealed that:

Firstly; when there is no secondary peak in the crystallization exotherm, there is no evidence of a transcrystalline region in the sample. Figure 3.9 shows this behaviour for POM on sodium benzoate substrate. Similar results were obtained for HDPE and nylon on sodium benzoate, saccharin or sorbitol. PB exhibits a rather different behaviour. The secondary peak is smaller compared to those obtained for PP with various substrates. The reason for this is that the heat of crystallization for PB is very low (7 cal/gr) compared to that of PP (23 cal/gr) so the calorimeter detects a very small change during the crystallization process. Microtomed sections reveal the formation of a transcrystalline region of lower density compared to that attained by polypropylene samples with talc, sodium

TABLE 3.1. Maximum crystallization temperature (degrees K) of pure polymers and polymer-substrate samples.

| POLYMER | PURE | WITH NUCLEATING AGENTS | | | | | |
|---|---|---|---|---|---|---|---|
| | | MAIN PEAK | SMALL PEAK | | | | |
| | | | TALC | SODIUM BENZOATE | BORON NITRIDE | SORBITOL | SACCHARIN |
| HDPE | 390.6 | 390.1 | 398.1 | NO PEAK | 396.3 | NO PEAK | NO PEAK |
| PP | 387.9 | 389.0 | 405.5 | 403.6 | 402.7 | 406.0 | 398.3 |
| PB | 347.3 | 347.9 | APPROXIMATELY 354 | | | NO PEAK | NO PEAK |
| POM | 418.6 | 418.5 | 423.9 | NO PEAK | REACTION | NO PEAK | NO PEAK |
| PET | 478.1 | 478.8 | 496.9 | 499.9 | 500.3 | 481.7 | MELTING OF NUCLEATING AGENT |
| NYLON 66 | 508.2 | 508.9 | 518.8 | NO PEAK | NO PEAK | MELTING OF NUCLEATING AGENT | |

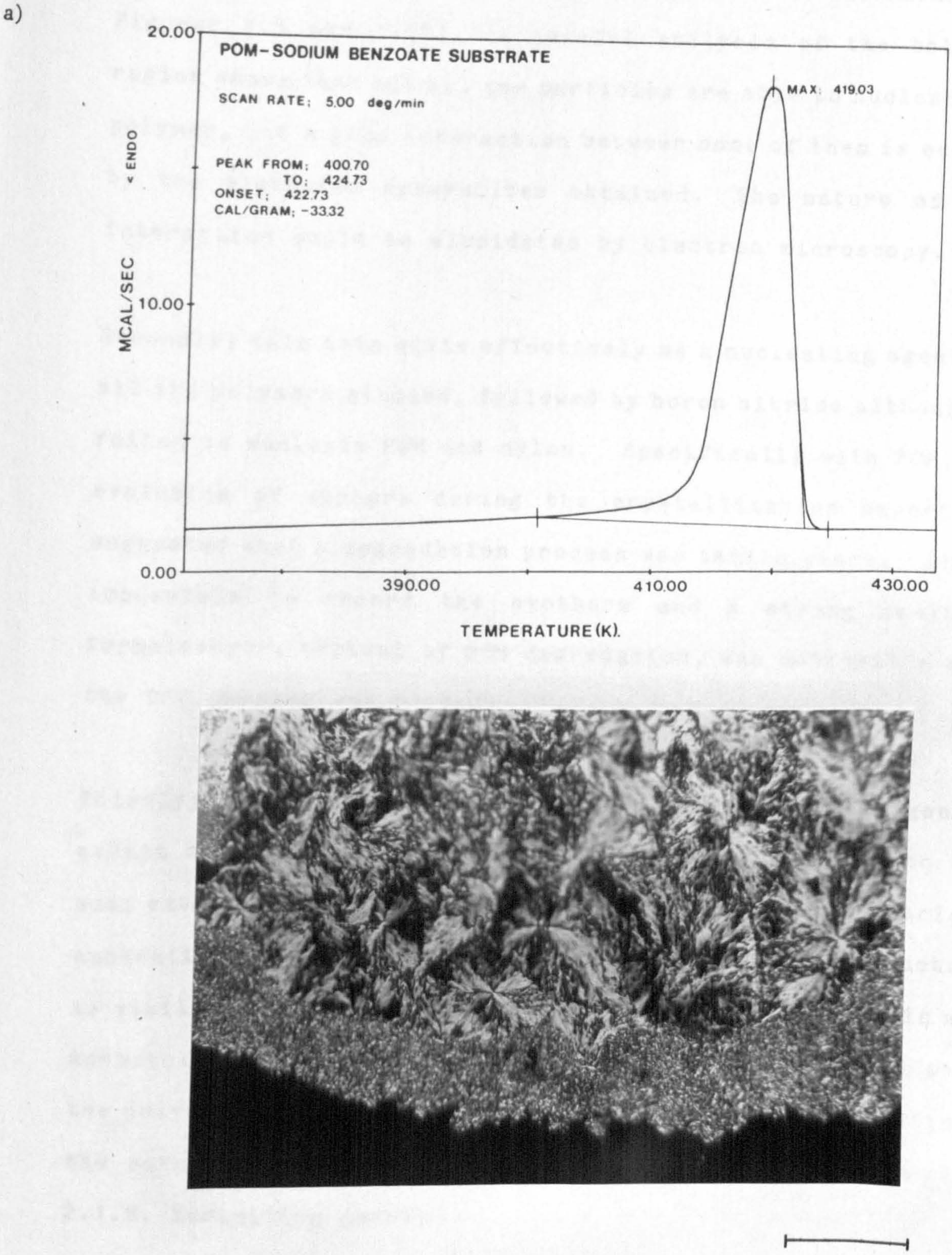


Fig. 3.9. a) crystallization exotherm of polyoxymethylene sodium benzoate substrate, melted at 470K and crystallized at 5$^{o}$/min. b) microtomed sample of polypropylene sodium benzoate substrate.

benzoate or boron nitride; but similar to that of saccharin (see Figures 3.8 and 3.10). A careful analysis of the columnar region shows that not all the particles are able to nucleate the polymer, but a good interaction between some of them is evident by the elongated spherulites obtained. The nature of this interaction would be elucidated by electron microscopy.

Secondly; talc acts quite effectively as a nucleating agent for all the polymers studied, followed by boron nitride although it failed to nucleate POM and nylon. Specifically with POM, the evolution of vapours during the crystallization experiment suggested that a degradation process was taking place. It was impossible to record the exotherm and a strong smell of formaldehyde, typical of POM degradation, was noticeable when the DSC chamber was opened.

Thirdly; for the same polymer different nucleating agents, except saccharin, were able to nucleate approximately to the same extent. This reveals that the interaction between various nucleating agents of different geometry and chemical structure is similar. Only in cases like PET and nylon 66, saccharin and sorbitol failed to nucleate. The reason for this is that when the polymer reaches its melting point prior to crystallization, the substrate is already molten and decomposed (see Chapter 2.1.B. Nucleating Agents).

These observations lead to the conclusion that by restricting the space for spherulitic growth, when nuclei are densely packed on substrate, a transcrystalline region, which is temperature - independent, could be obtained for various polymers. Those

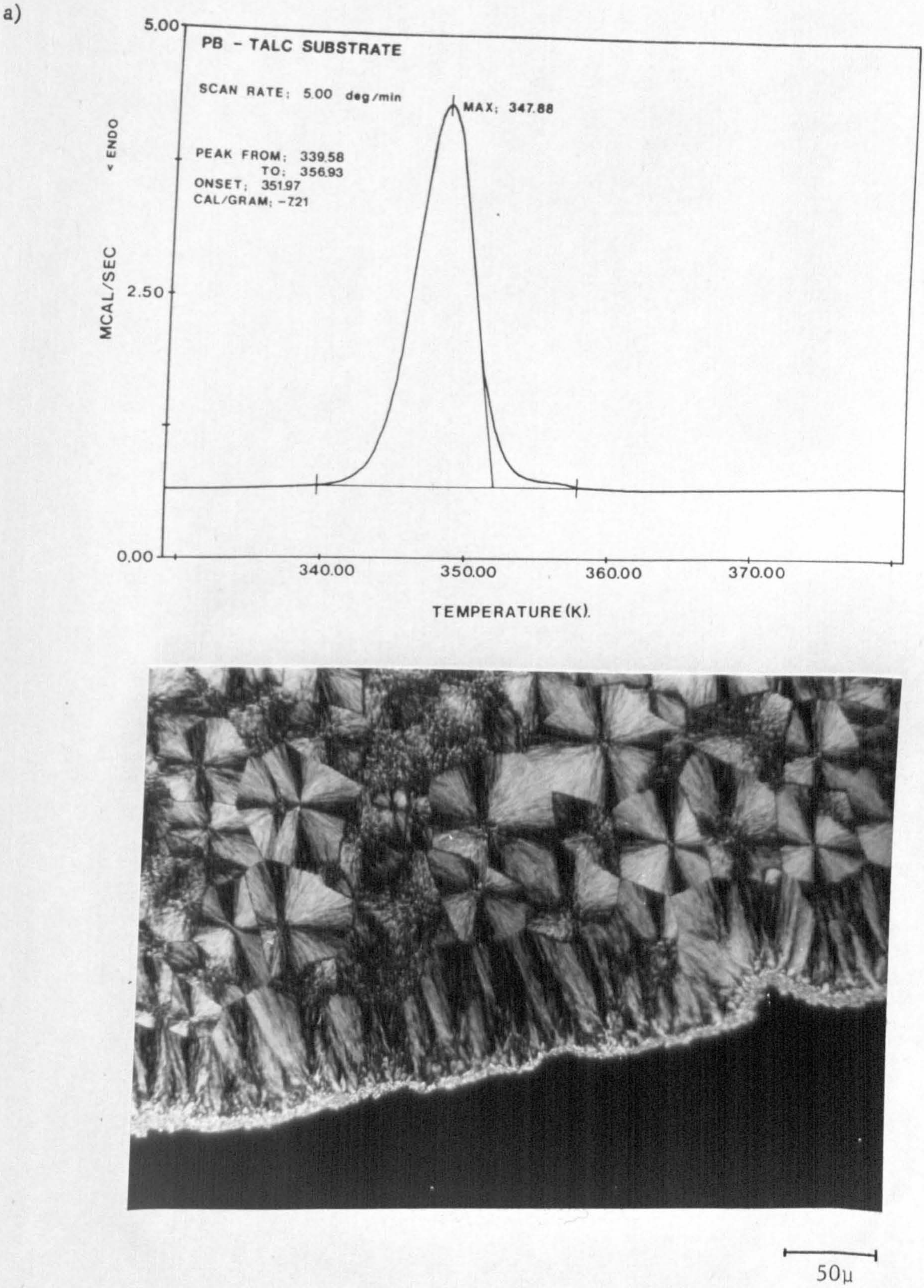


Fig. 3.10. a) crystallization exotherm of polybutene-talc substrate melted at 430K and crystallized at 5$^{o}$/min b) microtomed sample of polybutene-talc substrate.

morphologies can be used to characterize the nucleating ability of substrates qualitatively. The crystallization exotherms recorded simultaneously can be used to characterize the nucleating ability quantitatively by the presence of the secondary peak.

# CHAPTER 4

# 4. THE EFFECTS OF HETEROGENEITIES ON NUCLEATION OF POLYMERS

The effectiveness of nucleating agents has been explained in terms of the ability of the nucleant to increase the nucleation rate with the subsequent spherulitic growth rate remaining unchanged[69,70,71]. The change in the relative rates of nucleation and spherulitic growth has two main consequences. Firstly, the system reaches its maximum crystallinity at a much higher temperature and secondly; a fine homogeneous morphology is produced which is relatively independent of the crystallization temperature[59].

To date, the cause of the shift in crystallization temperature promoted by the nucleating agents has not been clearly established. Also it has not been explained why certain polymers undergo bigger shifts in their crystallization temperature than others.

The present study was undertaken to establish the nature of the shift in crystallization temperature due to presence of different nucleating agents. For this, various polymers were loaded at different concentrations of the nucleator and their effect on the crystallization temperature, morphology, nucleation density and spherulitic growth rate were examined. The results were interpreted by current theory and an extension to that theory is proposed.

## 4.1 RESULTS AND DISCUSSION

As described in the general introduction, in the crystallization of polymers from the melt one cannot rule out the possibility of occasional impurities in the polymer nucleating a few spherulites. Binsbergen[21] states that there is no decisive role played by catalyst residues left in the polymer after its inactivation and after the usual washing procedures. Chatterjee and Price[36] proved that the transcrystallinity induced by iPS or iPP was not due to catalyst residues but to the polymer itself. In the present investigation commercial polymers with occasional impurities are used and perhaps they are able to nucleate a few spherulites.

## 4.1.A SHIFT IN THE CRYSTALLIZATION TEMPERATURE

PP when cooled from the melt on a DSC exhibits an exotherm as shown in Fig. 4.1a. This is indicative of the enthalpy of crystallization as was first discussed by Beck and Ledbetter[62] on the crystallization of i-PP. The temperature at the peak of the exotherm (387.9K) is taken to be the optimum crystallization temperature, Tmax, and corresponds to the temperature at which the observed crystallization reaches its maximum rate[72]. All the crystallization measurements of the polymers and nucleated samples were made at a cooling rate of $5^o$/min. Following the previous results, conditions which ensure complete melting of the polymers were applied to the sample prior to crystallization. This means that the samples were melted 30 degrees above their melting point for 10 minutes.

The crystallization exotherms for nucleated PP were detected at higher T than the unnucleated polymer as shown in Fig. 4.1b. To prove the reproducibility of the above results five different samples of unnucleated PP were submitted to crystallization. The peak temperature and the onset temperature are reproducible to $\pm 0.5^o$, thus assuring an accurate response of the calorimeter

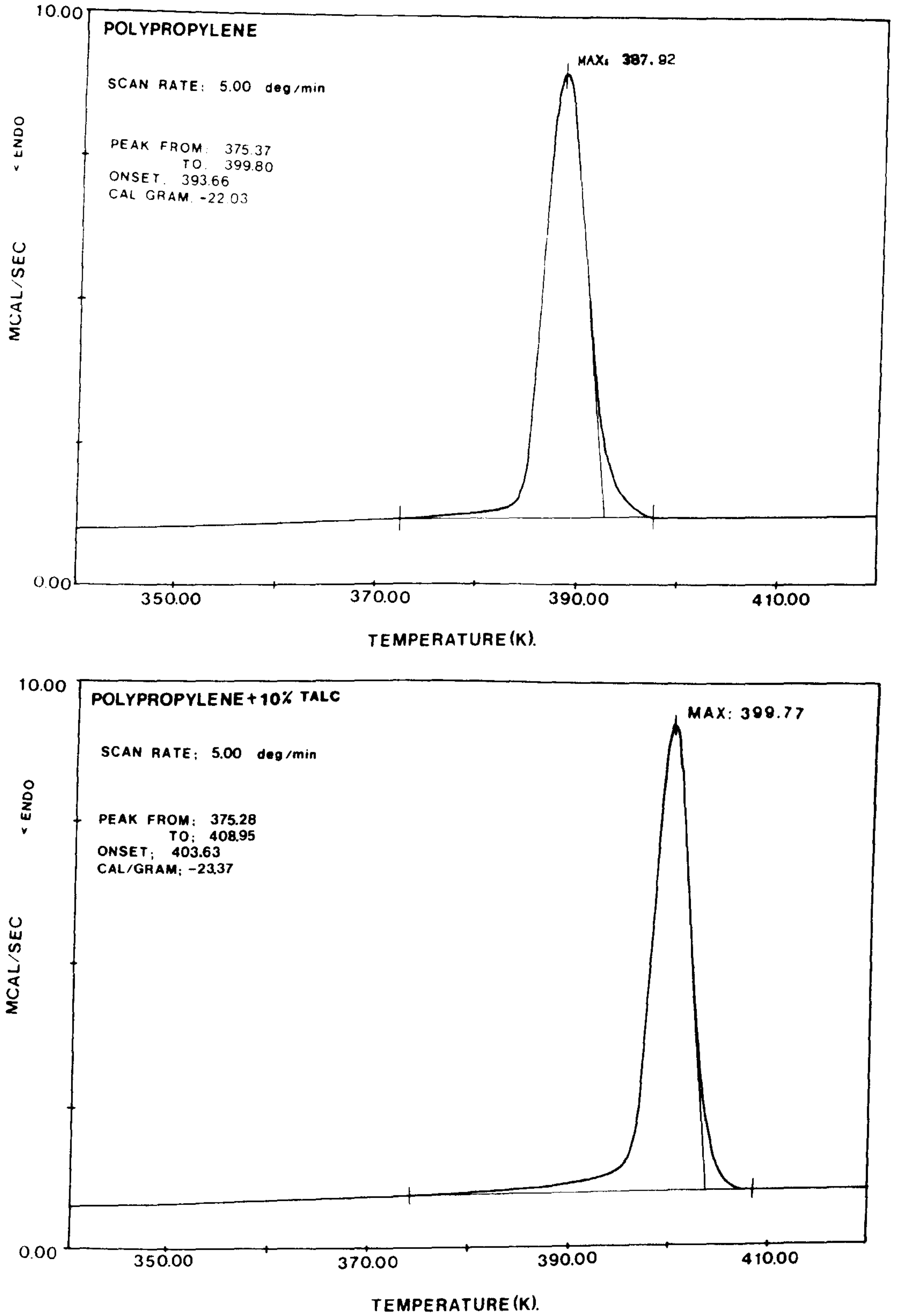


Fig. 4.1. Crystallization exotherms of a) pure polypropylene and b) polypropylene + 10% talc, melted at 470K and crystallized at 5°/min.

and homogeneity in the samples.

For nucleated samples, the peak temperature and the onset temperature are reproducible to 0.5° at loadings of 1,5 and 10% of nucleating agent. For lower loadings, e.g. 0.5%, the peak temperature was reproducible to 2° and the onset temperature to ±1°. The results here lead to the conclusion that maximum homogeneity in the samples, hence reproducibility of results, was achieved at loadings of 1% or more.

The peak temperature of the crystallization exotherms for nucleated PP was found to be dependent on the concentration of the nucleating agent. As can be seen in Fig. 4.2 a,b and c the crystallization temperature of PP increases with increasing nucleant content. It is also apparent in Fig. 4.2 that samples with similar nucleant content but different nucleating agents exhibit the same crystallization behaviour. At the same time it is clear from these figures that the change in crystallization temperature with increasing nucleant content is rather strong up to 1%; beyond this value increasing concentration of nucleant has little effect on the crystallization temperature.

Taking into account this "saturation" effect of the nucleant and to obtain maximum shift, the other polymers to be investigated were prepared at 1% and 10-% of nucleating agent. The results are summarized in Table 4.1.

Comparing the results obtained in Table 4.1 it reveals that HDPE is the only polymer to exhibit a secondary peak when nucleated with talc or boron nitride, rather than showing a shift in the

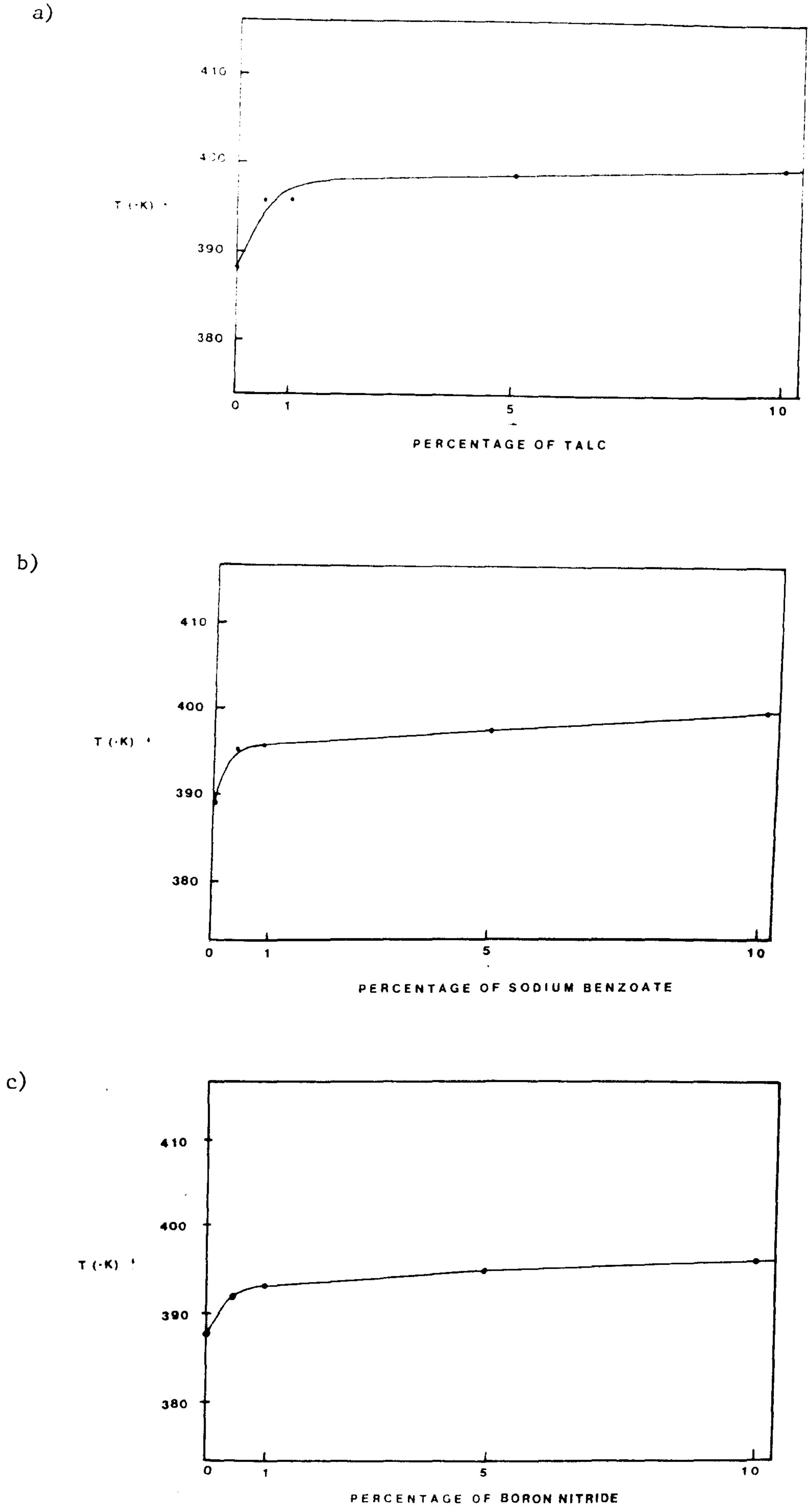


Fig. 4.2. Variation of maximum crystallization temperature of PP with concentration of nucleating agent a) talc b) sodium benzoate c) boron nitride.

TABLE 4.1 Maximum crystallization temperature (degrees K) of pure polymers and various compositions with a different nucleating agent. The temperature shift due to the presence of the nucleator is shown in brackets.

| POLYMER | PURE | NUCLEATING AGENT CONTENT (% W/W) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | TALC | | SODIUM BENZOATE | | BORON NITRIDE | | SORBITOL | | SACCHARIN | |
| | | 1 | 10 | 1 | 10 | 1 | 10 | 1 | 10 | 1 | 10 |
| HDPE | 390.6 | 390.6 | 392.3 ><br>401.2 | NO SHIFT | | 390.6 | 390.7 ><br>403.3 | NO SHIFT | | NO SHIFT | |
| PP | 387.9 | 395.7<br>(7.8) | 399.7<br>(11.8) | 396.1<br>(8.2) | 401.0<br>(13.1) | 392.6<br>(4.7) | 396.9<br>(9.0) | 396.5<br>(8.6) | 402.5<br>(14.6) | 393.0<br>(5.1) | 394.0<br>(6.1) |
| PB | 347.3 | 348.3<br>(1.0) | 354.6<br>(6.3) | 349.9<br>(2.6) | 354.3<br>(7.0) | 348.6<br>(1.3) | 353.0<br>(5.7) | 348.9<br>(1.6) | 353.7<br>(6.4) | NO SHIFT | |
| POM | 418.6 | 421.2<br>(2.6) | 422.3<br>(3.7) | NO SHIFT | | REACTION | | NO SHIFT | | NO SHIFT | |
| PHB | 373.3 | 382.1<br>(7.8) | 383.4<br>(10.1) | REACTION | | 391.0<br>(17.7) | 392.3<br>(19.0) | NO SHIFT | | NO SHIFT | |
| PET | 478.1 | 490.6<br>(12.5) | 494.2<br>(16.1) | 483.7<br>(5.6) | 497.3<br>(19.2) | 486.7<br>(8.6) | 495.0<br>(16.9) | 480.3<br>(2.2) | 482.1<br>(4.1) | NO SHIFT | |
| NYLON | 508.2 | 510.2<br>(2.0) | 515.2<br>(7.0) | NO SHIFT | | NO SHIFT | | NO SHIFT | | NO SHIFT | |

> two peaks observed

exotherm as the other polymers did. This secondary peak is not detected at 0.5, 1 or 5% loadings, but at 10% it is shown at around 401K and 403K for talc and boron nitride respectively (Fig 4.3b and c).

Compounds of HDPE with sodium benzoate, saccharin or sorbitol have not shown a secondary peak at any loadings.

In the present investigation, varying both the type and concentration of nucleating agent did not appear to affect the crystallization behaviour of LDPE.

Taking into account the results obtained in Table 4.1 it can be said that, firstly; talc acts quite effectively as a nucleating agent for all the polymers studied, followed by boron nitride. Secondly; for the same polymer different nucleating agents, except saccharin, have produced the same shift in crystallization temperature. For PP regardless of the type of nucleating agent used, the shift in crystallization temperature was approximately 12 degrees. The same may be applied to PB showing a shift of 7 degrees, and to PET with a shift of 17n degrees. But for PHB the shift was 19 degrees when boron nitride was the nucleating agent and 10 degrees when it was talc. Thirdly; the polymer that exhibits the smallest shift in crystallization temperature is POM with 4K, followed by nylon and PB (approximately 8K).

These results obtained for mixed samples (Table 4.1) and those summarized in Table 3.1 for polymers crystallized on substrates are in good agreement. For instance, the maximum temperature at

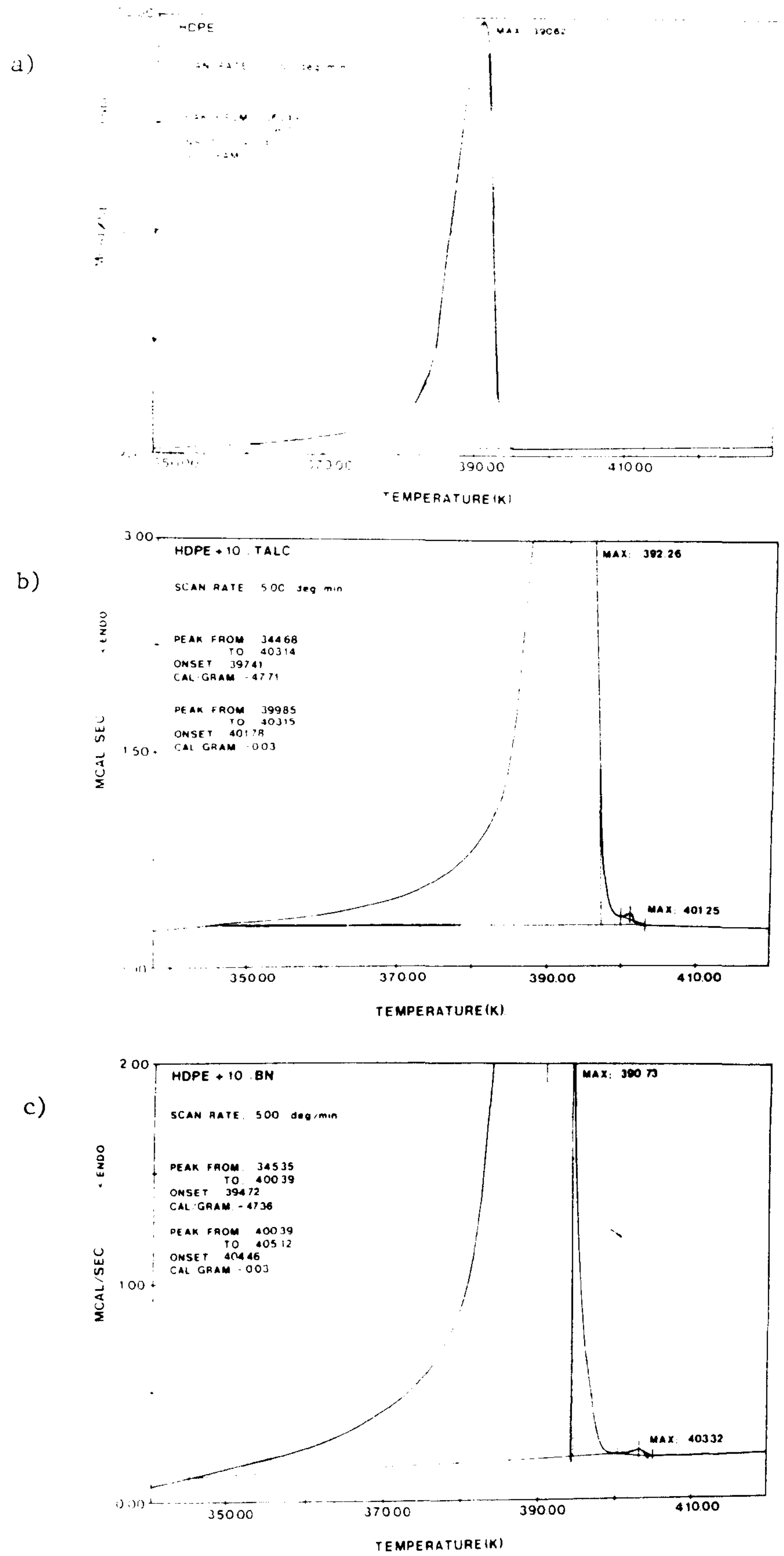


Fig. 4.3. Crystallization exotherms of a) HDPE b) HDPE with 10% of talc and c) HDPE with 10% boron nitride. Figures b and c have been expanded to show clearly the presence of a secondary peak.

which the secondary peak appeared for PP-talc substrate samples is 406K and samples with 10% loading of talc exhibit a peak at 400K. The difference in 6K is due to the fact that for substrate samples the particles of a nucleating agent are densely packed, so the number of nuclei formed is very high and is approaching a highly loaded sample with a good dispersion of the nucleating particles.

When there was no secondary peak and no transcrystalline region in substrate samples, the corresponding thorougly mixed samples have not shown a shift in the crystallization exotherm. These observations lead to the conclusion that the morphologies of crystallized polymers induced by substrates can be used to characterize the nucleating ability of the substrate qualitatively. The crystallization exotherms recorded simultaneously can be used to characterize their nucleating ability quantitatively by the presence of the secondary peak.

The necessary and sufficient conditions for an effective nucleating agent are not yet definitely established. But taking into account that different nucleating agents produce similar shifts in crystallization temperature for the same polymer, it can be concluded that the nature of the interaction is similar in all cases. This fact excludes the requirement of close matching of crystal lattice parameters of polymer and nucleating agent and similarity of crystallographic unit cell, since the various nucleating agents under study have different geometry, crystal lattice parameters and chemical structure and so have the polymers. These would be studied extensively by electron microscopy. The conditions for an effective nucleating agent must then be due to the presence of certain active sites on the particles.

It has also been found that the same nucleating agent is able to promote nucleation for different polymers. In each particular case the extent of the shift in crystallization temperature is characteristic for each polymer. For instance, talc promotes a shift of 12 degrees for PP, 7 degrees for PB and 16 for PET (see Table 4.1). The explanation for different shifts must be found in the inherent characteristic of the polymers, specifically its morphology. For this, polymer samples with increasing loadings of filler were investigated under light microscopy.

### 4.1.B MORPHOLOGY OF NUCLEATED POLYMERS

The addition of talc to i-PP significantly alters the morphology of a crystallized sample as it is clearly illustrated by comparing figure 4.4a and Figure 4.4c. The former shows a sample of unfilled i-PP that has been allowed to crystallize totally and hence impingment of the spherulites is complete. The spherulites that have been formed are relatively large (100-200μ) and the number of nuclei that developed into spherulites can be counted. However in Figure 4.4c, where the polymer has been loaded with 0.5% of talc, the Maltese Cross pattern can just be discerned. With loading of 5% of talc or more, instead of the Maltese Cross observed in Fig. 4.4a, the sample has a "granular" appearance and the number of nuclei formed impossible to count.

At loadings of 0.25% of talc, as it can be seen in Fig. 4.4b, the spherulites have shown a dramatic change in size; from values of

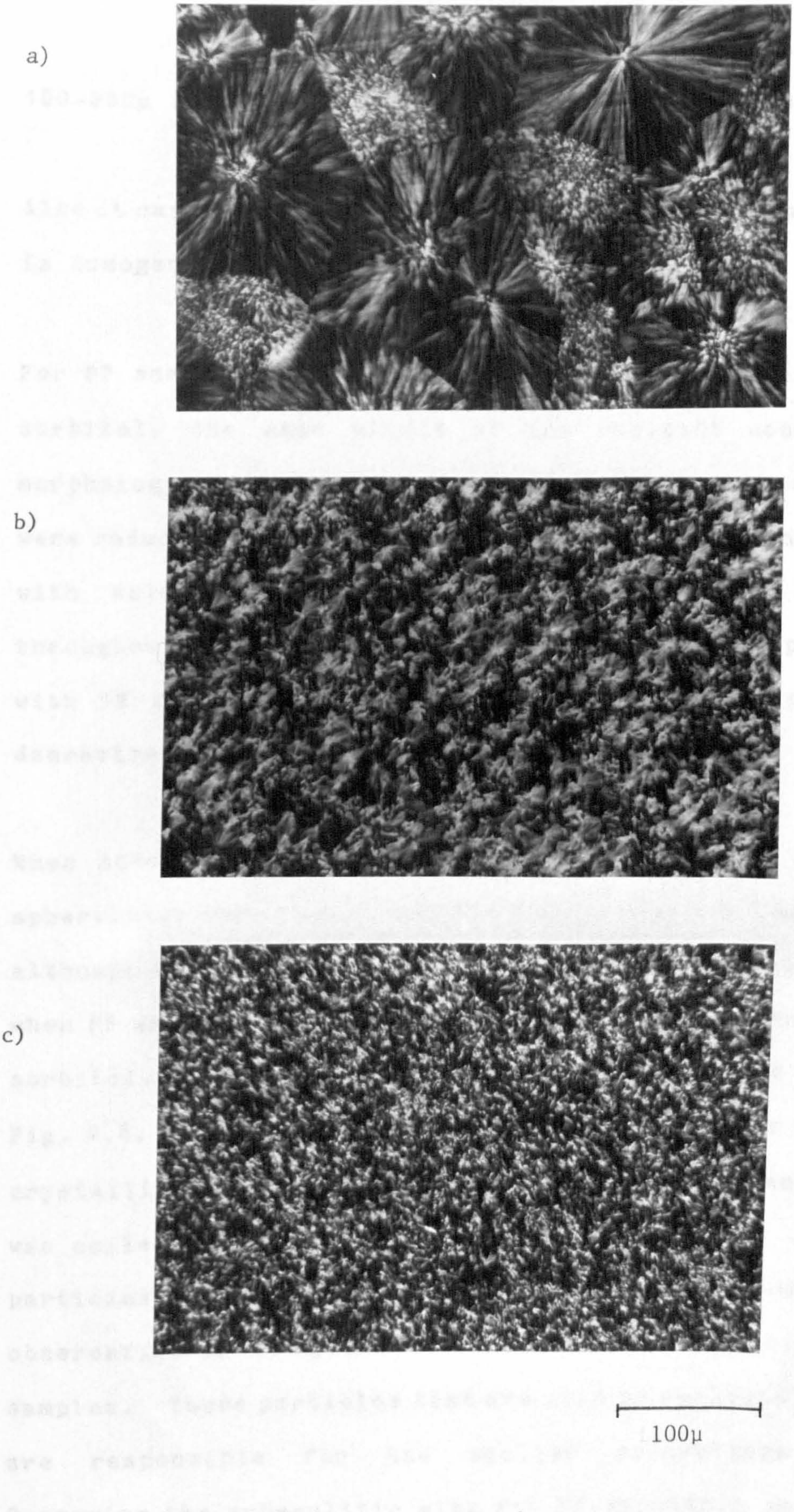


Fig. 4.4. Microtomed sample of i-PP and its composites crystallized at 5 degrees/minute. a) unfilled i-PP b) PP + 0.25% talc and c) PP + 0.5% talc.

100-200μ for unfilled polymer to values of 40-50μ.

Also it can be observed that the dispersion of the talc particles is homogeneous throughout the samples.

For PP samples loaded with sodium benzoate, boron nitride or sorbitol, the same effect of the nucleant content on the morphology of the polymer has been observed, the spherulities were reduced in size to the same extent as for PP samples loaded with talc. The dispersion was found to be homogeneous throughout the sample as is shown in Fig. 4.5. A picture of PP with 5% loading of talc was taken without the polarizer to demonstrate the good dispersion.

When saccharin was used as a nucleating agent for PP, the spherulites were found to be reduced in size for loadings of 5%, although the change in morphology was not as dramatic as it was when PP was filled with talc, sodium benzoate, boron nitride or sorbitol. The spherulites vary very much in size as shown in Fig. 4.6. For loadings of 10% there was no further shift in the crystallization temperature assuring the achievement of what was called "saturation effect" of the nucleator. Not all the particles were able to bring about nucleation and this observation is in agreement with that for saccharin substrate samples. Those particles that are able to nucleate the polymer are responsible for the smaller spherulites obtained. Comparing the spherulitic size for PP-saccharin samples (Fig. 4.6) with that for PP samples loaded with 0.25% and 0.5% talc (Fig. 4.4 b and c), it can be observed they are similar. The temperature shift of 394K for PP + 5% saccharin is in between that

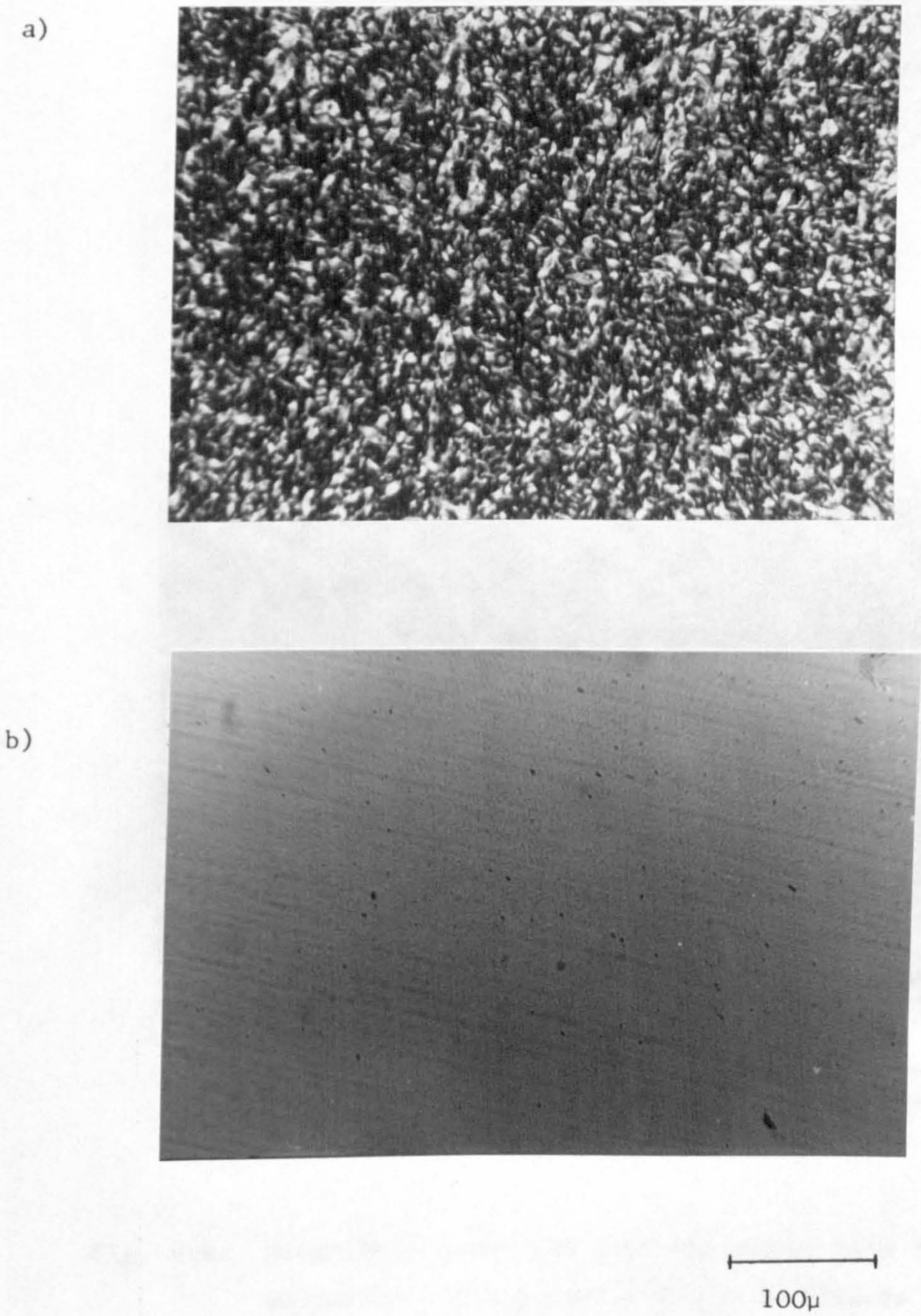


Fig. 4.5.a)Microtomed sample of i-PP nucleated with 5% talc b) Picture taken without the polarizer.

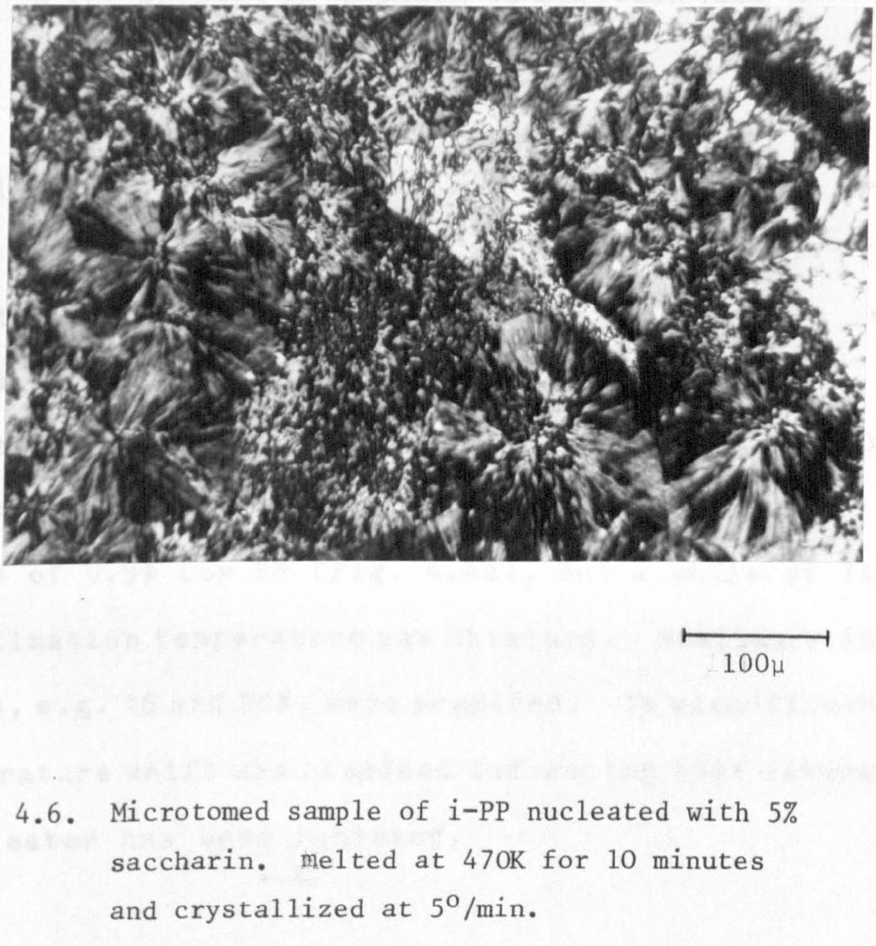


Fig. 4.6. Microtomed sample of i-PP nucleated with 5% saccharin. melted at 470K for 10 minutes and crystallized at $5^{o}$/min.

for PP + 0.25% talc of 392 and that for PP + 0.5% talc of 397 (see Fig. 4.2a). These results indicate that once the particle is able to interact with the polymer to create a stable nuclei, the extent of the shift in the crystallization temperature is related to the amount of new nuclei that can be formed by the nucleating agent. Obviously the more nuclei present, the smaller would be the spherulites formed. Other polymers studied in the present work would be analysed from this point of view.

The addition of sodium benzoate to PB has altered the morphology of a crystallized sample as illustrated in Fig. 4.7. With increasing content of the nucleating agent, the spherulitic size has been reduced. The extent of this reduction is not as homogeneous and dramatic as for PP. At loadings of 10% (Fig. 4.7c) still few spherulites are not as small as they are at loadings of 0.5% for PP (Fig. 4.4c), but a shift of 7K in the crystallization temperature was obtained. Samples with higher loadings, e.g. 15 and 20%, were prepared. No significant change in temperature shift was obtained indicating that saturation of the nucleator has been achieved.

A factor which plays an important role in the crystallization process of PB is the difficulty in obtaining a homogeneous dispersion of the nucleating agent. From Fig. 4.7b and c it can be observed that sodium benzoate forms "aggregates" in the polymer matrix. This was also observed for boron nitride and talc. Fig. 4.8 shows an area of a PB sample loaded with 1 % boron nitride where the dispersion is very poor.

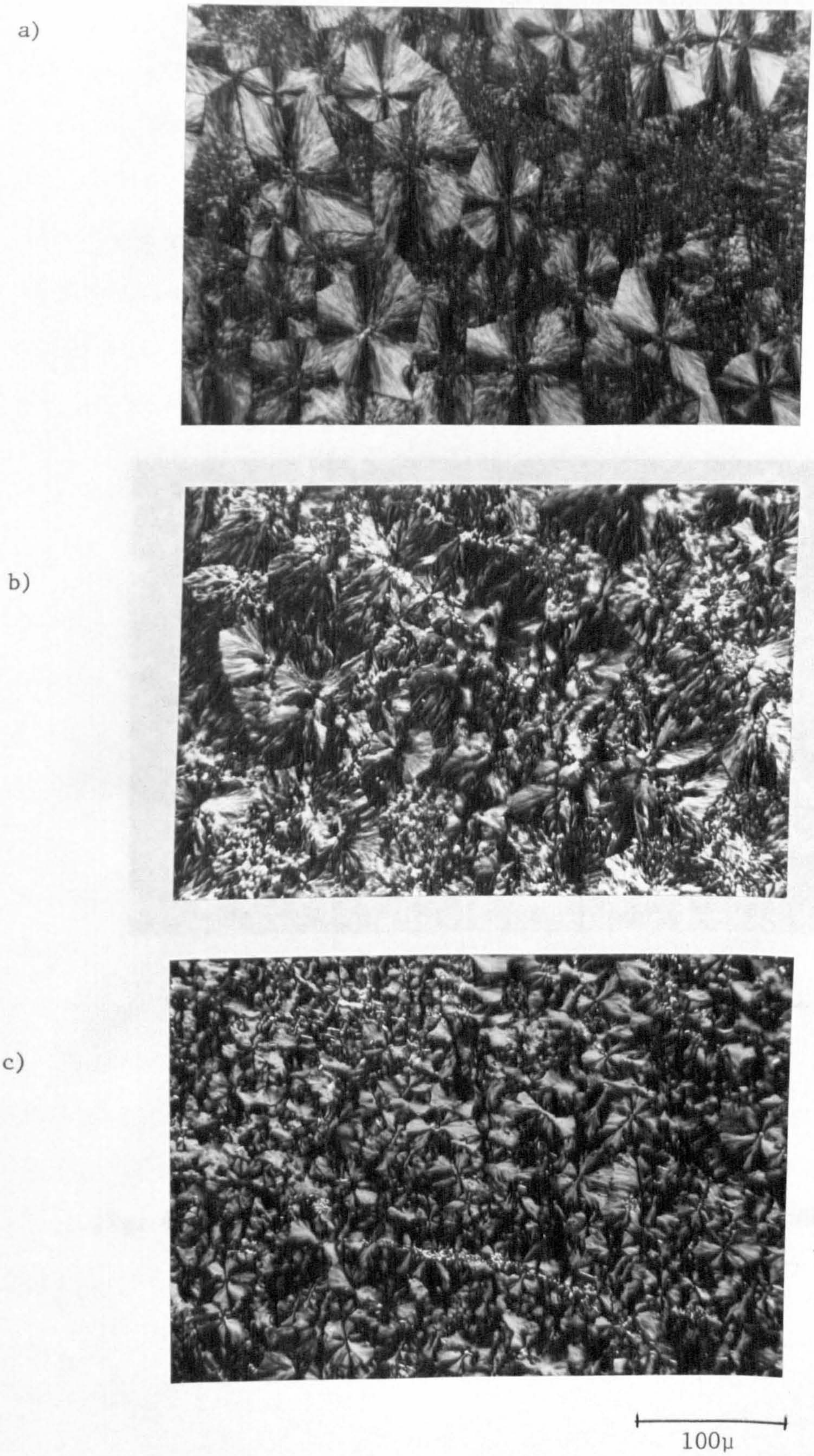


Fig. 4.7. Microtomed sample of PB and its composites crystallized at 5 degrees/minute a) unfilled PB b) PB + 1% sodium benzoate and c) PB + 10% sodium benzoate.

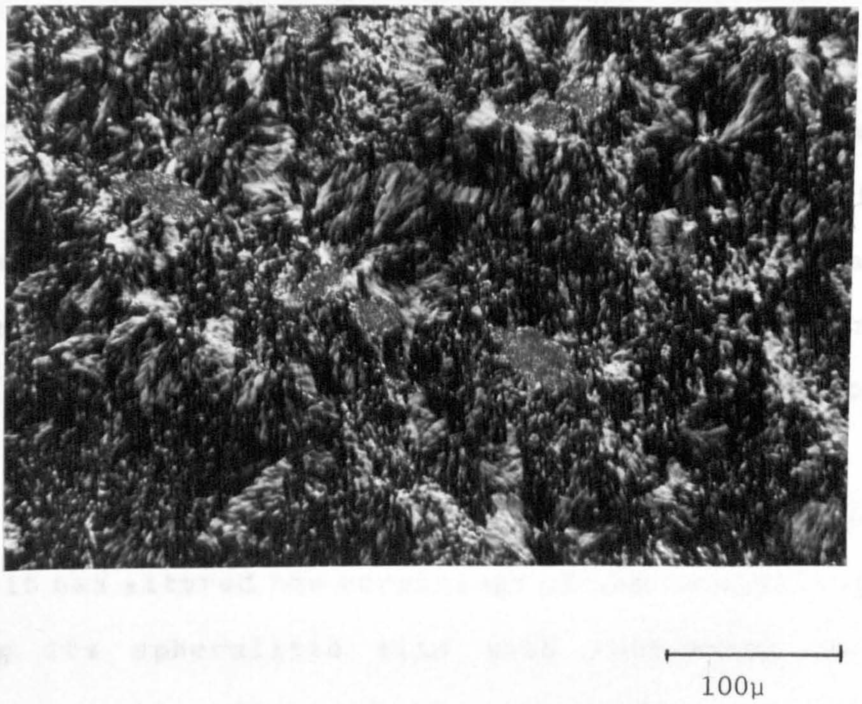


Fig. 4.8. Microtomed sample of PB + 10% boron nitride, crystallized at 5 degrees/min.

PB has a higher melt viscosity compared to that of PP hence loading the samples was more difficult. When the mixing process was done 40 degrees above the melting point of the polymer (instead of 20 degrees as it was done for all the samples) no significant change in the crystallization temperature was obtained. The difficulty to obtain homogeneous dispersion causes a broadening of the crystallization curve as shown in Fig. 4.9.

The small shift of 7 degrees in the crystallization temperature for PB compared to that of 12 degrees for PP may be attributed to the pure polymer exhibiting smaller spherulites initially. In fact comparing Fig. 4.7a and Fig. 4.4a, it can be seen that in average PB spherulites are half the size of those for PP.

The addition of talc to POM shows the same effect observed for PP and PB; it has altered the morphology of the crystallized sample reducing its spherulitic size with increasing content of nucleating agent. Figure 4.10 demonstrates this effect and also points out the fact that starting with a large number of nuclei or small spherulites in the unfilled material, the shift in the crystallization temperature that can be achieved by loading the polymer is small. For POM this shift was only 4K.

The dispersion of the nucleant was found to be homogeneous so the effectiveness of the nucleating agent was at its maximum.

The correlation put forward previously between the initial size of the spherulite of the unfilled polymer and the extent of the shift in crystallization temperature that can be obtained for

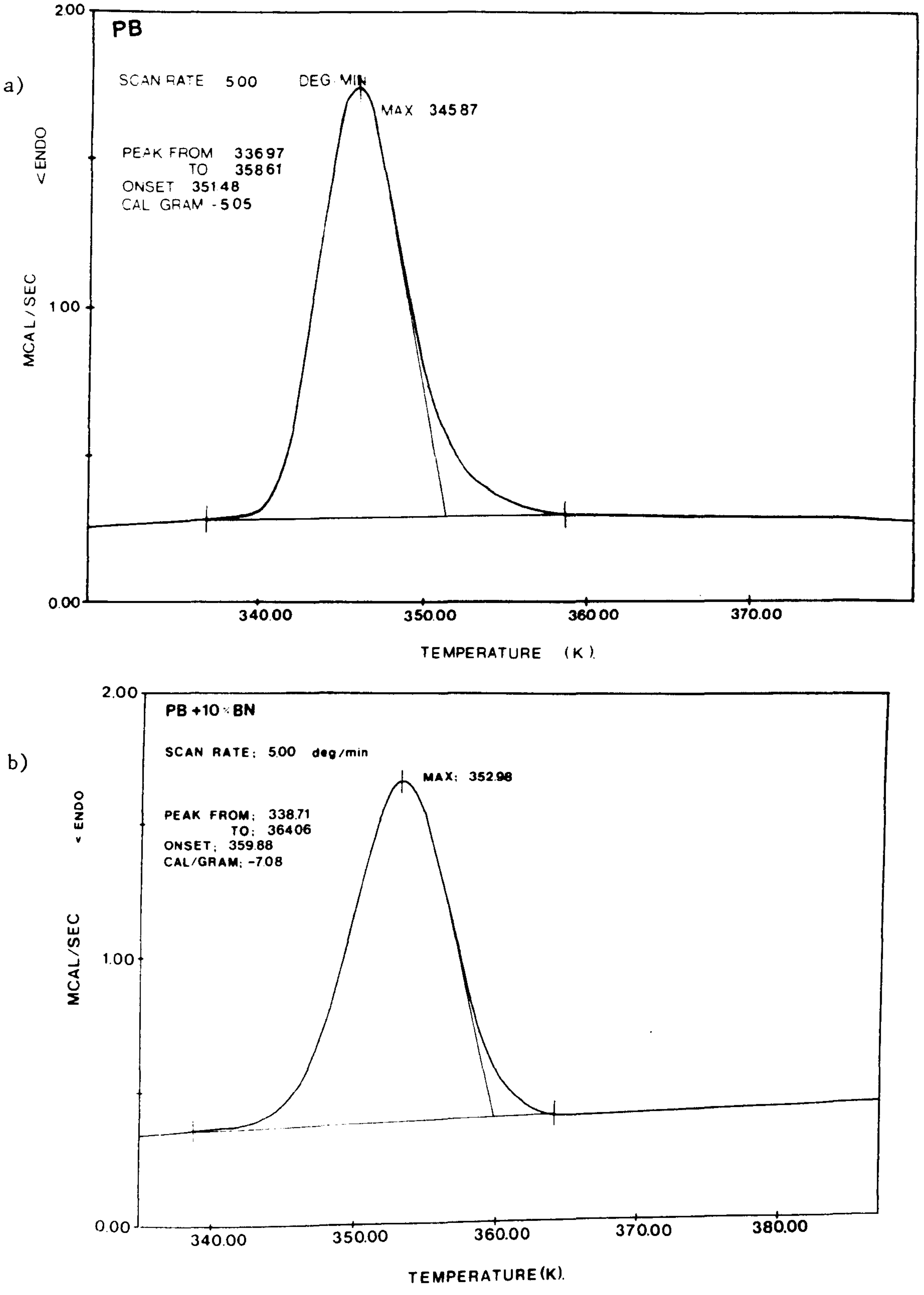


Figure 4.9. Crystallization exotherms of a) PB and b) PB + 10% BN crystallized at 5 degrees/minute.

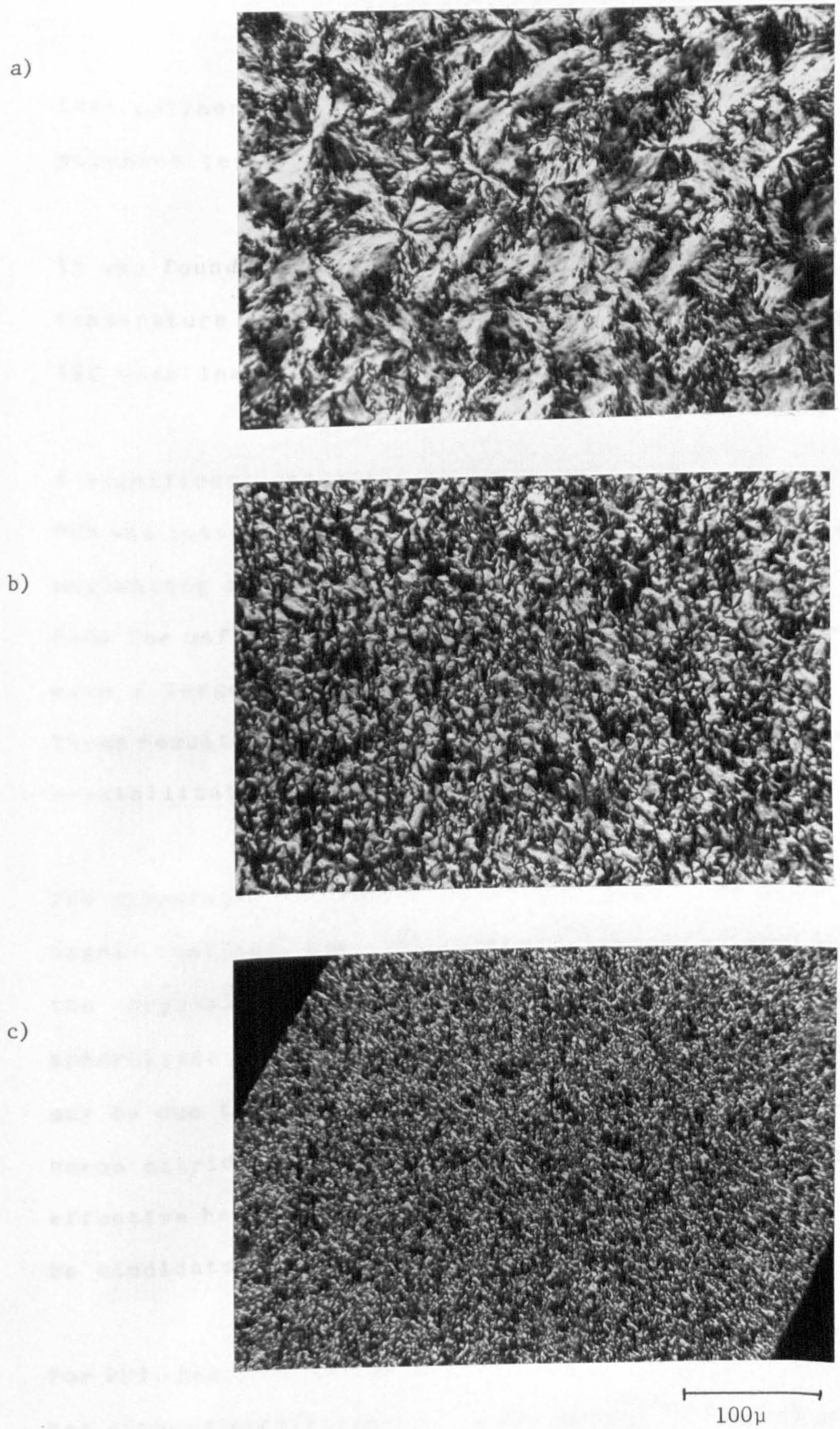


Fig. 4.10. Microtomed sample of POM and its composites crystallized at 5 degrees/minute. a) unfilled POM b) POM + 1% talc and c) POM + 10% talc.

that polymer, reached the higher value for PHB in the series of polymers tested in the present work.

It was found, according to table 4.1, that the crystallization temperature of PHB was shifted 10K when loaded with 10% talc and 19K when loaded with 10% boron nitride.

A significant reduction in spherulitic size was achieved when PHB was loaded, as shown in Fig. 4.11. When talc was used as the nucleating agent, the spherulites were reduced from about 500-600µ for unfilled polymer to about 200µ. But for boron nitride even a larger reduction to approximately 100µ was obtained. These results are in good agreement with the respective shifts in crystallization temperature of filled PHB.

The dispersion of the nucleants was found to be homogeneous and higher loadings, e.g. 15%, have not caused any further shift in the crystallization temperature or any decrease in the spherulitic size. The bigger shift obtained with boron nitride may be due to a better interaction with the polymer. Perhaps boron nitride possess the surface structure necessary for an effective heterogeneous nucleation of PHB. This aspect has to be elucidated by electron microscopy.

For PET, the addition of talc or sodium benzoate or boron nitride has altered significantly the morphology of the sample, this is clearly illustrated by comparing Fig. 4.12a and Fig. 4.12c. Although the unfilled material does not start with such big spherulites at PHB, a shift of 17K has been obtained, but at loadings of 1% the spherulites were much smaller than for PHB

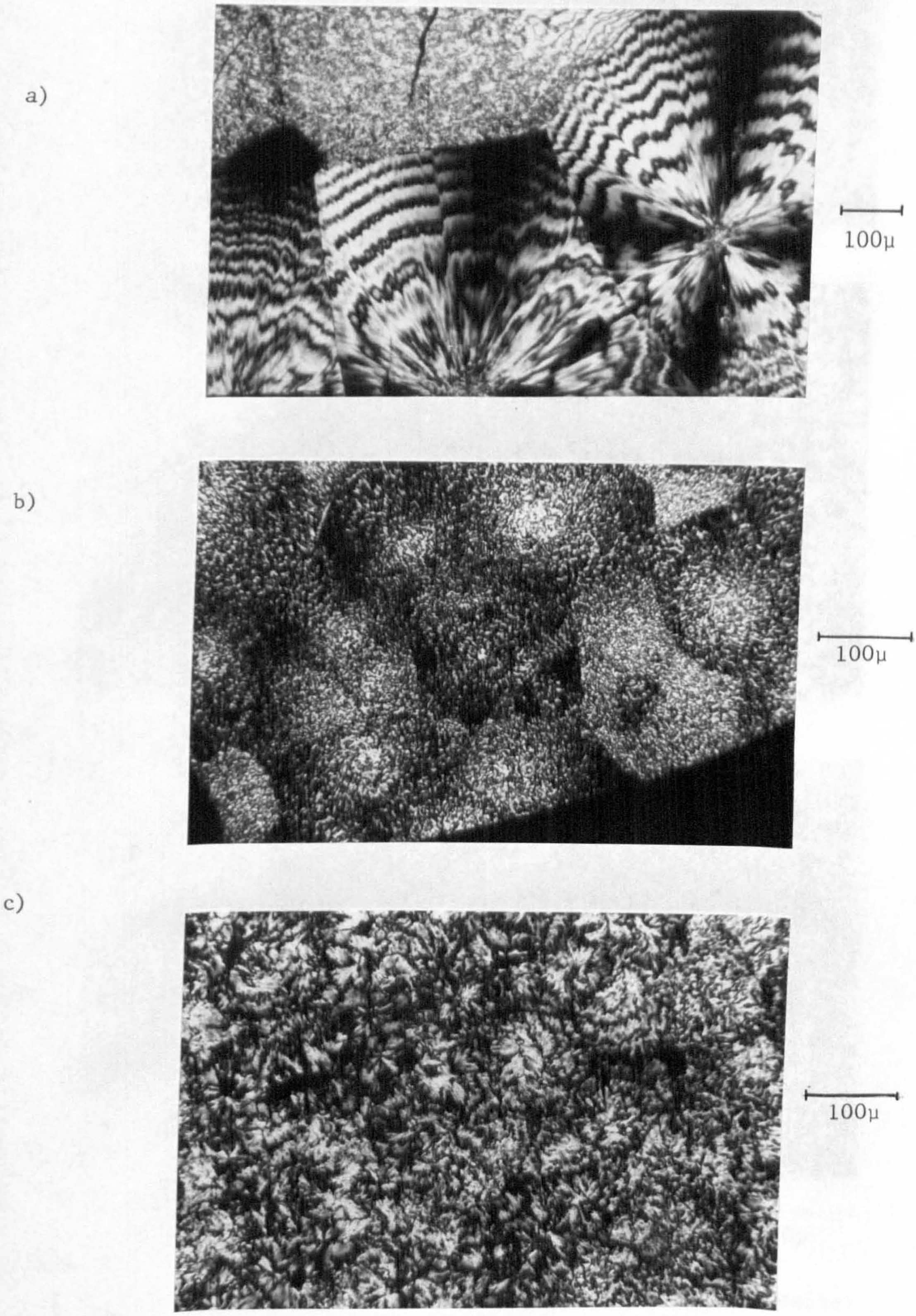


Fig. 4.11. Microtomed sample of PHB and its composites crystallized at 5 degrees/minute a) unfilled PHB b) PHB + 10% talc and c) PHB + 10% BN.

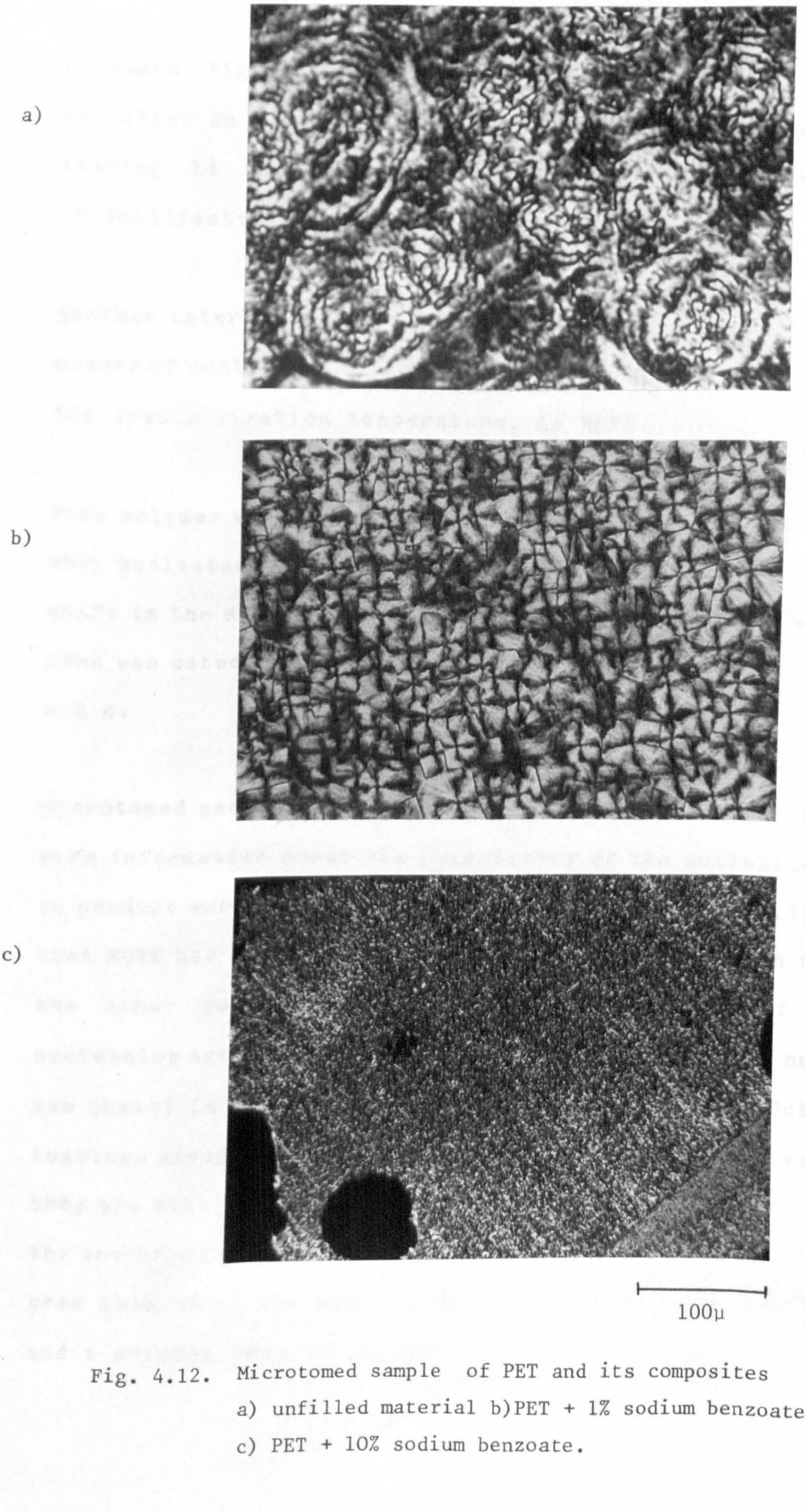


Fig. 4.12. Microtomed sample of PET and its composites
a) unfilled material b)PET + 1% sodium benzoate
c) PET + 10% sodium benzoate.

(compare Fig. 4.11c and Fig. 4.12c). Proportionally the reduction in spherulite size has been similar for PHB and PET leading to similar results in temperature shift of the crystallization process.

Another interesting example that corroborates the effect of the number of nuclei formed by the nucleating agent with the shift of the crystallization temperature, is HDPE.

This polymer was the only one which exhibited a secondary peak when nucleated with talc or boron nitride, rather than showing a shift in the exotherm as the other polymers did. The secondary peak was detected only at 10% of loadings as shown in Fig. 4.3b and c.

Microtomed sections of samples with various loadings disclosed more information about the possibility of the nucleating agent to produce more nuclei in the polymer matrix. Fig. 4.13a shows that HDPE has a greater number of nuclei to start with than all the other polymers studied here. At loadings of 1% the nucleating agent is not able to introduce a significant number of new nuclei in comparison to those already present. But at 10% loadings enough new nuclei are brought about by the nucleator and théy are able to grow at faster speed as shown by the presence of the secondary peak. Immediately the rest of the nuclei start to grow because of the small undercooling characteristic of HDPE and a primary peak is formed.

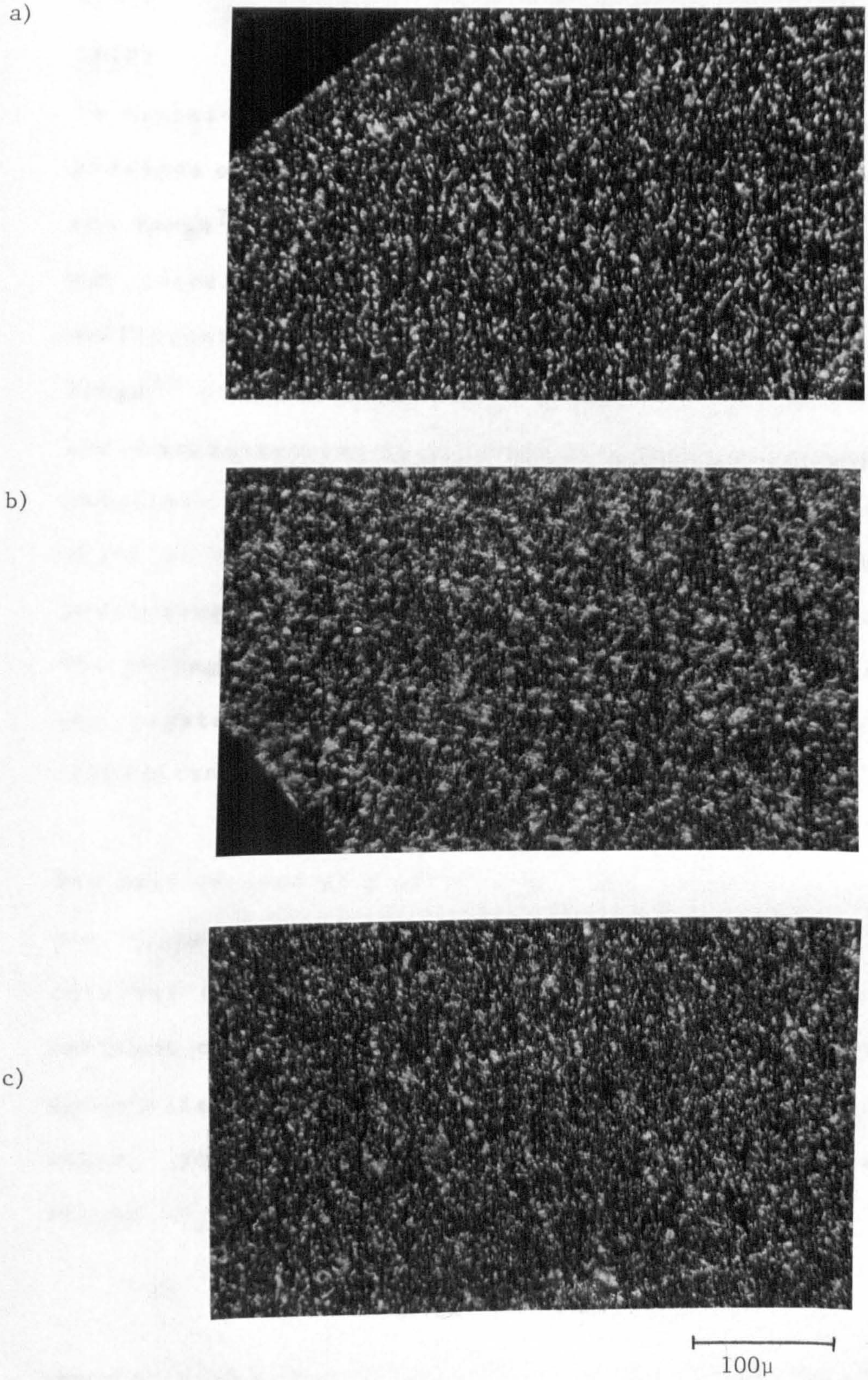


Fig. 4.13. Microtome samples of HDPE and its composites crystallized at 5 degrees per minute. a) unfilled HDPE b) HDPE + 1% BN and c) HDPE + 10% BN.

## 4.1.C. THE EFFECT OF NUCLEATION DENSITY ON THE TEMPERATURE SHIFT

To explain the shift in crystallization temperature due to the presence of a nucleating agent it has been postulated by Menczel and Varga[73] that a nuclei can be formed at a higher temperature and therefore the induction time which is needed to form a sufficient number of nuclei is decreased. Binsbergen and de Lange[69] obtained a different result in the interpretation of their measurements; they insist on the absence of any detectable induction time. An attempt will be made here to explain the shift of the DSC cooling curves to higher temperatures with increasing percentage of the nucleating agent by a decrease of the average distance between the nuclei formed; assuming that the crystallization will commence at the same temperature regardless if the polymer has been nucleated or not.

The heat evolved at a particular time interval is dependent on the volume of polymer which is crystallizing at that time interval ( $\frac{dV_c}{dt}$ ) . For a constant crystallization rate and a constant cooling rate, a maximum is reached when the growing spherulites reach their maximum size and start to touch each other. For spherulitic growth, the change in the crystallized volume ($V_c$) can be calculated as:

$$dV_c = N\,4\pi r^2 dr \tag{4.1}$$

where N is the number of spherulites growing simultaneously and r is the spherulitic radius. This radius is dependent on the time (t) measured from the beginning of crystallization and on the rate of crystallization v(T), which is temperature dependent.

$$r = v(T)\ t \tag{4.2}$$

The rate of crystallization is usually expressed as in Equation 1.23.

$$V = V_o \exp\left(-\frac{E_D}{kT}\right) \exp\left(-\frac{4\sigma\, \sigma_e\, b_o\, T^o_m}{kT\, \Delta H_v\, \Delta T}\right)$$

It is not easy to use this equation as it contains some parameter which are difficult to measure accurately. It would be therefore easier to rely on experimental measurements. When the crystallization is performed on a substrate (see Chapter 3), the heat evolved from the transcrystalline region is given by

$$\frac{dV_c}{dt} \sim \frac{Adx}{dt}$$

Where A is the area of the substrate and x is the distance of the solid/melt interface. It is apparent that the measured heat evolved is directly proportional to the rate of crystallization. The rate is changing with the undercooling and the DSC cooling curve is in this case directly related to the temperature dependence of the crystallization rate:

$$\frac{dV_c}{dt} \sim v\,(\Delta T)$$

In Figure 4.14, the experimental curve and the calculated curve assuming that $v(\Delta T) \sim \Delta T^3$ are in good agreement if the crystallization process started at 418K. The small peak is due to the initial growth of the transcrystalline region in the spherulitic form and hence the rate of crystallization is different.

For a constant rate of cooling of 5 degrees/min, $\Delta T \sim t$ so the rate of crystallization is proportional to $t^3$. Therefore equation 4.2 can be written as

$$r = C_1\, t^4$$

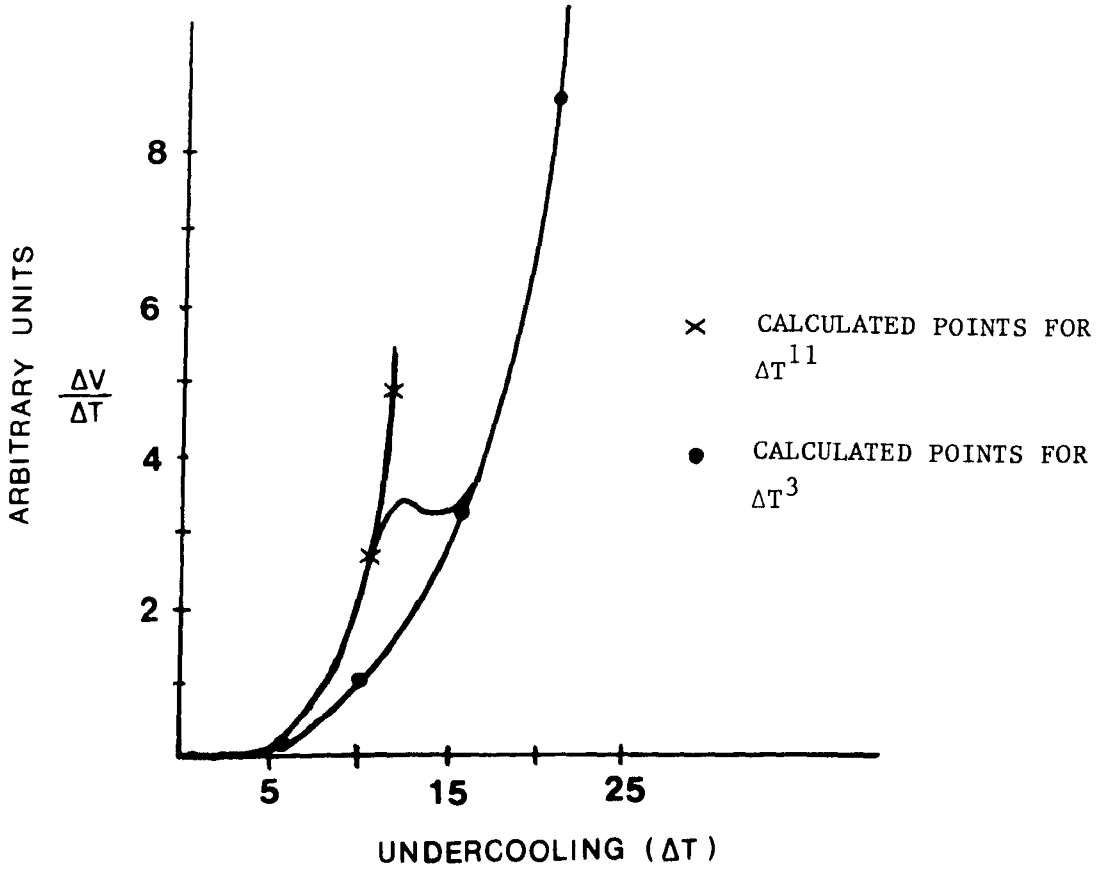


Figure 4.14. First part of Fig. 3.6 of the DSC cooling exotherm for PP on a talc substrate. The measured graph has been extrapolated to differentiate between the two nucleation processes. The calculated points are ● for $\Delta T^3$ and × for $\Delta T^{11}$.

and

$$dr = 4\ C_1\ t^3\ dt \qquad (4.3)$$

substituting Equation 4.3 in Equation 4.1

$$\frac{dV_c}{dt} \sim N\ 4\ \pi (C_1\ t^4)^2\ (C_2\ t^3)$$

or

$$\frac{dV_c}{dt} \sim N\ C\ t^{11} \qquad (4.4)$$

where $C_1$, $C_2$ and C are constants. The heat evolved per time is therefore proportional to $t^{11}$. The small peak in Fig. 1.14 is due to a shorter crystallization distance on the substrate and is related to the nucleation density. The initial growth is spherulitic and therefore the heat would be evolved more rapidly at the beginning, but the speed will change from $t^{11}$ to $t^3$ abruptly when the spherulites touch each other given rise to the transcrystalline region. Hence the small peak corresponds to a thin layer of the order of 0.5 - 1μ in contact with the nucleating agent.

In figure 4.15 the experimental DSC cooling curves for pure polypropylene and samples loaded with 1 and 10% of talc are similar, only their maximum appears at different temperatures. This observation allow us to assume that the crystallization of nucleated and unnucleated samples occurs at the same temperature dependent rate. Comparing the experimental curves with the calculated curves using Equation 4.4 (see Figure 4.15) it can be observed that they are in good agreement and it is thus possible to explain the effect of the nucleating agent by simply assuming that the number of nucleating centers is changing by up to 2½ orders, which corresponds well to our observations.

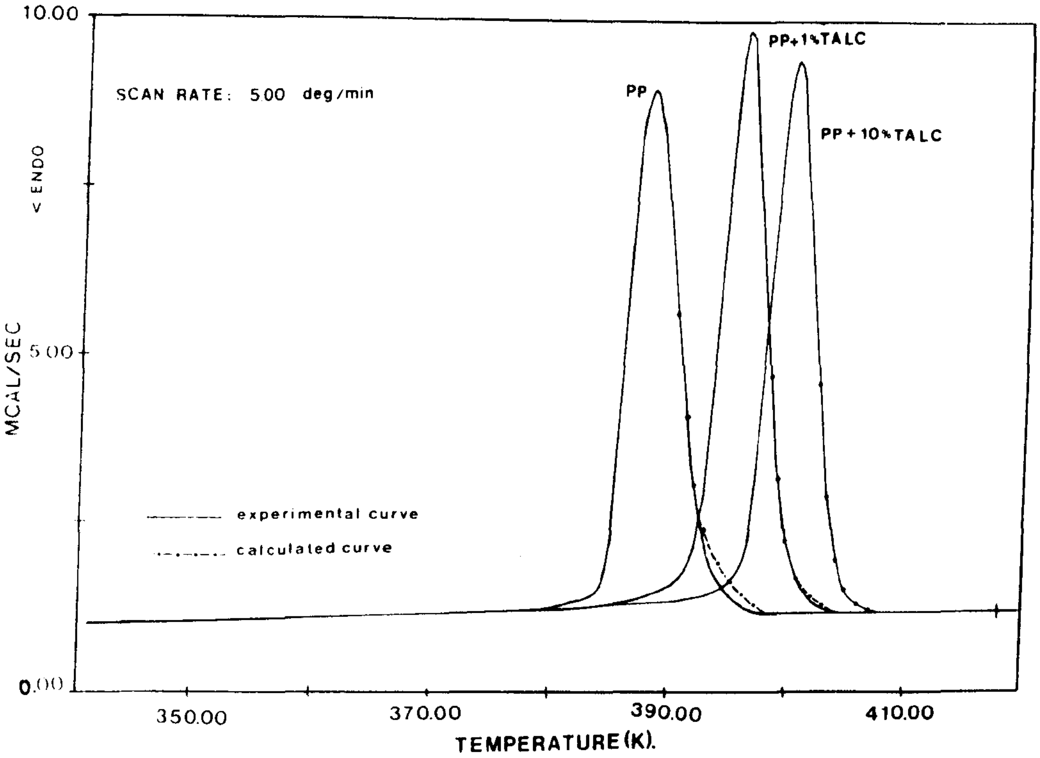


Figure 4.15. DSC cooling curves for pure PP and samples loaded with 1 and 10% of talc.

It can be concluded from the above analysis that the increase in the temperature of crystallization can be explained by the density of nuclei formed. Also the extent of the shift in the crystallization temperature of heterogeneously nucleated polymer is related to the initial number of spherulites present in the pure polymer. The bigger the spherulites of the polymer to start with, the higher would be the shift in crystallization temperature due to the presence of the nucleating agent.

# CHAPTER 5

## 5. SELF NUCLEATION OF POLYMERS FROM THE MELT

One aspect of polymer crystallization that has been extensively investigated is the influence of various thermal pretreatments of the melt on the isothermal crystallization kinetics. Turska and Gogolewski[64] studied the crystallization behaviour for nylon 6, Boon et al[65] for i-Polystyrene, Rybnikar[75] for i-Polypropylene and Hartley et al[76] for polyethylene terephthalate. In all such cases it was found that as the melt temperature was increased, the number of nuclei was reduced and thus the nucleation rate. Rybnikar[75] found that for i-PP the number of nuclei decreased sharply with increasing the melting temperature to 220°C and then remained practically constant. These effects are generally attributed to incomplete melting of highly crystalline fragments or to the persistance of small crystalline regions trapped in cavities of solid impurities that can act as nuclei on subsequent cooling.

This particular type of primary nucleation caused by polymeric crystals which are chemically identical to the crystallizing polymer, but have survived the prior dissolution or melting, is called self-nucleation.

In the present study the self-nucleation behaviour of various polymers was utilized to elucidate the effect of heterogeneous nuclei on the temperature shift. For this purpose previously crystallized polymers were melted close to and at the melting temperature and subsequently crystallized. The shift in the crystallization temperature would be a consequence of the nucleating effect of chemically identical fragments remaining after the melting treatment. This would ensure that the shift obtained represents the maximum shift attainable by the polymer, since the requirements for a close matching of crystal lattice parameters and similarity in crystallographic unit cell that allow the polymer to grow, are fulfilled.

A comparison between the crystallization temperature shift in self-nucleated polymers and in heterogeneously nucleated polymers would establish if the nucleating agents used in the present investigation are causing the possible maximum shift or if still a better nucleator can be found for each polymer.

## 5.1 RESULTS AND DISCUSSION

### 5.1.A EFFECT OF MELTING TEMPERATURE ON SELF-NUCLEATION

In the previous section it was found that the shift in the crystallization temperature is due to the crystallization distance between the nucleated spherulites. With increasing nucleant content more new nuclei are formed until a saturation is achieved with a maximum shift in crystallization temperature. Taking into account this fact, it was necessary that the samples submitted to self-nucleated crystallization would have initially the same number and size of spherulites. The conditions chosen were the same as for heterogeneously crystallized polymers (Section 3), that means melted 30 degrees above their melting point and crystallized at 5 degrees per minute. After this previous treatment various samples were melted close to and at the melting temperature and subsequently crystallized at 5 degrees per minute. When the samples were melted above and at the melting point, the enthalpy of crystallization, calculated with the TADS system, remain approximately constant. At a certain temperature below the melting point it decreased dramatically. This point was taken as the temperature where self-nucleation was not possible (Fig. 5.1 a and b).

After the DSC thermograms were obtained, the samples were microtomed at different levels throughout their volume and investigated with light microscopy.

The crystallization temperatures for self-nucleated polymers are plotted in Figure 5.1a and b. According to those results, an increase in crystallization temperature coincides with the melting temperature of each polymer investigated except PHB. In cases like PE, PB, POM, Nylon 66 and PP the maximum shift is obtained within a melting range of 5 degrees or less. For polymers like PHB and PET the range is $20^{\circ}$ and $15^{\circ}$ respectively. For melting times of 2,5 and 10 minutes, there was no significant change in the crystallization temperature for the various polymers investigated except PHB. This polymer exhibits a decrease of $4^{\circ}$ in the crystallization temperature if the melt is held at 480K for 5 minutes instead of 2 minutes. At 10 minutes of melting time there is a scatter of $2^{\circ}$ in the crystallization temperatures. For this reason in the present study PHB was held in the melt for 10 minutes while the rest of the polymers were held for 5 minutes.

Vidotto[48] et al studied in detail the self-nucleation behaviour of PE and PB. They found that the number of nuclei decreases rapidly with the increasing melting temperature to the melting point after which a constant limit is reached. For PE their range of 3o for melting temperature coincides with that obtained

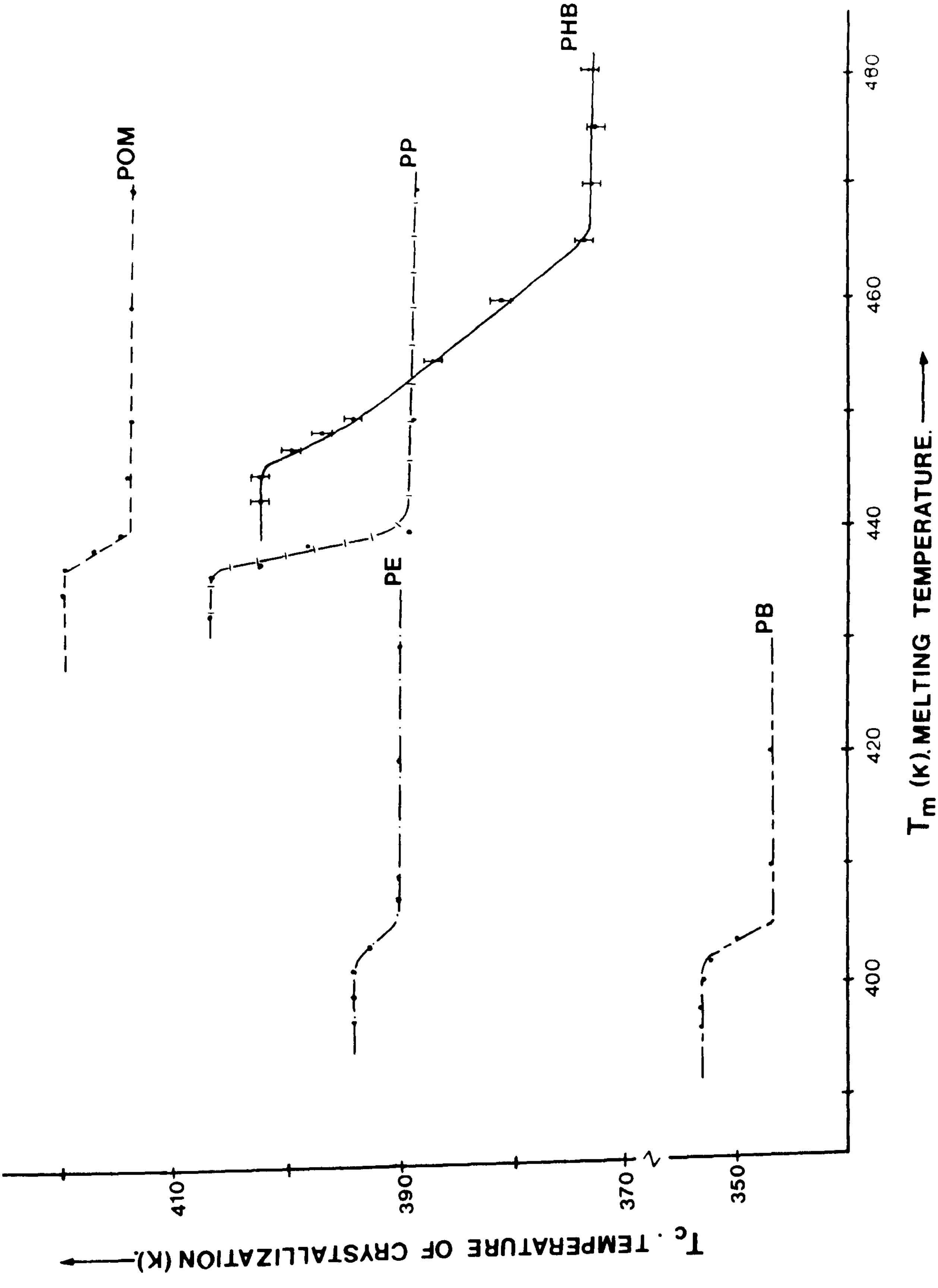


Figure 5.1a. Variation of maximum crystallization temperature of various polymers with melting temperature. Polymers crystallized at $5^{o}$/min

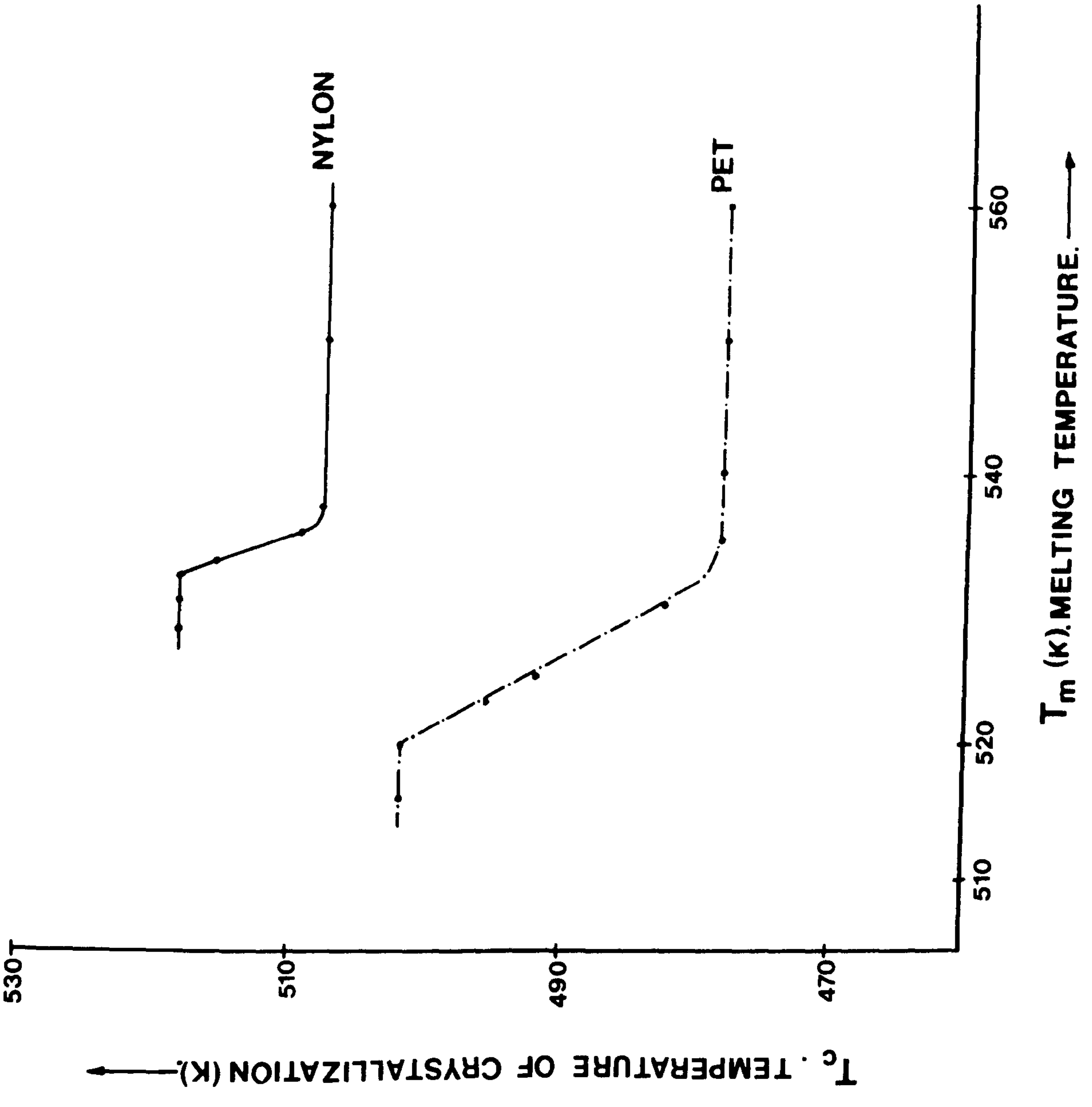


Figure 5.1b. Variation of maximum crystallization temperature with melting temperature for a)PET and b) Nylon 66.

in the present work. A special case was found for PB as this polymer crystallizes in two crystal forms. Form 1 is the stable crystal form and form 2 crystallizes at high temperature from the melt. The conversion of form 2 to form 1 occurs with maximum rate at 25°C. The limit of self nucleation of form 2 reported by Vidotto et al[48] is 131°C and 141°C for form 1. According to the present results (Figure 5.1a), the limit for self-nucleation is 132°C so only form 2 is formed which would be converted to the stable form 1 at room temperature. The melting range for self-nucleation obtained by Vidotto et al is 3°C which is in good agreement with that of 2.5° obtained in the present study.

In the following table, the maximum shift in crystallization temperature for self-nucleated samples and for heterogeneously nucleated samples are summarized.

TABLE 5.1 <u>Maximum shift in crystallization temperature for nucleated polymers.</u>

| | | HETEROGENEOUSLY NUCLEATED | |
|---|---|---|---|
| POLYMER | SELF NUCLEATED | MIXED | SUBSTRATE |
| HDPE | 4° | 4° | 4° |
| PP | 18° | 14° | 18° |
| PB | 7° | 7° | APPROXIMATELY 7° |
| POM | 5° | 4° | 5° |
| PHB | 29° | 19° | 17° |
| PET | 23° | 19° | 22° |
| NYLON | 11° | 7° | 11° |

Comparing the maximum shift in crystallization temperature in Table 5.1 for self-nucleated samples with the shift for heterogeneously nucleated samples it can be observed that the shifts are in most cases similar. When the nucleating agent is densely packed (substrate samples), the number of nuclei formed is very high and the temperature shift obtained is the same as for the self-nucleated samples, except for PHB with a difference of 10°. For samples with well dispersed nucleating particles the maximum shift in crystallization temperature is approximately 4° below that for self-nucleated samples.

The samples subjected to self-nucleation show clearly the effect of melting temperature on their morphology (Fig. 5.2). Initially the PP samples had an average spherulitic size of 100μ and their number of nuclei that developed into spherulites can be counted. After remelting the specimen at one or three degrees below their maximum melting point (440K) and crystallized at 5 degrees/minute, the structure had a "granular" appearance and the number of nuclei formed were difficult to count. It is apparent that at temperatures just below the melting point the incomplete melting of crystalline fragments can act as nuclei on subsequent cooling and hence increasing dramatically the number of spherulites obtained.

As discussed in the previous chapter, decreasing the crystallization distance between the spherulites leads to an increase in crystallization temperature. In fact as shown in Fig. 5.2b, self-nucleated PP sample melted at 437K with a small spherulitic size crystallizes at a temperature of 407K i.e. higher than 398K for the sample with larger spherulites melted at

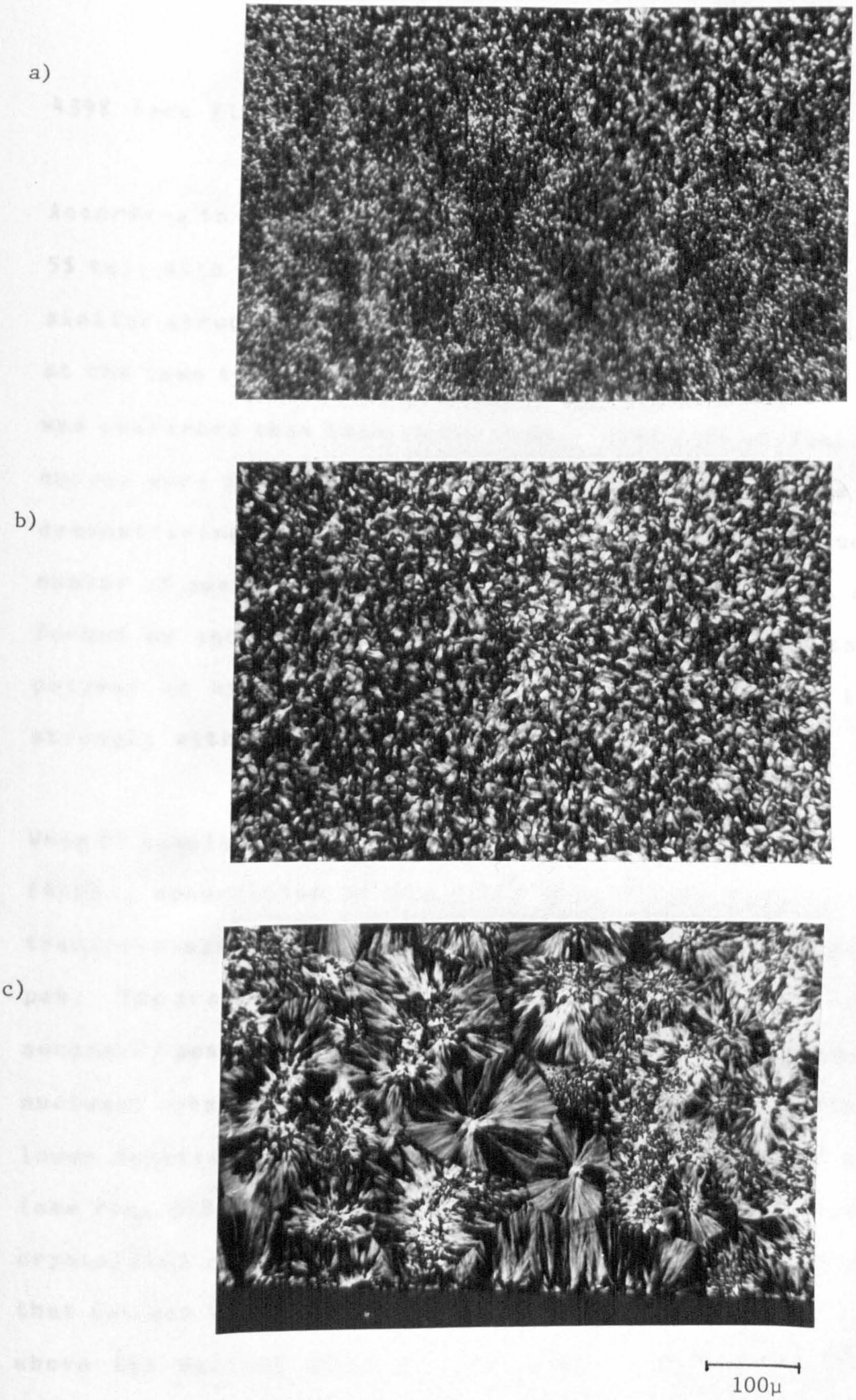


Fig. 5.2. Microtomed samples of self-nucleated PP melted at a) 437K b) 439K and c) 440K and crystallized at 5 degrees/minute.

439K (see Fig. 5.1 c).

According to these results one should expect that a sample of PP + 5% talc with a good dispersion, nucleated at 398K, would have a similar structure as a self-nucleated sample which crystallized at the same temperature. Comparing Fig. 4.5a with Fig. 5.2b it was confirmed that this is the case. Also both crystallization curves were identical in shape for samples of the same weight, demonstrating then that the extent of the shift is due to the number of nuclei present in the polymer. Those nuclei could be formed by incomplete melting of crystalline fragments of the polymer or by the presence of heterogeneities that interact strongly with the polymer.

When PP samples were self-nucleated at their melting temperature (440K), spherulites of about 80μ were formed together with a transcrystalline region at the melt interface with the aluminium pan. The presence of transcrystallinity does not give rise to a secondary peak on the crystallization curve as in the case of PP-nucleant substrate samples. This transcrystalline region is of lower density compared to that of substrate nucleated samples (see Fig. 5.2 and Fig. 3.2b) and is due to persistance of small crystalline regions trapped in cavities of the aluminium pan that can act as nuclei on subsequent cooling. At temperatures above the melting point of the polymer, the self-nucleation effect disappears and the number of nuclei remains constant with no further shift in the crystallization temperature.

Some of the polymers under study have achieved similar shifts in crystallization temperature either by self-nucleation or heterogeneous nucleation. But for PP, PET and nylon there is a difference of 4° between them (see Table 5.1). This difference was reduced when mixed samples were melted below and at the melting point of the polymer. Fig. 5.3 describes the additional effect of self-nucleation in previously heterogeneously nucleated samples of polypropylene with 10% talc. The same effect was observed for PET and for nylon. POM and PB nucleated with talc have not shown any additional increase in their temperature of crystallization by self-nucleation because the samples already attain the maximum shift exhibited by the polymer when self-nucleated. For PE it was difficult to observe any shift in the crystallization temperature of talc nucleated samples submitted to self-nucleation because of the two peaks present in the crystallization exotherms (see Fig. 4.3).

Among the polymers studied, PHB is the only one that can be self-nucleated within a wide range of melting temperatures. Varying the melting temperature of a previously crystallized samples from 445K to 470K, the crystallization temperature decreases 30° as shown in Fig. 5.1a. In a recent study Barham and Keller et al[77] estimated the equilibrium melting point of PHB and reported a value of 470K. This result is in good agreement with the temperature where the limit for self-nucleation was observed in the present study.

Microtomed sections taken at different levels throughout the structure of various PHB samples, self-nucleated at different melting points, showed a dramatic change in spherulitic size. Figure 5.4a shows a PHB sample remelted at 448K with a spherulitic size of about 5µ. At a higher melting temperature

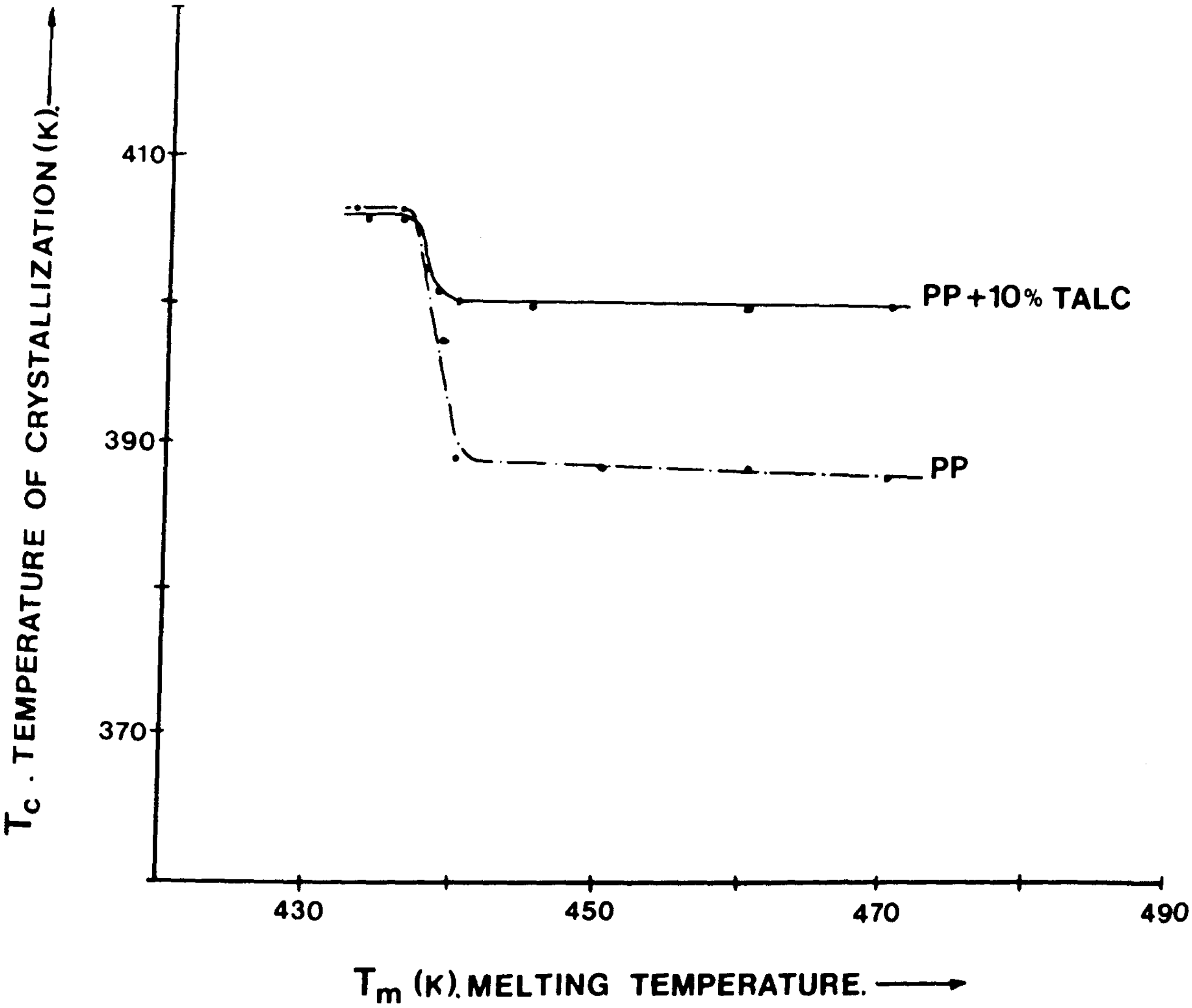


Figure 5.3. Variation of maximum crystallization temperature with melting temperature of a)pure polypropylene and b) polypropylene + 10% talc.

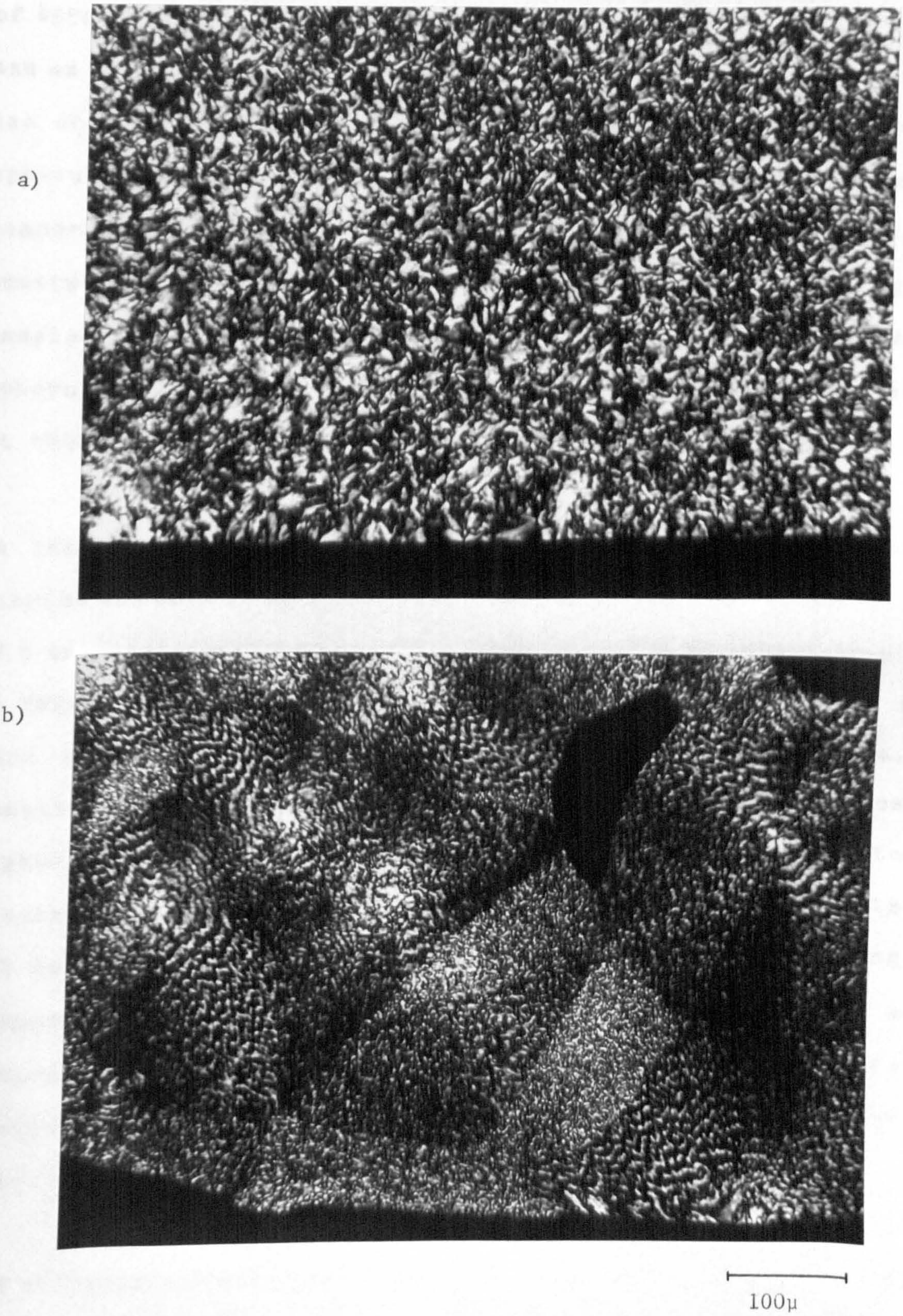


Fig. 5.4. Microtomed samples of self-nucleated PHB melted at a) 448K and b) 455K. Crystallized at 5 degrees/minute.

of 455K (Fig. 5.4b), the spherulitic size is approximately 250μ and as an expected consequence, the crystallization temperature has droped from 399K to 387K (see Fig. 5.1a). The number of spherulites present continues to decrease, with the melting temperature increasing to 470K, and then remains practically constant. Figure 5.5a shows spherulites of about 350μ for samples remelted at 465K and figure 5.5b shows the maximum spherulite size (approx. 400μ) reached by a PHB sample remelted at 480K and crystallized at 5 degrees/minute.

In the previous section (Chapter 4) it was found that boron nitride was able to nucleate PHB. At a constant rate of cooling of 5 degrees/minute a PHB sample loaded with 10% BN crystallized at 392K; 19 degrees above the crystallization temperature of a pure sample melted at 475K. For a self-nucleated sample, remelted at 445K, the crystallization temperature is 29 degrees higher than that of a sample melted at 475K. It was possible to obtain a similar crystallization temperature for a sample with 10% BN if it was submitted to a self-nucleation at a melting temperature of 445K. Figure 5.6 shows the behaviour of a heterogeneously nucleated sample that has been also self-nucleated. For 453K and lower melting temperatures the curve coincides with that of a pure self-nucleated polymer.

The difference between the spherulitic size achieved by the PHB sample loaded with 10% BN (Fig. 4.11c) and the self-nucleated PHB sample remelted at 448K (Fig. 5.4) explains the 10° difference in crystallization temperature. The nucleating agent is not able to reduce the crystallization distance to a sufficient extent as to obtain a smaller spherulitic structure than about 5μ. This

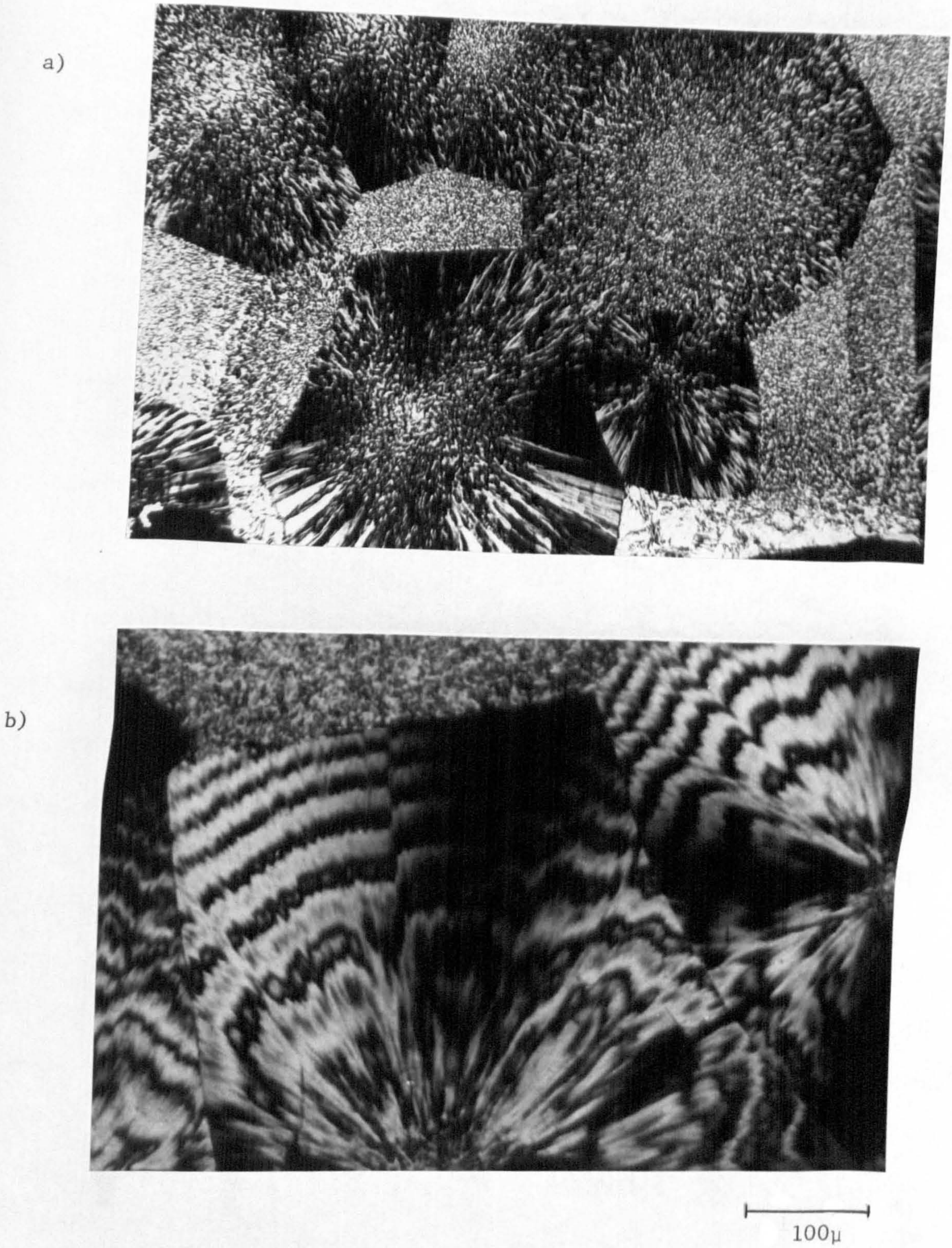


Fig. 5.5. Microtomed samples of self-nucleated PHB melted at a) 465K and b) 480K. Crystallized at 5 degrees/minute.

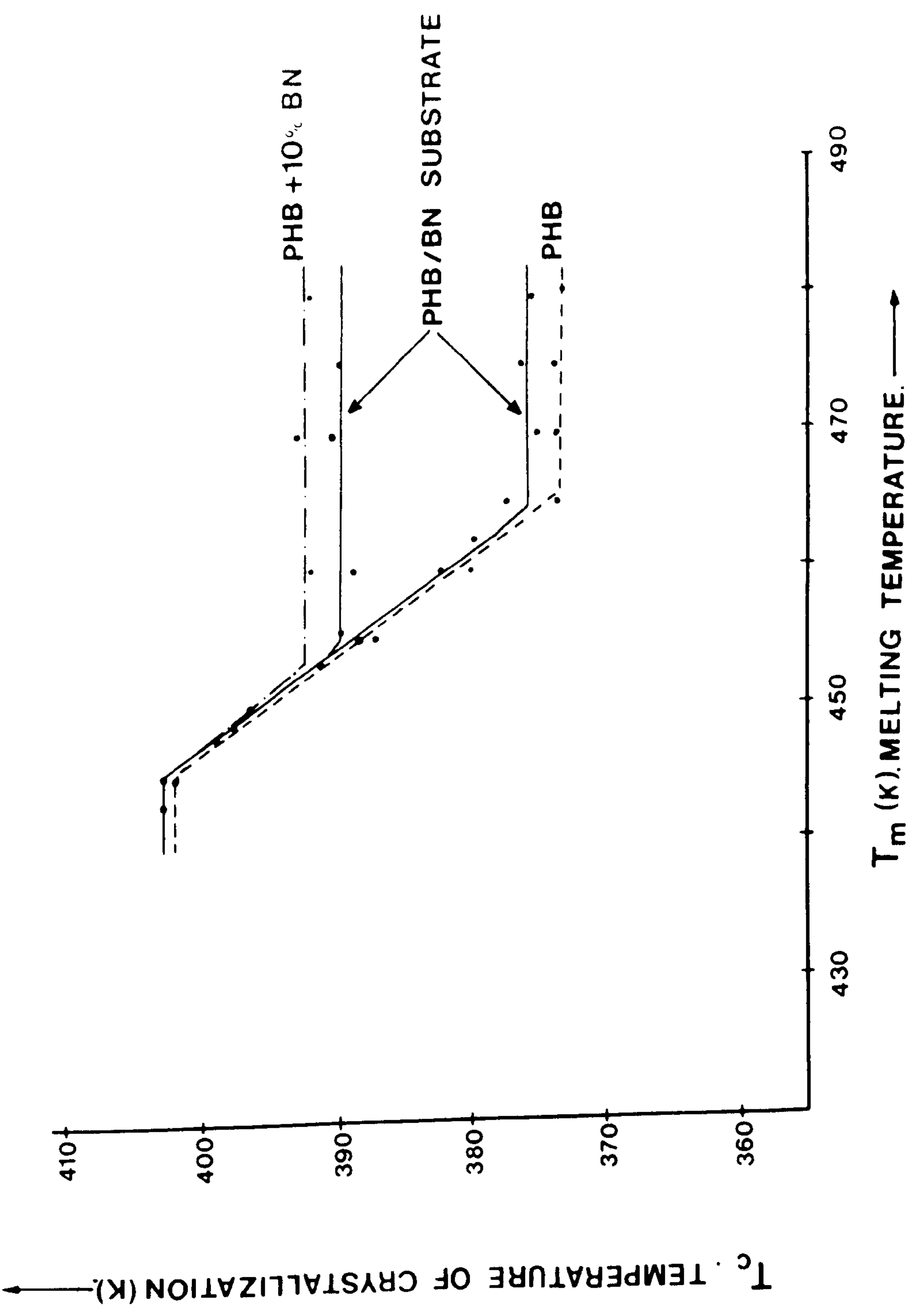


Figure 5.6. Variation of maximum crystallization temperature with melting temperature for a)pure PHB b)PHB-BN substrate and c)PHB + 10% BN.

inability might be due to the fact that not all the particles are able to interact with the polymer because they do not possess suitable facets or active sites to promote nucleation. This will be studied later by electron microscopy.

When PHB was nucleated on a boron nitride substrate, two peaks were obtained in the crystallization curve between a melting range of 455K and 475K. Figure 5.6 for PHB-BN substrate samples shows that the polymer in contact with the substrate crystallizes at 390K for various remelting temperatures and the rest of the material crystallizes at 376K as the pure polymer does. The microtomed section for a sample remelted at 475 (Fig. 5.7c) demonstrates the presence of a transcrystalline region due to the nucleating effect of boron nitride and the unrestricted growing of spherulites above the transcrystalline region. At melting temperatures below 465K the polymer which is not influenced by the nucleating effect of boron nitride, undergo self-nucleation up to 455K where the two curves (Fig. 5.6) join. Then the whole sample follows the self-nucleation curve between melting temperatures of 455K to 445K. Figures 5.7a anb b show the decrease in spherulitic size by decreasing the melting temperature. The spherulite sizes are comparable to those obtained for pure PHB self-nucleated samples (see Fig. 5.4 and 5.5).

Another nucleating agent used in the present study was saccharin. This compound was unable to nucleate PHB when thoroughly mixed with 10% of crushed powder. Figure 5.8 shows that at all melting temperatures, the pure PHB curve and PHB + 10% saccharin run almost parallel to each other. Similar results

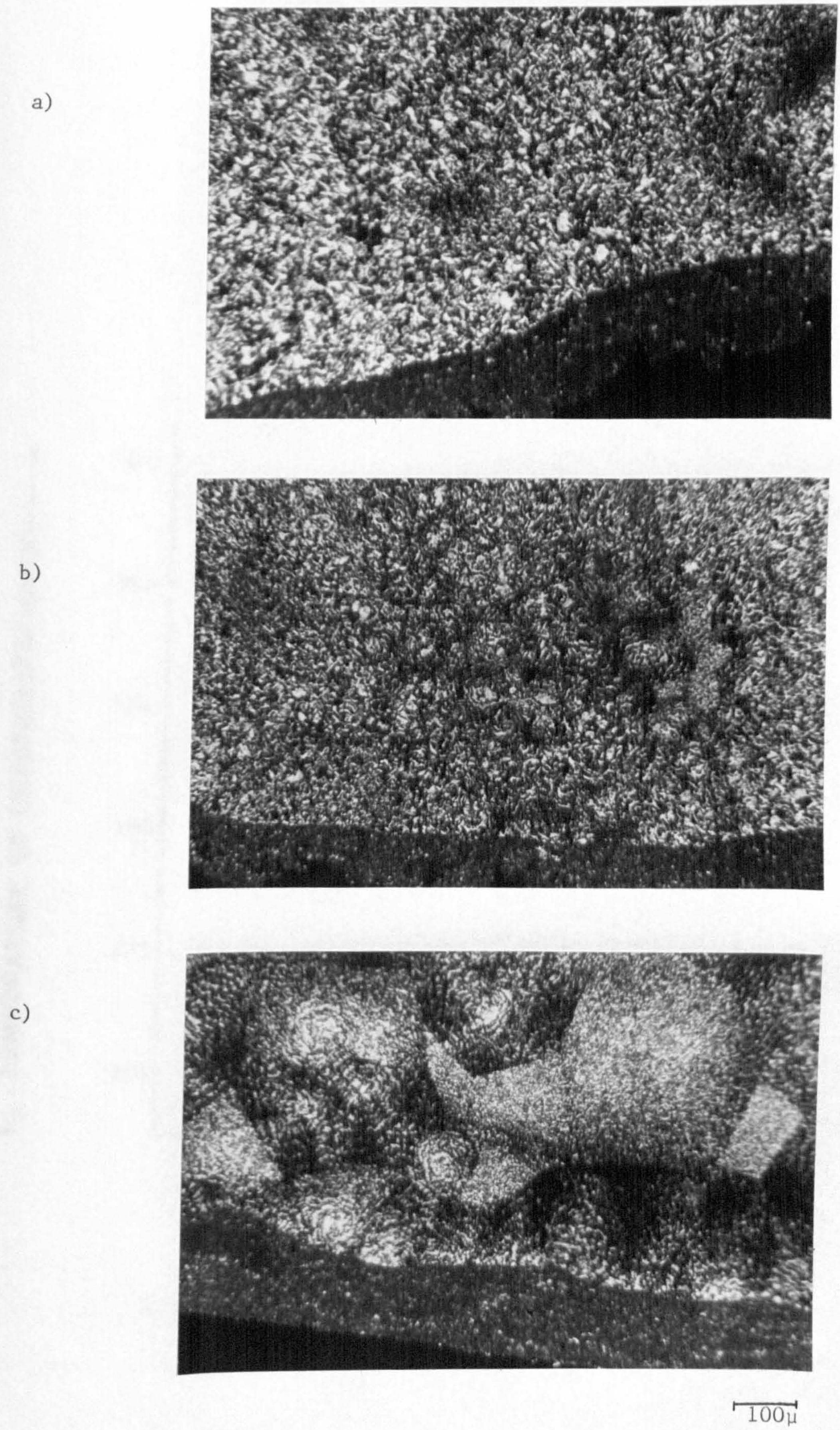


Fig. 5.7. Microtomed samples of self-nucleated PHB-BN substrate melted at a)448K and b) 450K and c)475K. Crystallized at 5 degrees/minute.

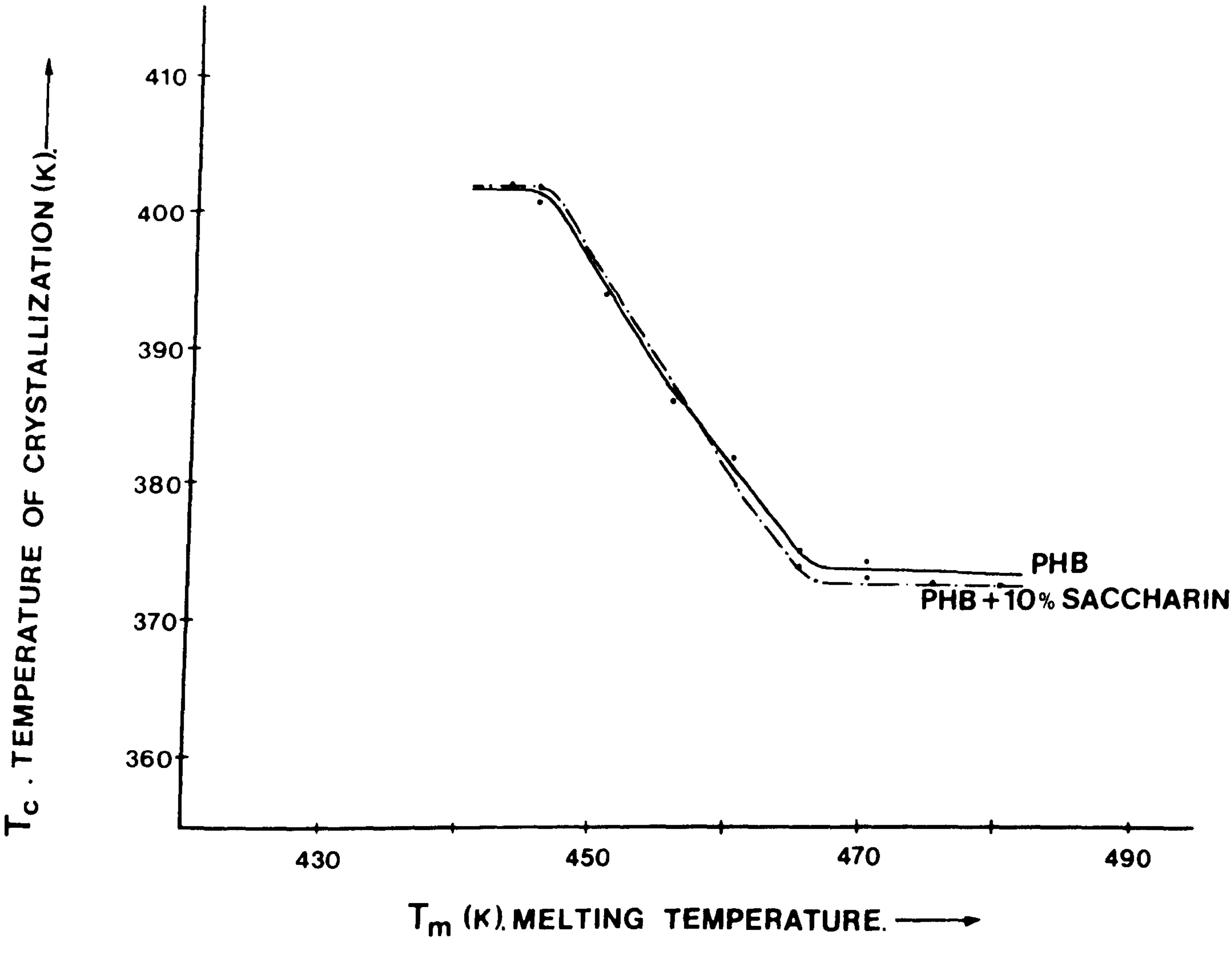


Figure 5.8. Variation of maximum crystallization temperature with melting temperature for a) pure PHB and b) PHB + 10% saccharin.

were obtained when PHB was nucleated on saccharin substrates. In a following paper, Barham[78] has reported nucleation of PHB by saccharin whether the polymer has first been allowed to crystallize around the saccharin particles and subsequently melted and recrystallized or whether it has been added directly to the melt. The reason why we have not obtained any nucleation might be due to the fact that the saccharin crystals used in this work were previously crushed and the suitable crystal facets which promote nucleation could have been destroyed.

In the present study samples of PHB + 10% talc have shown a shift of 10° in the crystallization temperature (see table 4.1) but no transcrystallinity was observed when the polymer was crystallized in contact with a talc substrate. These results are in good agreement with those obtained by Barham[78]. He reported that nucleation of PHB by talc has been observed after PHB has previously crystallized around the talc particle. In our experiments the mixed samples were first crystallized during the dispersion of the nucleator on the glass slide, before they were crystallized in the DSC. Substrate samples, on the other hand, were crystallized in the DSC without previous crystallization.

Barham[78] explained that this behaviour is due to local increase of the crystal melting point. The PHB molecules will form a semi-permanent crystalline layer around the talc particles, thus leaving a polymer crystal substrate for subsequent nucleation. From our results it is clear that talc is not as effective nucleating agent as boron nitride since the latter has caused a shift of 17° as compared to 10° for talc in the crystallization temperature. An attempt will be made (Chapter 6) to investigate by electron microscopy if the talc particles have the right facets to promote nucleation of PHB.

### 5.1.B EFFECT OF TEMPERATURE GRADIENT ON SELF-NUCLEATION

Barriault and Gronholz[79] reported that extruded nylon 66 has shown surface transcrystallinity under nearly all cooling conditions and this, they believed, indicated that a nucleating agent is not required for nucleation and proposed that a temperature gradient is sufficient to induce a high nucleation density on the surface.

Eby[80] reported transcrystallinity in polyethylene, crystallized under a temperature gradient; the thickness of the transcrystalline region could be increased by increasing the gradient between the surface and the melt. Schonhorn[81] has used specially treated materials to induce surface nucleation. Others have reported that highly oriented polyethylene and polypropylene have been prepared using techniques derived from zone-melting[82,83,84].

In the present investigation a simple apparatus with an accurate control of the temperature gradient was conceived (see Chapter 2.5) for studying the influence of such gradient on the crystallization process of various polymers.

Polymer specimens of even thickness and with a well developed spherulitic structure have been partially molten in a predetermined temperature gradient. After the experiment was performed, a transition band has been observed that has begun at a cooler face and has proceeded outwards into the melt. The width of the band corresponds to a certain temperature gradient (see Fig. 5.9). This gradient in the band was calculated from the measured temperature gradient graph. The study of the microstructure indicated that a temperature gradient is reflected principally in a size distribution of the spherulites, the smaller spherulites are close to the cold front and the larger ones to the hot front. These differences in spherulitic size can be attributed, as in the case of self-nucleation, to incomplete melting of highly crystalline fragments that can act as nuclei on subsequent cooling. The spherulites near the cold front are only partially molten which allow them to act as new nuclei. The spherulites in the inner part of the molten zone, which is at a higher temperature, are completely molten and the number of nuclei which can be formed is smaller. It is thus apparent that the melting temperature and not the temperature gradient is responsible for the degree of self nucleation.

In the following table, the temperature range and the transition range for the temperature shift as measured by DSC are summarized.

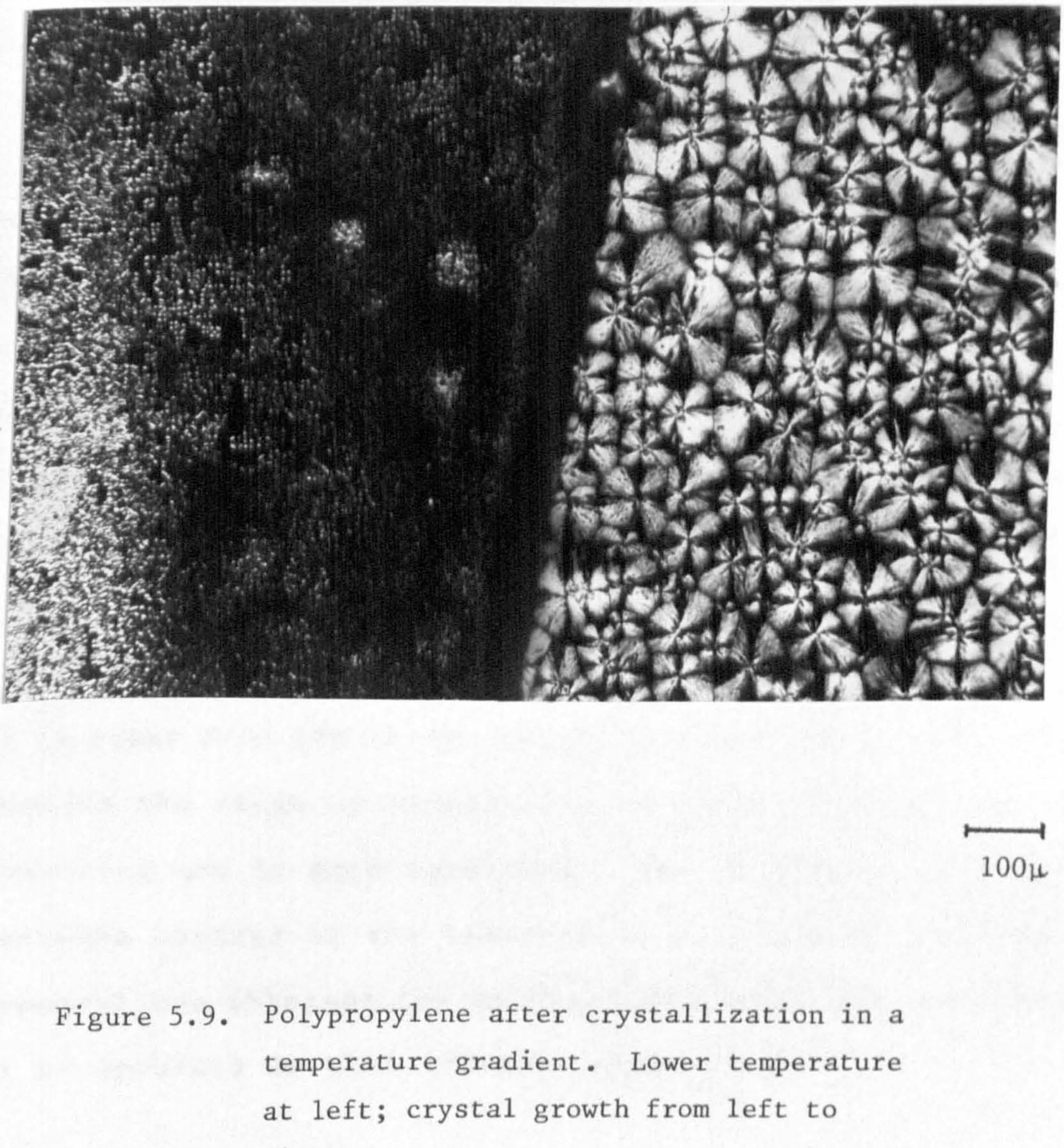


Figure 5.9. Polypropylene after crystallization in a temperature gradient. Lower temperature at left; crystal growth from left to right.

TABLE 5.2. Temperature range for self nucleation and temperature range for DSC temperature shift for various polymers.

| POLYMER | TEMPERATURE RANGE FOR SELF-NUCLEATION (o) | TEMPERATURE RANGE FOR DSC TEMPERATURE SHIFT (o) |
|---|---|---|
| PE | 2.6 | 2.5 |
| PP | 3.8 | 3.5 |
| PB | 2.3 | 2.5 |
| POM | 2.0 | 2.5 |
| PHB | 20.4 | 20.0 |
| PET | 14.8 | 15.0 |

It is clear from the above results that the two methods used to measure the range of temperature in which self-nucleation is occurring are in good agreement. The apparatus built has an accurate control of the temperature gradient so the range of temperatures obtained for self-nucleation of various polymers is as accurate as that obtained with the DSC.

Comparing the crystallization temperature shift in self-nucleation polymers with that obtained for heterogeneously nucleated polymers (Table 5.1), it can be concluded that the nucleating agents used in the present investigation (except saccharin) are causing the possible maximum shift in crystallization temperature for all the polymers studied except

PHB where a difference of $10^{o}$ exists. Electron microscopy studies will explain the reason for this difference.

# CHAPTER 6

## 6.1 THE NATURE OF THE INTERACTION IN THE POLYMER-NUCLEANT INTERFACE

The introduction of solid crystalline materials into polymer melts often has an effect on the molten phase and consequently can modify the nucleation process. The macroscopic effects of such modifications may be observed both by the rate of volume crystallization and by the structural properties of the solidified mixture. This interaction was first reported by Willems[85] and Fisher[86] who observed the alignment of polyethylene molecules along the sodium chloride crystal planes. Subsequently, epitaxy of several synthetic polymers and model biopolymers has been reported[87,88,89]. Polymer epitaxy has generally been achieved by deposition from solution and more recently it has also been reported from the melt[90] and from vapour deposition of a sublimated monomer, followed by solid-state polymerization[91]. Other inorganic substances, aside from alkali halides, have been used to grow polymer crystals epitaxially, including mica[44], graphite[42] and condensed aromatic hydrocarbons[43]. In every case mentioned above, the polymer chain axis was oriented parallel to the substrate surface.

Numerous organic and mineral additives have been used for their nucleating ability towards polyethylene and other polyolefins. Various molecular and crystallographic parameters have been investigated. Beck[24] and Binsbergen[25] found that several salts of organic acids were very active leading to a model nucleating agent consisting essentially of alternated polar and apolar parts. These studies have not, however, revealed specifically what types of interaction with the polymers render the nucleating agent active. Epitaxy has been recurrently invoked but it has never been firmly established; on the contrary it has been rejected as a possible explanation in the nucleating ability of these agents. Wittman[96] in his recent paper studied the nucleating effect of benzoic acid for various polymers. This acid was taken as a substitute for its alkali halide-metal salt (sodium benzoate) because the crystal structure of the salt could not be obtained. He reported an epitaxial relationship between polyethylene, n-paraffins or aliphatic polyesters and benzoic acid. it was characterized by a unique orientation of the polymer mass parallel to the substrate plane. However the crystallographic nature of the polymer/substrate interaction has not been well established.

Rybnikar[97] observed orientation of the rod like polyethylene crystals on talc and kaolin, and assumed that molecular segments were oriented in an extended zig zag conformation and attached to the substrate in [110] direction of the substrate. He could not confirm this because of experimental difficulties in obtaining the electron diffraction patterns

The present investigation was undertaken to establish the nature of the interaction in the polymer-nucleant interface and to correlate these results with those obtained on crystallization kinetics with DSC and light microscopy techniques.

### 6.1.A. SUBSTRATE STRUCTURE

Talc has a hexagonal unit cell with a= 5.26Å and c= 18.96 Å and is obtained in the form of large platelets as seen in Figure 6.1.a. The average particle size is about 5-10μ. Boron nitride is also

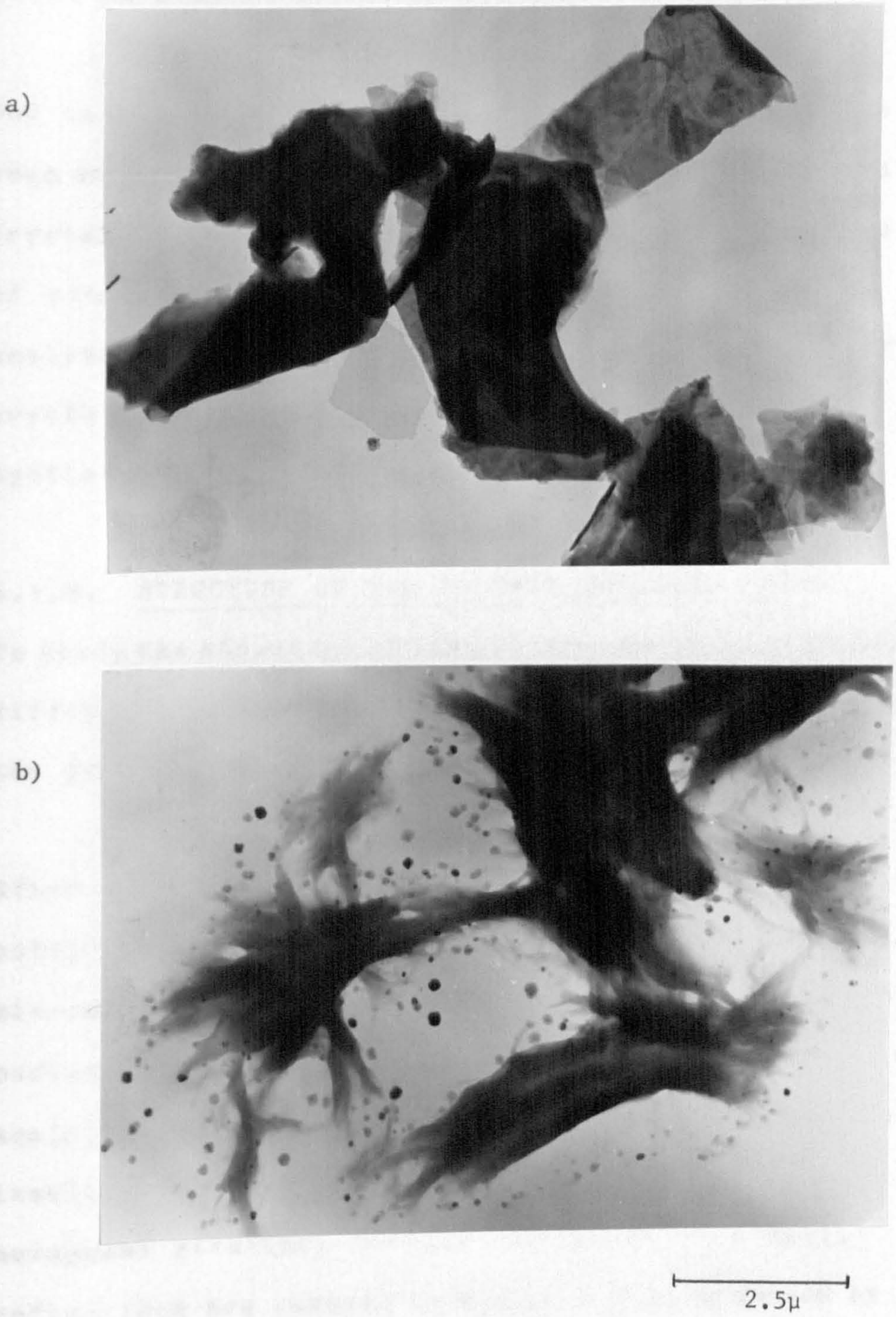


Figure 6.1. TEM micrographs of powders supported on a carbon film.
a) Talc particles; layered structure is clearly visible.
b) Sodium benzoate particles; most crystals form scrolls. Small cubic crystals are NaCl remaining from the synthesis.

hexagonal with a=2.50 Å and c=6.66 Å and the same average particle size of about 5-10μ.

Due to extreme sensitivity of sodium benzoate to the electron beam and their scroll form, it was not possible to establish its crystallographic structure. Figure 6.1.b shows large crystals of sodium benzoate surrounded by small particles. An X-ray analysis performed on these particles have shown that they are crystals of sodium chloride presumably originated from the synthesis of sodium benzoate.

### 6.1.B. STRUCTURE OF THE POLYMER-NUCLEANT INTERFACE

To study the structure of the polymer-nucleant interface several diffraction patterns were taken for each particular sample. In the present study only one pattern from each set is shown.

After melting and recrystallization of solvent cast films of polypropylene (PP) mixed with the talc particles, electron micrographs, as well as microdiffractions were taken from the particles which formed the centers of the spherulites. Their analysis clearly indicates that the orientation of the PP lamellae (Figure 6.2) and the diffraction spots for the hexagonal structure of talc correlate very well. The main reflections are indexed in Figure 6.3 as proposed by Keith and Padden[93] and by Turner et al[94]. The $\alpha$ form of PP has been obtained in all cases and the direction of growth of the spherulites corresponds to the (040) crystal plane with the polymer chain axis oriented parallel to the surface of the substrate.

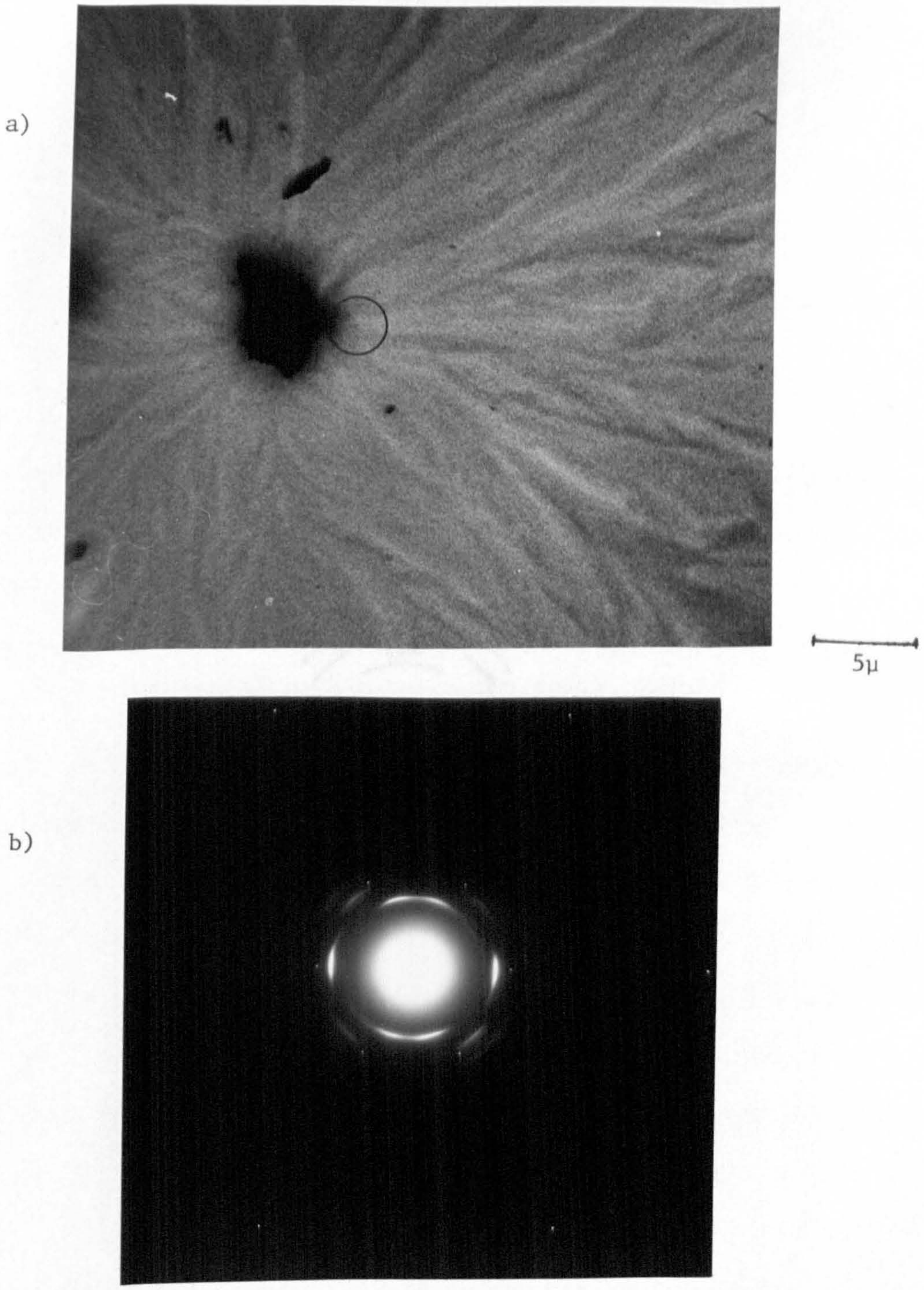


Figure 6.2. a) Polypropylene + talc particle image of spherulite and b) diffraction pattern taken from a).

The circle indicates the area from which the diffraction pattern was taken.

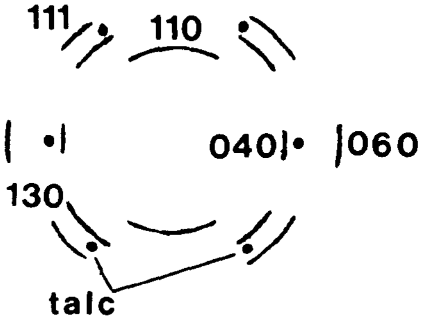


Figure 6.3. Schematic diagram of a diffraction pattern from PP/talc with the main reflection indexed.

The lattice parameters obtained for i-polypropylene (a = 6.9 Å and b = 20.3 Å) are in good agreement with those previously proposed by Natta and Corradini[95]. The direction of the facets on the talc particle were approximately 30° and 90° to the direction of growth of the spherulites. Particles smaller than 3μ do not seem to nucleate the polymer.

The underlying epitaxial relationship of the polymer is shown in Figure 6.4 by a two dimensional lattice matching of the polymer and the talc substrate. It can be observed that the repeated configuration has a periodicity of nine polymer chains.

A similar behaviour has been observed on polypropylene nucleated with boron nitride. The diffraction pattern shows a correlation between the boron nitride spots and the (040) crystal plane of the polymer. The growth direction of the spherulites also corresponds to the (040) crystal plane (see Figure 6.5). In the case of boron nitride the repeated configuration has a periodicity of thirteen polymer chains as shown in Figure 6.6.

Although it was not possible to find a direct correlation between polypropylene and sodium benzoate, due to the extreme electron beam sensitivity of the latter, Figure 6.7. shows an image of a spherulite growing on a certain facet of the nucleator. The lamellae are growing on the (040) crystal plane of the polymer. This plane has been proven to be the nucleating facet for polypropylene nucleated either by talc or boron nitride.

In the present investigation the diffraction patterns have shown

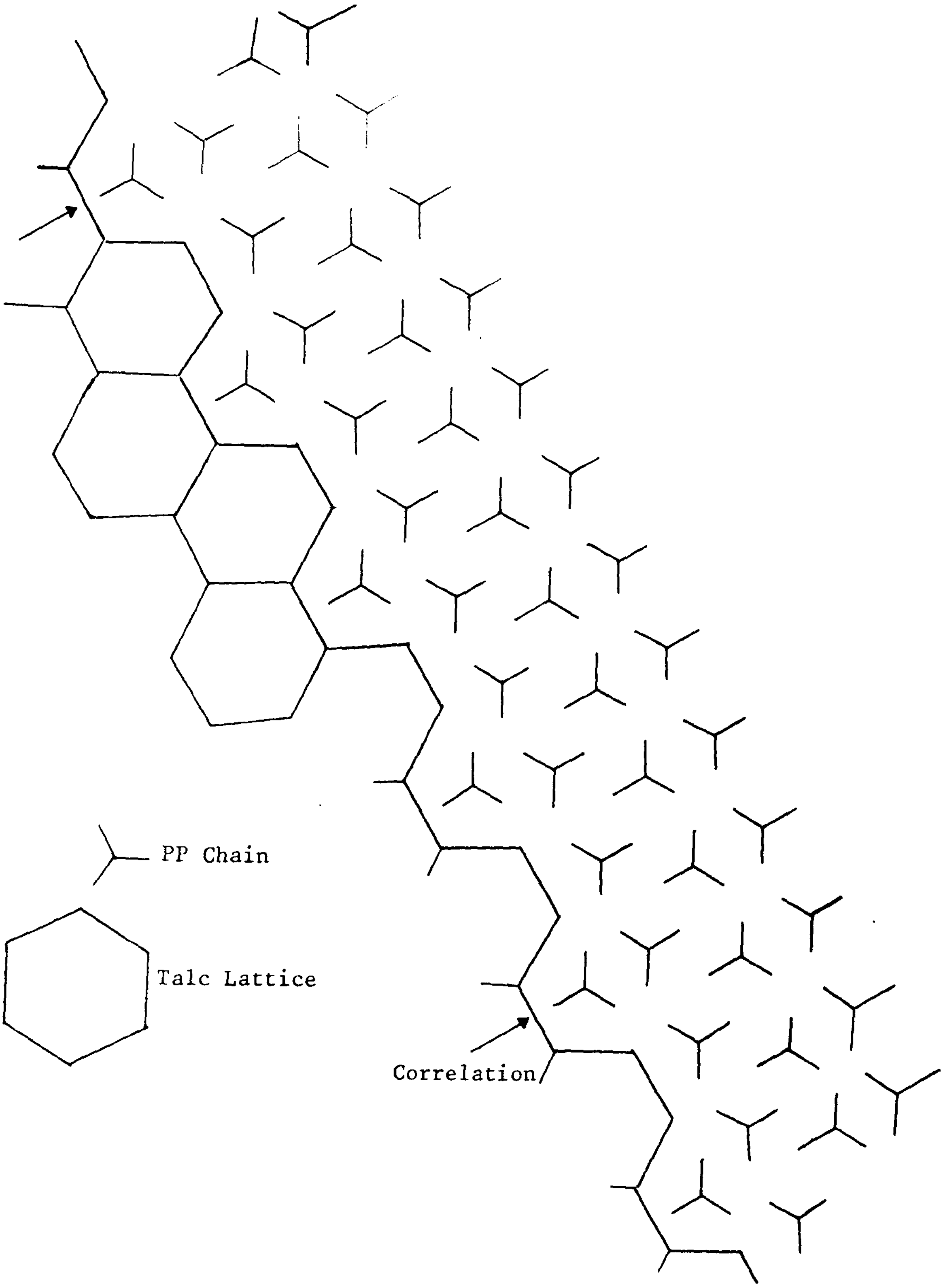


Figure 6.4. Two dimensional lattice matching of polypropylene and the talc substrate.

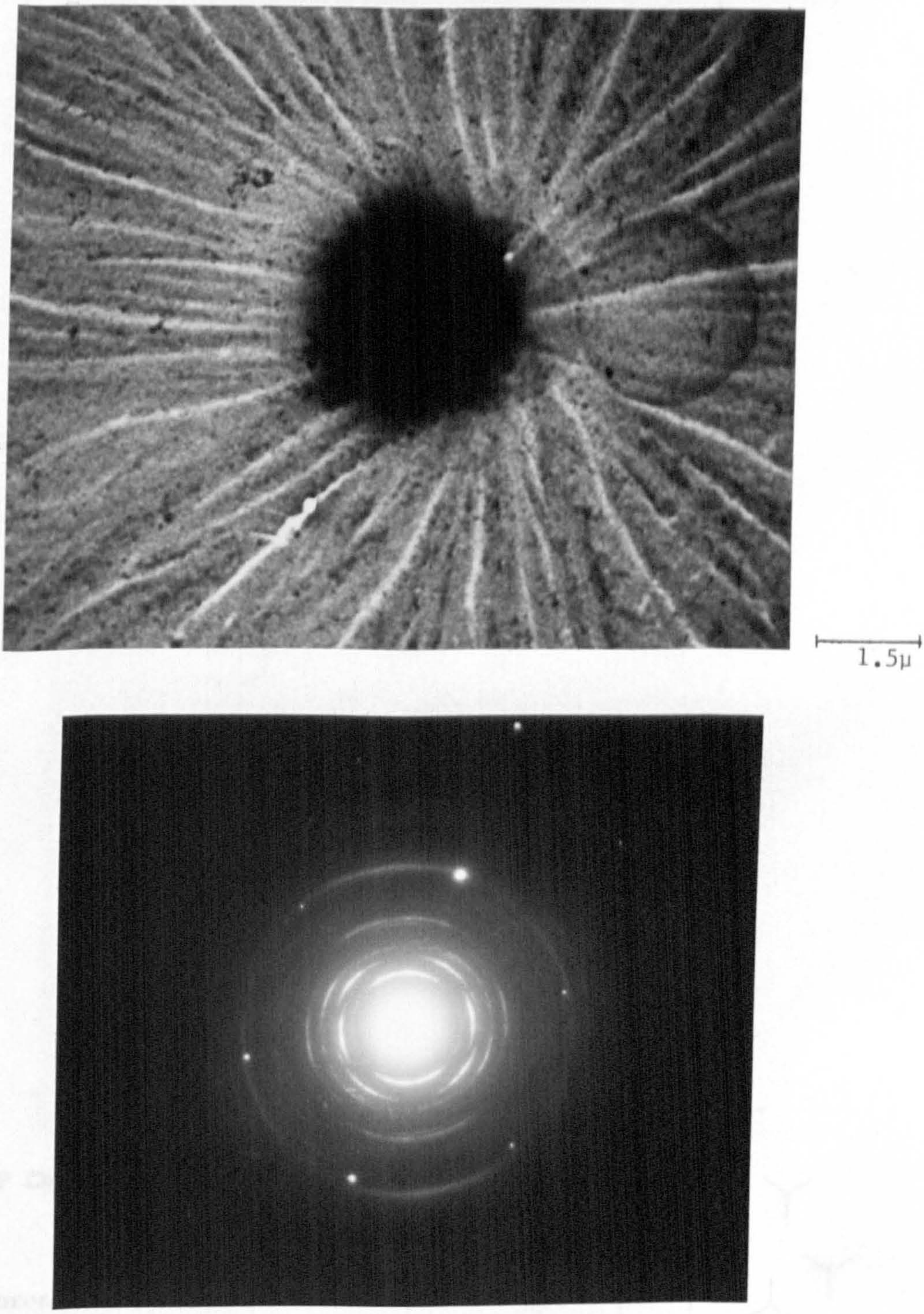


Figure 6.5. a) Polypropylene + boron nitride image of spherulite and b) diffraction pattern taken from a).

The circles are the contamination marks showing the areas from which the diffraction patterns were taken.

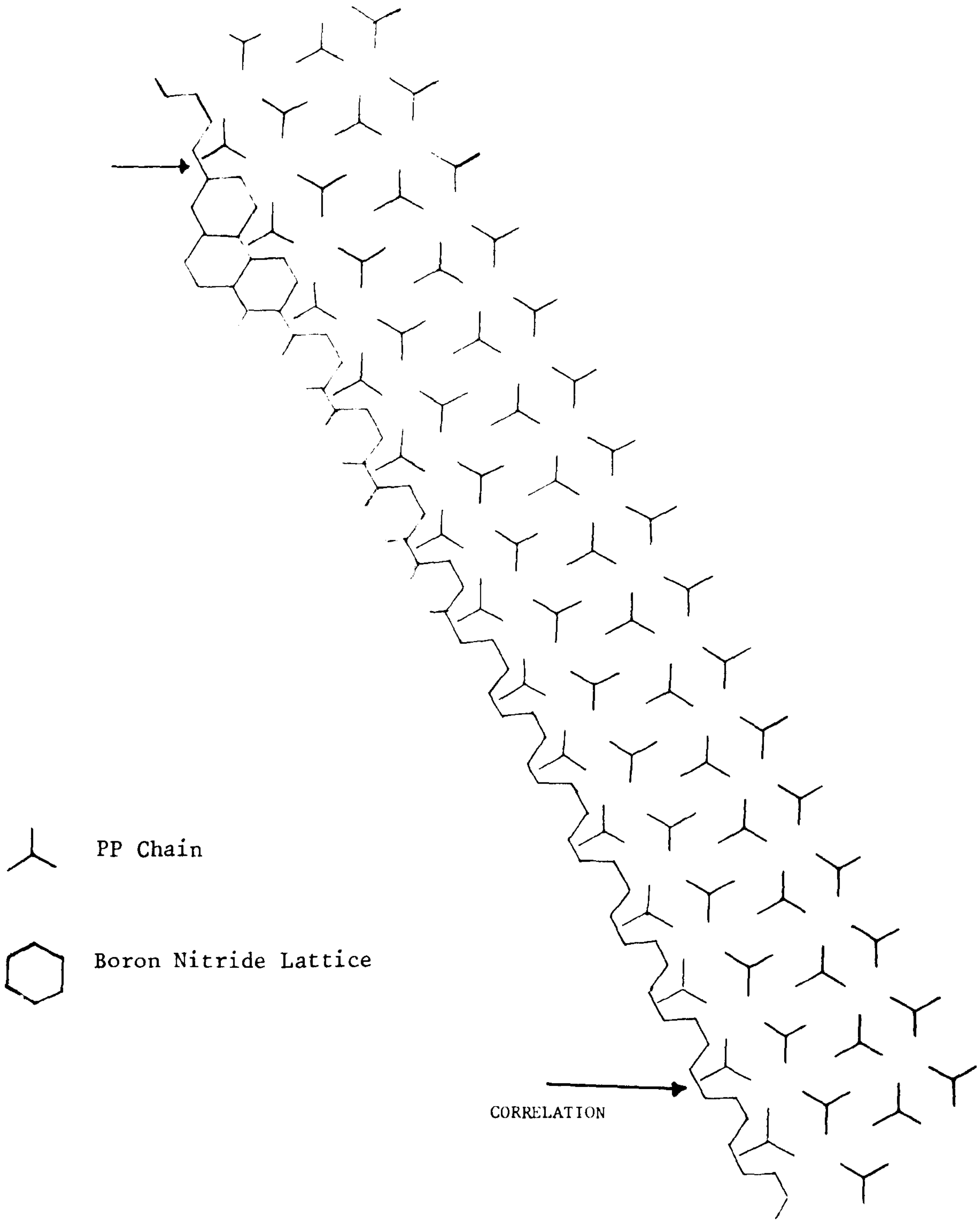


Figure6.6. Two dimensional lattice matching of polypropylene and boron nitride substrate.

Figure 6.7. Polypropylene + sodium benzoate image of spherulite.
The sodium benzoate particle appears white as a result of mass loss due to the electron beam damage.

unambiguously that polyethylene crystallizes epitaxially on talc and on boron nitride particles. Figure 6.8b shows diffraction spots for the hexagonal structure of talc and Figure 6.9b. for boron nitride with an excellent correlation to the polymer struture. The main reflections are indexed in Figure 6.10 showing that the direction of growth of the spherulites (see Figures 6.8a and 6.9a) nucleated with talc or boron nitride corresponds to the (020) crystal plane. The correlation between the talc spots or the boron nitride spots is in the (110) crystal plane. Another correlation is found perpendicular to the (110) plane demonstrating thus a close epitaxial growth of the polymer with an excellent crystal matching between the polymer and the substrate.

POM nucleated with talc exhibits an excellent correlation between the polymer and the substrate as shown in Figure 6.11a and b. The lamellar crystals have specific orientations in the [110] directions of the substrate. The correlation is found in the (110) crystal plane of the polymer as shown in Figure 6.11c. Also another correlation is found perpendicular to the (110) crystal demonstrating thus a close epitaxial matching between the polymer and the substrate.

PHB nucleated with talc exhibits a correlation at the (021) crystal plane of the polymer as shown in Figure 6.12. The main diffractions are indexed in Figure 6.12c according to Okamura[99] and the direction of growth of the spherulite correspond to the (021) crystal plane (see Figure 6.12a). The underlaying epitaxial relationship of the polymer is shown in Figure 6.13 by a two dimensional lattice matching of the polymer and the

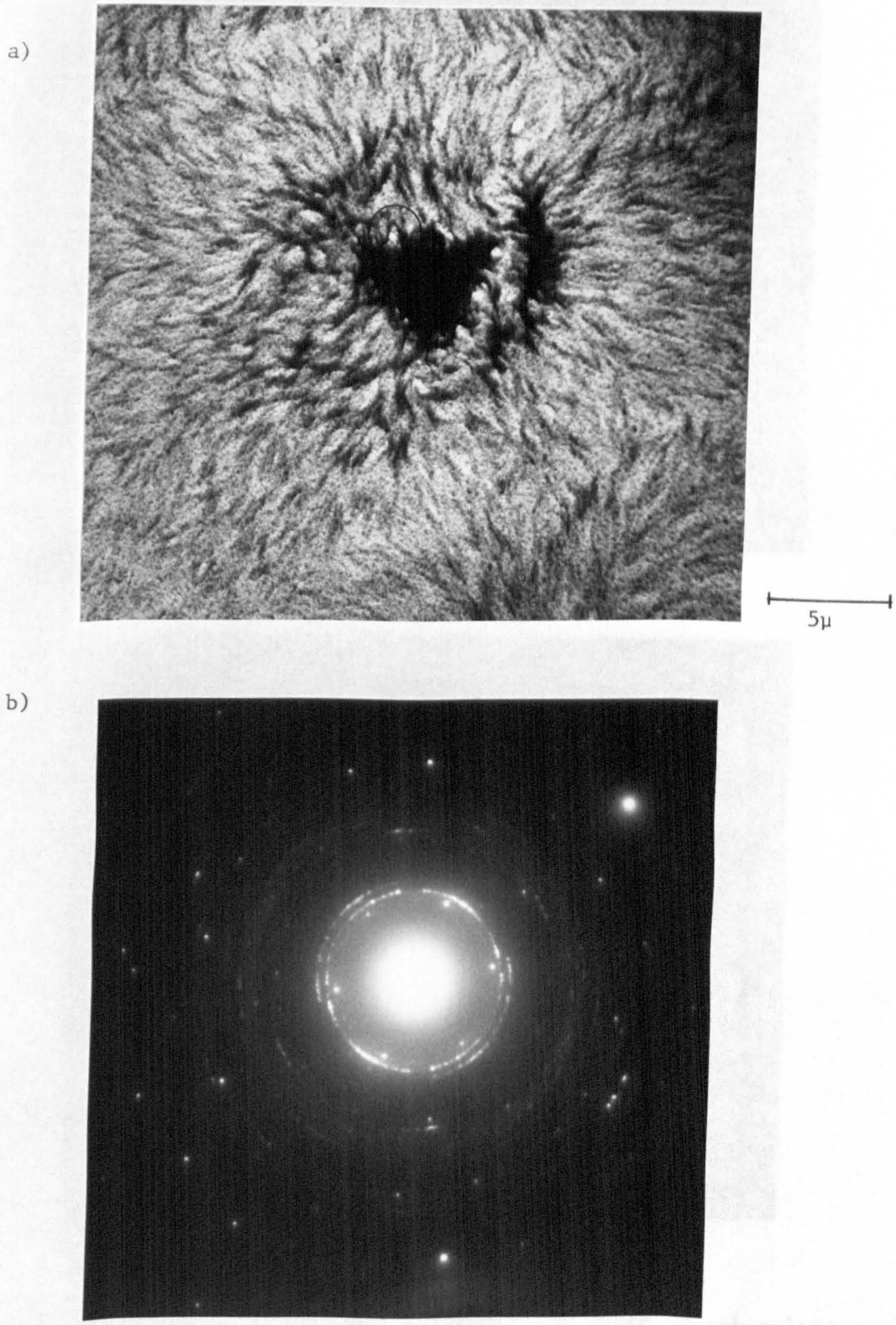


Figure 6.8. a) Polyethylene + talc image of spherulite and b) diffraction pattern taken from a).

The circle indicates the area from which the diffraction pattern was taken.

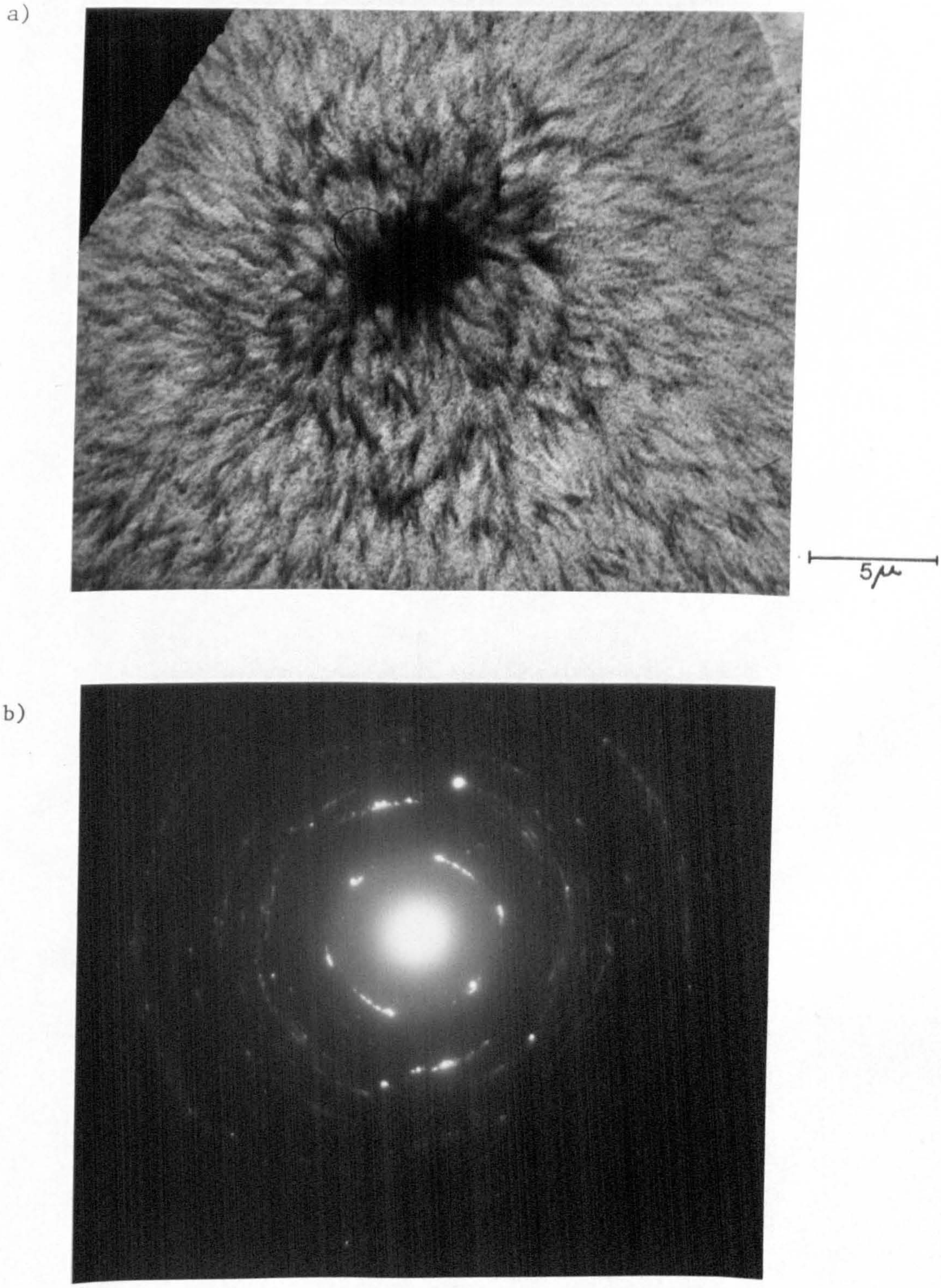


Figure 6.9. a) Polyethylene + boron nitride image of spherulite and b) diffraction pattern taken from a).

The circle indicates the area from which the diffraction pattern was taken.

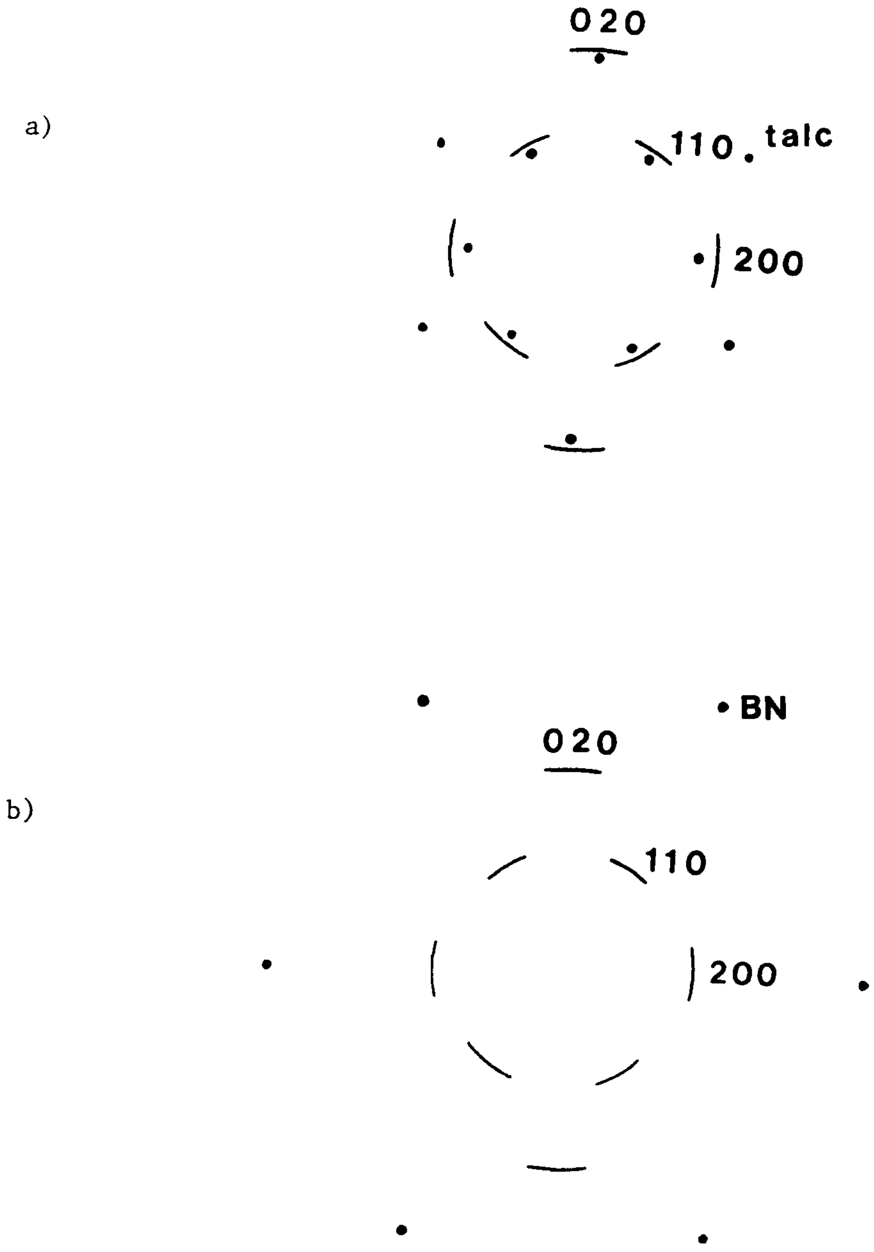


Figure 6.10. Schematic diagram of a diffraction pattern from a) PE/talc and b)PE/BN with the main reflections indexed.

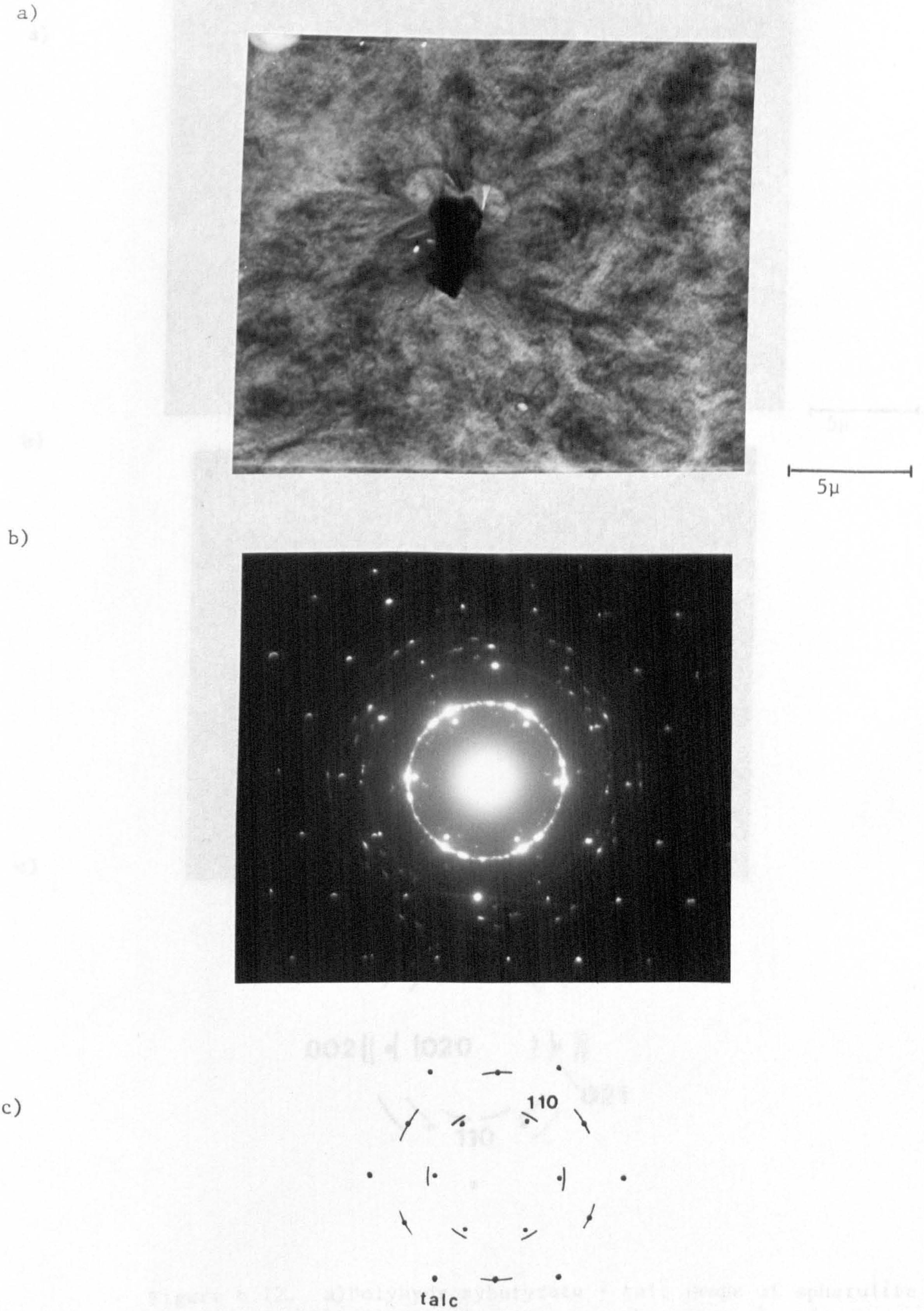


Figure 6.11. a) Polyoxymethylene + talc image of spherulite
b) diffraction pattern taken from a) and
c) the main reflections indexed.

The circles are the contamination marks showing the areas from which the diffraction patterns were taken.

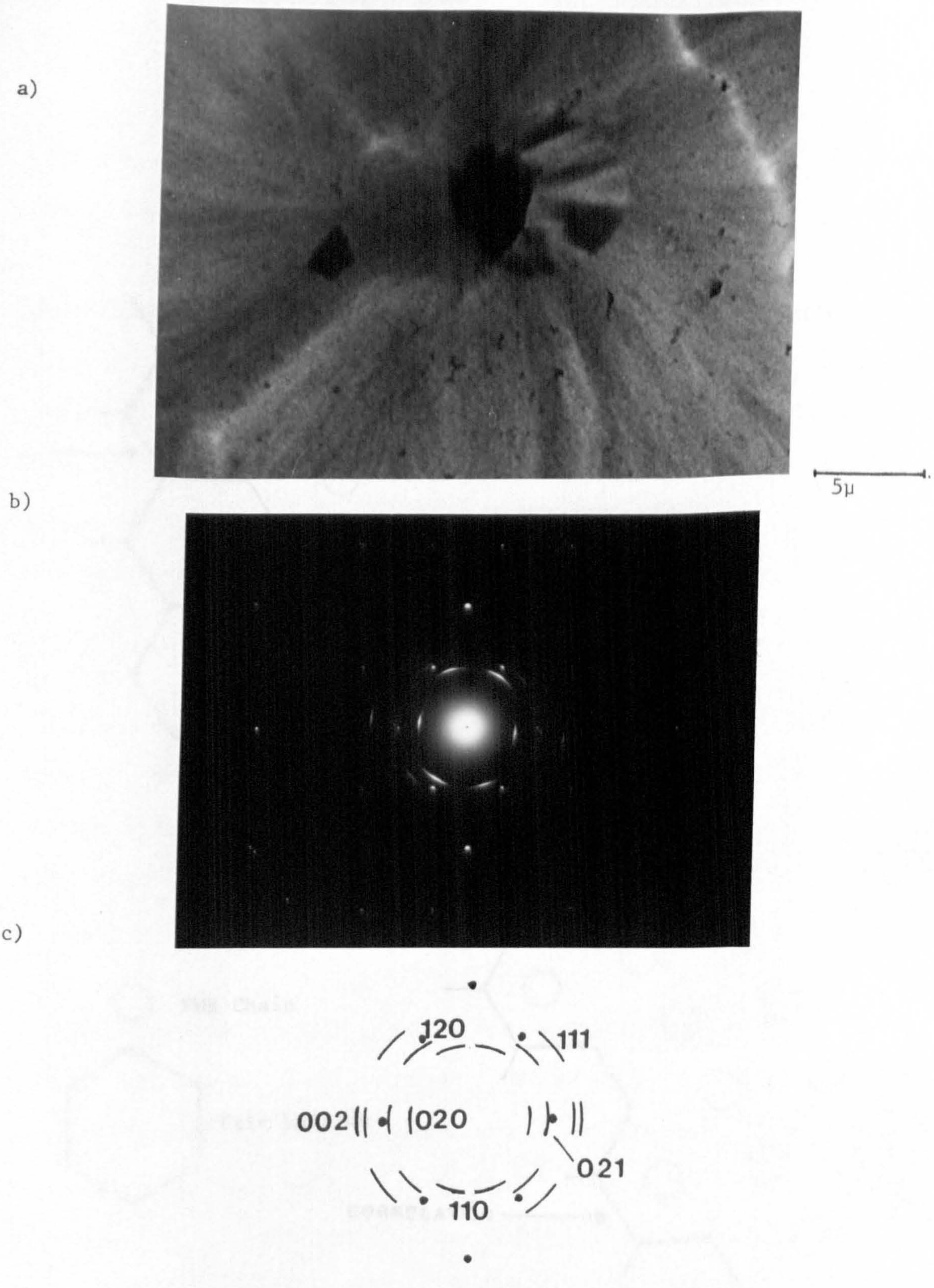


Figure 6.12. a) Polyhydroxybutyrate + talc image of spherulite
b) diffraction pattern taken from a) and
c) the main reflections indexed.

The circle is the contamination mark showing the area from which the diffraction pattern was taken.

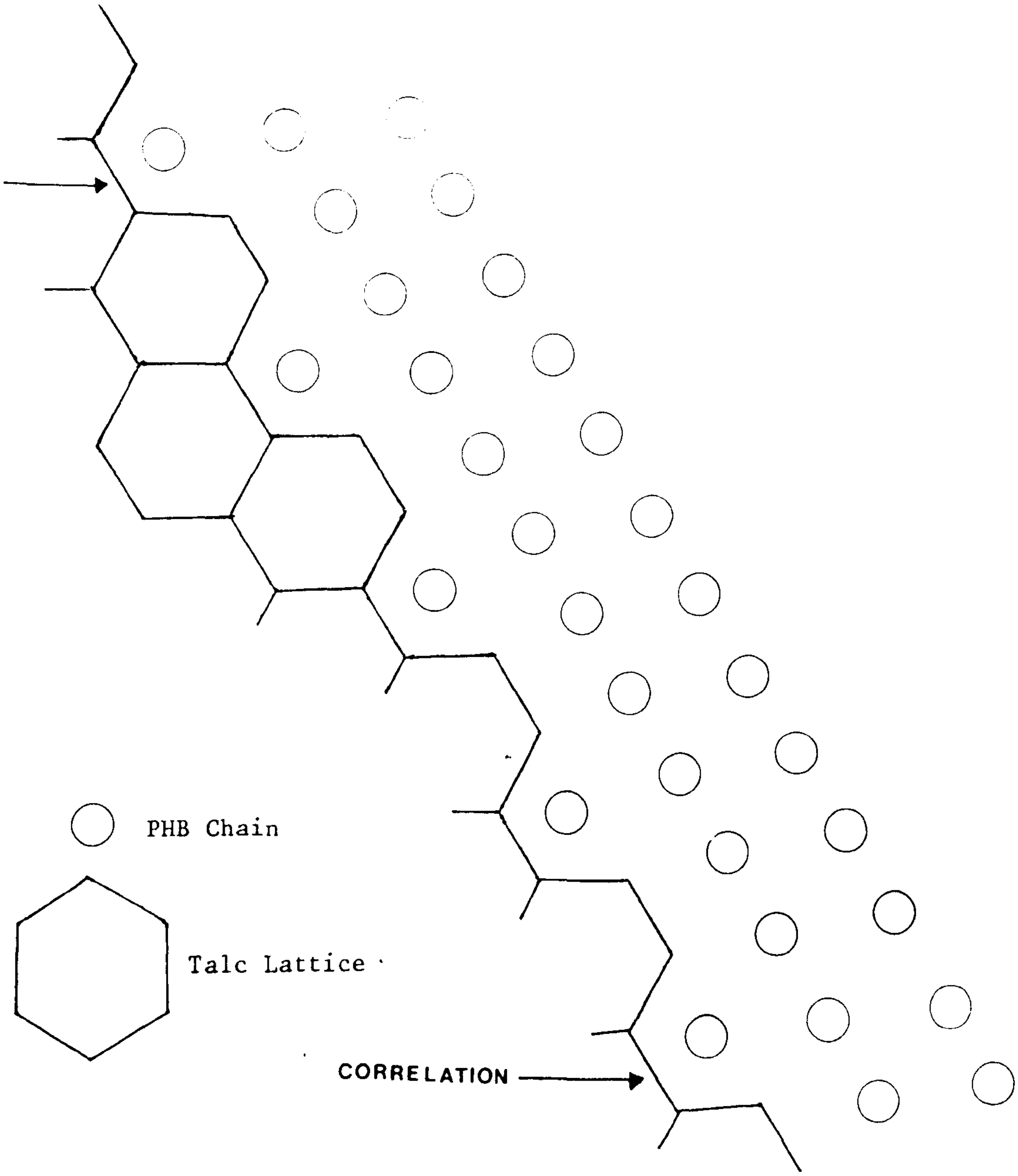


Figure 6.13. Two dimensional lattice matching of PHB and talc substrate.

substrate. It can be observed that the repeated configuration has a periodicity of eleven polymer chains.

When PHB is nucleated with boron nitride a similar situation is observed. A correlation on the (021) crystal plane of the polymer is obtained as shown in Figure 6.14a and b and the direction of growth corresponds to the same plane. In this case the underlaying epitaxial relationship has a periodicity of four polymer chains (see Figure 6.15).

In Chapter 4 (Table 4.1) it was found that the temperature of crystallization of PHB is shifted 10$^o$ when nucleated with talc, and 19$^o$ when nucleated with boron nitride. This difference can be explained by the difference in the periodicity of the repeated configuration in the epitaxial growth of the polymer on the substrates.

Those polymers in which a close epitaxy have been observed (e.g. PE and POM) have also exhibited the maximum possible shift in their crystallization temperature (see Table 5.1) due to the nucleating effect of the substrate. In other cases, such as PP nucleated with talc and PHB nucleated with boron nitride where the epitaxy in every nineth or fifth polymer chain, respectively there is still a difference between the shift in crystallization due to the presence of the nucleator and the maximum possible shift that the polymer can attain. For polypropylene that difference is only 4 degrees but for PHB is 10$^o$. A better nucleator with a close crystal match to the polymer must be found.

Due to the toxicity of the solvent used for PET and nylon (O-chlorophenol), it was not possible to prepare solvent casted films for electron diffraction studies. Ultramicrotomy was an alternative way of obtaining thin section but the materials could not be cut sufficiently thin and without damage.

It can be concluded from the above results that the epitaxial growth is the most probable mechanism of induced nucleation in a polymer and that a perfect crystal matching of the polymer and substrate will ensure maximum shift in the crystallization temperature.

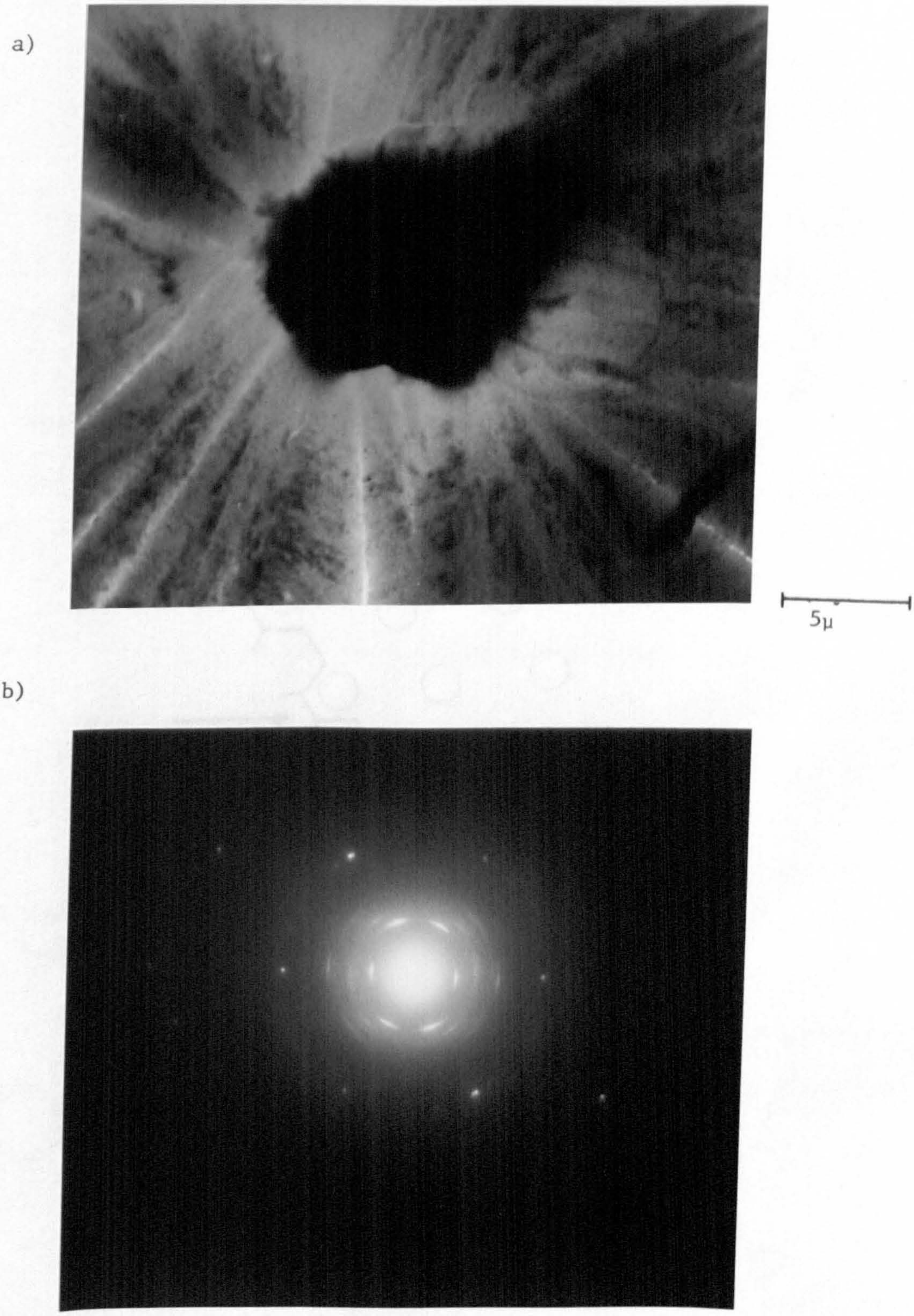


Figure 6.14. a) Polyhydroxybytarate + boron nitride image of spherulite b) diffraction pattern taken from a).

The circle is the contamination mark showing the area from which the diffraction pattern was taken.

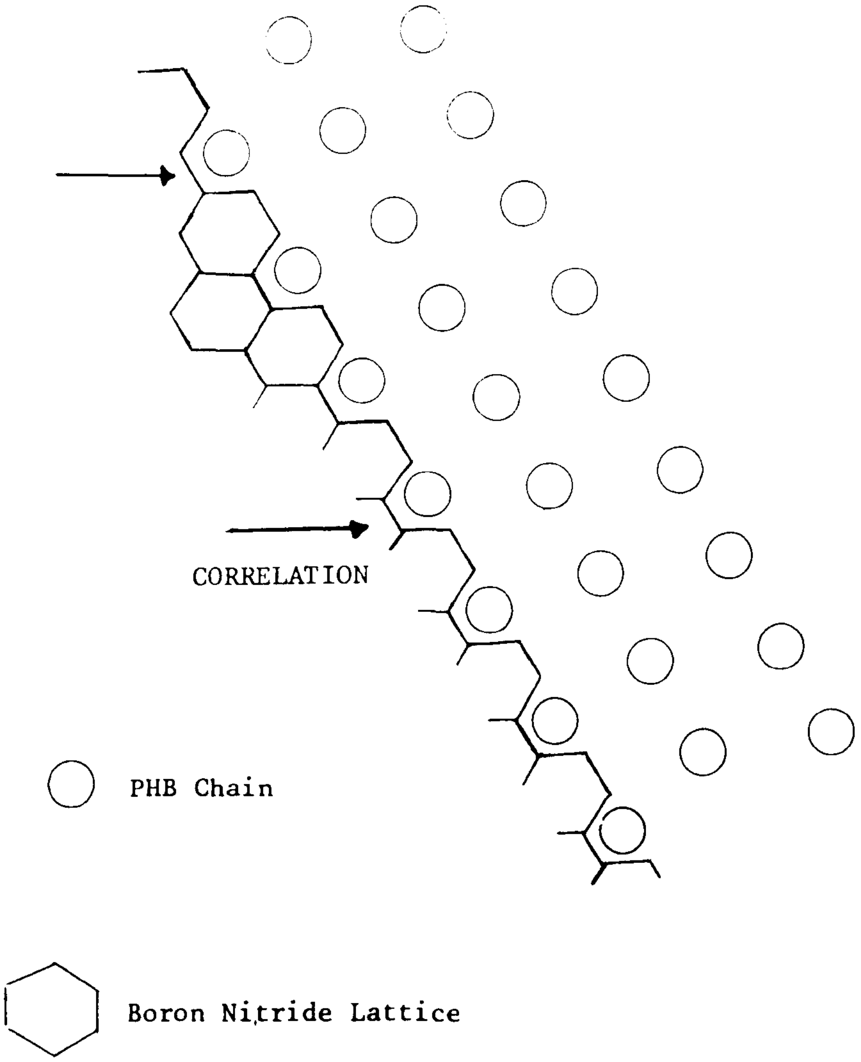


Figure 6.15. Two dimensional lattice matching of PHB and boron nitride.

## CONCLUSION

The nucleation of the crystalline phase in molten polymers is a complex process, dependent on many parameters which are not yet fully understood. There is still some confusion and uncertainty in the published literature but a clearer image is slowly emerging. The present work is an attempt to clarify some aspects of the nucleation process. As a result of new and systematic experimentation it is now possible to conclude what are the most important properties of the nucleant and of the nucleated polymer which are required for a commercially successful system.

The first and perhaps the most important conclusion is that the presence of a nucleant will not alter the crystallisation kinetics of the polymer. The whole volume of the polymer melt will start to crystallise at a temperature which is close to its melting point, regardless whether the nucleant is present or not. The crystallization will be completed when the growing spherulites touch each other. For a constant cooling rate, the temperature at which this occurs is dependent on the average distance between the nuclei. High density and homogeneous dispersion of nuclei is thus needed for the most efficient nucleation. Polymers, which form small spherulites naturally (e.g. due to impurities) cannot be nucleated further. The highest possible nucleation density can be achieved by selfnucleation of a partially molten polymer.

The second important conclusion is that for the most efficient nucleation epitaxial growth is required. A perfect crystallographic correlation between the growth planes of the spherulite lamellae and the low index plane of the nucleating particles has always been found, but a perfect match of the molecular spacing along this plane has been found only for the most active nucleants, e.g. talc and BN. The size and the geometry of the nucleating surfaces, as well as the forces acting on the polymer molecules are not known. It is however obvious that the attraction must be sufficiently strong to form nuclei at temperatures above the melting point of the polymer.

The properties of a good nucleating agent, which are required for the nucleation of a polymer can be summarised as follows:

1) homogeneous and easy dispersion in the polymer
2) small particles with a narrow size distribution
3) well developed cleavage or growth facets of a suitable size
4) epitaxial correlation across the particle-polymer interface
5) sufficiently high melting point and chemical stability

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