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The γ-phase of high molecular weight isotactic polypropylene: III. The equilibrium melting point and the phase diagram

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The equilibrium melting point of polypropylene has been determined as a function of pressure. For pressures of crystallization below 0.5 kbar the melting point observed is characteristic of the α-phase, whereas for crystallization pressures above 0.9 kbar the values are typical of the γ-phase. The principal technique used, to be reported in this paper, was the Hoffman Weeks plot of melting point versus crystallization temperature. Unlike the α-phase, the γ-phase does not show significant levels of abnormal lamellar thickening and the use of the Hoffman Weeks plot is accurate, correlating well with results from small angle X-ray scattering studies. Results demonstrate that the equilibrium melting point of the γ-phase, when extrapolated back to atmospheric pressure, is similar to that of α-polypropylene. The heat of fusion has been determined using the Clapeyron equation and the phase diagram constructed using the Gibbs equation. Reasons for the relative stability of the phases are proposed.

(Keywords: isotactic polypropylene; crystallization; equilibrium melting point)

INTRODUCTION

Although first studied in the 1960s[1–8] the γ-form of isotactic polypropylene is not very well understood. Additional, more in-depth studies of the form were initiated as result of the need for high pressure studies of regime transitions, the existence of modern polypropylenes and the suggestion of a completely new type of crystal structure to account for its X-ray diffraction spectrum.

Early studies had associated the formation of the γ-phase with chemical heterogeneity in the polypropylene chain caused by atacticity or by copolymerization[9]. More recent studies[10] have demonstrated that the γ-phase is produced at elevated pressures from high molecular weight homopolymers and that it has the same diffraction patterns as the low molecular weight polymers crystallized at atmospheric pressure. This study has also confirmed that the γ-phase is not the result of some unexpected degradation reaction at elevated pressures. The analysis of Turner-Jones[9] considered some copolymers of propylene with ethylene (as well as other comonomers) and found that the presence of a comonomer enhanced the formation of the γ-phase. The polymers that were available for study at that time contained atactic material, and there was no *a priori* way of separating the effects of atacticity from the effects of copolymerization, which would be complementary. More recent studies, conducted by Mezghani and Phillips[11] using variable amounts of ethylene content in $> 98\%$ isotactic propylene copolymers, not only confirmed the results of Turner-Jones but also indicated that the amount of the γ-form is proportional to the ethylene content and to the crystallization temperature. Accordingly, the amount of the γ-form is higher at low supercoolings.

Since its description 6 years ago[12,13] the orthorhombic γ-phase of polypropylene has been an enigma. Its structure, being composed of sheets of parallel chains juxtapositioned next to one another so that non-parallel chains are generated normal to the sheets, is unique to polymer science[12–14]. Unexplained is the fact that the α-phase is normally encountered at atmospheric pressure. It was reported in the first paper of this series that as the pressure of crystallization is increased the proportion of the γ-phase present increases from zero at atmospheric pressure to close to 100% at 2 kbar[10]. In that paper a model was proposed for crystallization in which the two crystals deposit within the same lamellae through an epitaxial process. A question not yet answered is why it should require an elevated pressure for the γ-phase to be formed.

When varying the pressure only the α- and γ-forms are observed[3,10]. As the crystallization pressure increases from atmospheric the γ-form begins to form, and to coexist with the α-form, until it becomes dominant at 2 kbar[10]. Furthermore, it appears from experiment that the lower the supercooling the higher is the amount of the γ-form produced at a specific pressure.

On the spherulitic level, no studies of pure γ-form had been reported until the publication of Part II of this series[15]. It has now been shown that the γ-form exhibits both positive and negative birefringence. However when α- and γ-forms are present in the same sample the morphological features become complex. The optical studies of microtomed sections as reported by Campbell, Phillips and Lin[10] show no evidence of Maltese cross formation when less than 10% of the material is in the γ-form, whereas when more than 60% γ-form is present, a clear Maltese cross exists. In addition, optical and electron microscope studies of etched specimens reveal no cross-hatching in a specimen with $> 60\%$ γ-crystals. Studies of the pure γ-form crystallized at

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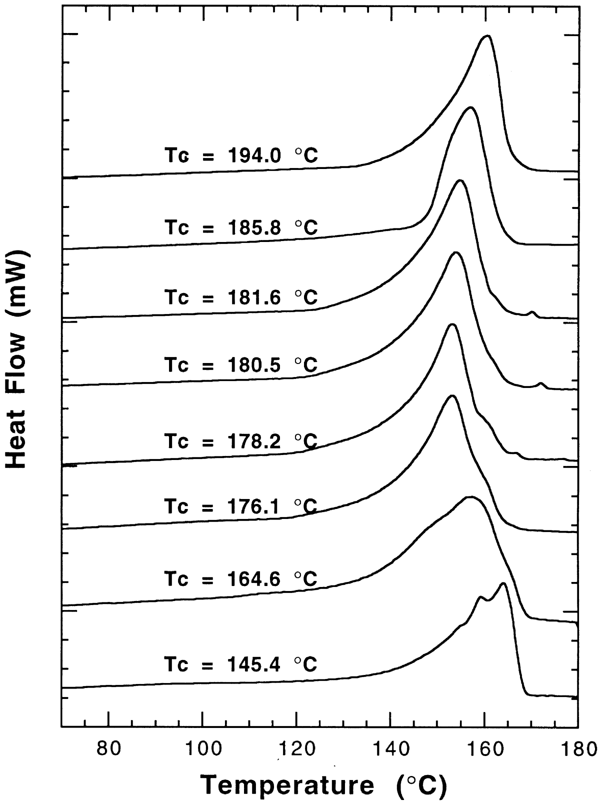

Figure 1 Melting curves of the γ-form at atmospheric pressure; samples were prepared at 200 MPa and at the isothermal crystallization temperatures indicated

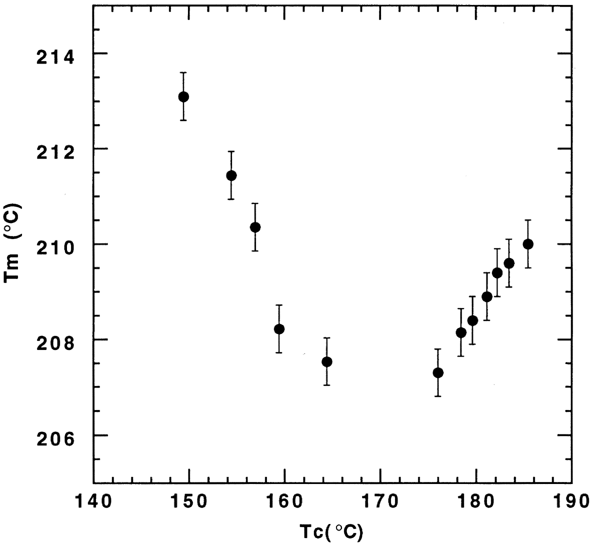

Figure 2 Melting point versus crystallization temperature at 125 MPa; the data were collected after a short crystallization time; high supercooling samples were composed of totally impinged spherulites

200 MPa[15] have shown that the birefringence changes from positive to negative to positive as supercooling is increased. It was also shown that spherulites grown at low supercoolings take the form of large 'featherlike' structures, apparently caused by massive self-epitaxy.

The melting point of the γ-form is mostly reported in the range from 125 to 150°C for low molecular weight samples. In the case of pressure-crystallized samples, with high molecular weight isotactic polypropylene (iPP), the melting occurs above 150°C. In this paper are described experiments conducted to determine the pressure dependence of the equilibrium melting points of both phases. They have been sufficiently successful for the equilibrium melting point of the γ-phase at atmospheric pressure to be extrapolated with acceptable precision. It is demonstrated that the melting point of the γ-phase is slightly higher than that of the α-phase. The heat of fusion has also been obtained from the Clapeyron equation. The relative stability of the two crystals has been determined, as has the phase diagram. It is demonstrated that the α-phase is the most stable phase at atmospheric pressure because of the low value of the heat of fusion of the γ-crystal.

EXPERIMENTAL

Materials

iPP was supplied by Exxon Corporation and had an isotactic pentad content of 90.7% and structural irregularities of 1.26%, as characterized by Dr L. Mandelkern. In order to correlate results it is necessary to assume that most crystallizing molecules are close to 99% isotactic, whereas some of the molecules are highly atactic. During crystallization the atactic molecules will be rejected from the lamellar growth front: consequently, their effects on lamellar thickness will be negligible. Since the melting of polymers is directly related to the lamellar thickness then the melting behaviour of this type of material should not be affected by their presence. It is not known if there are any specific effects resulting from the detailed atactic chain sequences generated by the use of Zeigler Natta catalysts in the polymerization process.

The values of M_n, M_w and M_z were respectively 72k, 257k, and 528k, the material being supplied as 3 mm cylindrical pellets.

Sample preparation

The polymer samples were first prepared as thin films using a Wabash model 12-12-2TB 12 ton melt press. The resin pellets were placed between two clean sheets of Kapton which in turn were placed between two stainless steel platens. The whole set was positioned between the preheated mobile and fixed plates of the press. The polymer chips were allowed to melt at a temperature of 200°C for about 5 min and then pressed with an applied pressure of about 0.8 tons in^{-2} for 2 min. Later, the polymer sample was taken out and allowed to cool to room temperature. Usually a 0.1 mm thick film is obtained by this process; when needed, thinner films were made using a longer dwell time in the press under pressure.

Differential scanning calorimetry

A Perkin-Elmer series 7 differential scanning calorimeter (DSC) was used to determine the melting behaviour of iPP using a rate of 10°C min^{-1}. Two melting points, the peak and the modified return-to-the-baseline (MRB), were taken each run. All samples were prepared at 2 kbar (200 Mpa) in the high pressure equipment.

High pressure equipment

The experimental unit is composed of a temperature control unit, a high pressure control unit and a recording system[16]. The high pressure cell is mounted on a microscope under cross-polar conditions. A binocular is used, one beam passing to a video camera, the second being used for direct observation. The polymer sample was placed

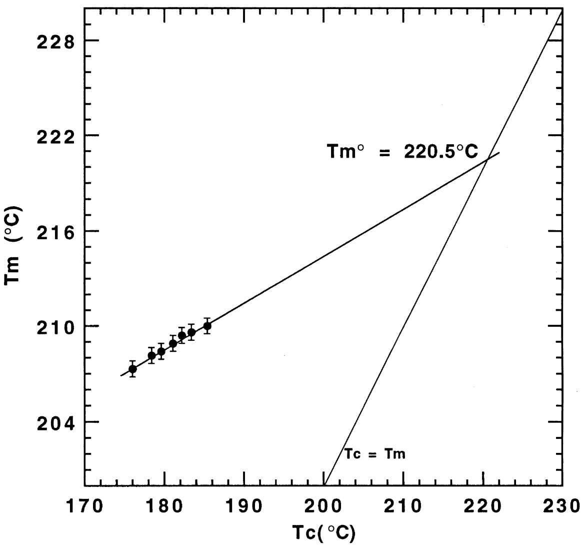

Figure 3 Melting point versus crystallization temperature at 125 MPa (points correspond to those shown in Figure 2)

between two quartz or sapphire windows inside the pressure cell[15]. In situ melting studies at elevated pressures were conducted using the transmitted depolarized light intensity method (DLM). First, the sample was melted at 200°C for about 10 min, then it was rapidly cooled to the desired crystallization temperature. The temperature was then allowed to equilibrate using a Mettler controller. As soon as thermal equilibrium was attained, the pressure was applied. This procedure assured the isothermal and isobaric crystallization of the specimen. The bulkiness of the pressure cell limited the maximum heating rate possible to 3°C min^{-1}. For melting experiments the sample was allowed to crystallize for a short time only, to prevent the thickening phenomena observed in α-crystals at atmospheric pressure[17], and was then heated at a rate of 3°C min^{-1} with the aid of the Mettler controller, the entire process being recorded on video for later analysis.

X-ray diffraction and scattering studies

Wide angle X-ray diffraction (WAXD) studies were carried out using a Rigaku Denki diffractometer. Samples were isothermally and isobarically prepared for both WAXD and small angle X-ray scattering (SAXS) analysis in the high pressure cell. SAXS studies were carried out at the Center for Small Angle Scattering at Oak Ridge National Laboratory[10] and will be described in detail in a later publication. Conventional analyses resulted in the acquisition of lamellar thickness values. The estimation of the γ-content from WAXD was carried out as described earlier[10,15].

RESULTS

Melting of the γ-form

The DSC melting curves at atmospheric pressure of samples crystallized at 200 MPa (2.0 kbar) and at different crystallization temperatures are shown in *Figure 1*. The samples were heated from 50°C to 200°C at a heating rate of 10°C min^{-1}.

The transformation of the γ-form to the α-form has been reported by several authors[12,14,18]. All studies have indicated that this phenomenon occurs at temperatures above 140°C and is time dependent. For example, according to Campbell[18], when the WAXD was conducted at 155°C of a sample prepared at 100 MPa and 50°C supercooling, the WAXD peak of the γ-form disappeared after 30 min. Also, according to Pae[19], the γ to α transformation occurs very slowly and cannot be detected by DSC run at 10°C min^{-1}. Consequently, the DSC melting curves presented in *Figure 1* represent melting of the γ-form rather than transformation of the γ- to the α-form.

Unusual behaviour is observed in *Figure 1* where the melting points of samples crystallized below 176.1°C tend to increase with decreasing crystallization temperature. For example the sample which was crystallized at 145.4°C has a higher melting temperature than the one prepared at 164.4°C. This behaviour can be related to the amount of

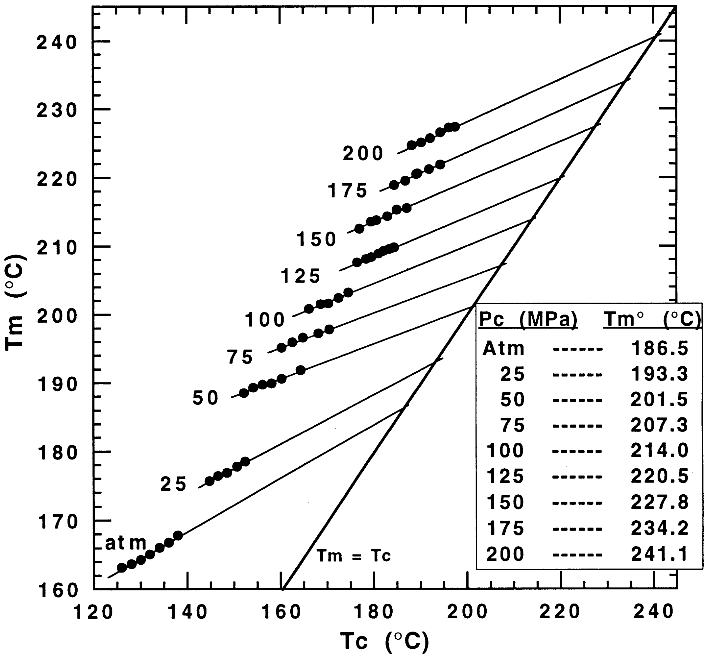

Figure 4 Melting point versus crystallization temperature as a function of pressure (both crystallization and melting carried out at the pressure indicated), using only the points corresponding to low supercoolings

the α-form that coexists with the γ-form (*Figure 2*). The result is the highly unusual V-shaped Hoffman Weeks plot, which is common to specimens of iPP crystallized at elevated pressures. As will be shown in the section on X-ray analysis the low supercoolings correspond to predominant γ-crystal formation. Data obtained from crystallization at low supercoolings can therefore be used to estimate the equilibrium melting point of the γ-phase at elevated pressures.

The melting temperatures of the specimens that were crystallized and melted at a pressure of 125 MPa at low supercoolings are presented in *Figure 3*. The line does extrapolate linearly to a value of the equilibrium melting point. Similar data are presented in *Figure 4* for all pressures studied where it can be seen that acceptable extrapolations are obtained at each pressure and that the equilibrium melting points increase with pressure as expected.

WAXD studies

The results of WAXD experiments (*Figure 5*) of samples prepared at 125 MPa (1.25 kbar) and at 200 MPa at different isothermal crystallization temperatures show that the lower the supercooling the higher the amount of the γ-form produced (*Figures 6 and 7*). Similar data were obtained for other crystallization pressures but are not presented for brevity. These results provide the justification for extrapolations such as those shown in *Figures 3 and 4*.

DISCUSSION

Formation of the γ-phase at elevated pressures

As discussed earlier, the γ-form of polypropylene can be generated by several methods. It is easily produced by crystallization at elevated pressures. As the crystallization pressure increases the γ-form increases from zero content at atmospheric pressure, coexisting with the α-form, until it becomes dominant at 200 MPa (2 kbar)[10]. The results of WAXD experiments of samples prepared at 125 MPa (1.25 kbar) and at different isothermal crystallization temperatures show that the lower the supercooling the higher the amount of the γ-form produced (*Figure 5*). The result is illustrated in *Figure 6*, which shows the variation of the γ-content from 62% to 96% as a function of the crystallization temperature. The γ-content increases with crystallization temperature until it reaches a plateau of 96% for temperatures above 165°C. For studies of content to be definitive total isothermal crystallization of the sample is imperative, this condition being attainable at low crystallization temperatures where the rate of crystal growth is very fast. At low supercoolings, the growth rate is relatively slow and although total impingement was observed, the achievement of total crystallization is not certain, because secondary crystallization cannot be followed effectively with optical microscopy. Consequently, small portions of these samples are likely to have crystallized during slow cooling to room temperature, generating some α-crystals.

It is possible that changes of the peak intensities of the WAXD spectrum are caused by crystal orientation at the surface of the specimens. When crystal orientation at the surface is observed, the orientation factor should not be the same in the diffraction and transmission modes of WAXD experimentation. Some of the samples crystallized at high pressures were studied using both transmission and diffraction modes. The results showed very similar intensity peak variation for each sample over the whole spectrum range (10° to 30°) and definitely in the critical region from

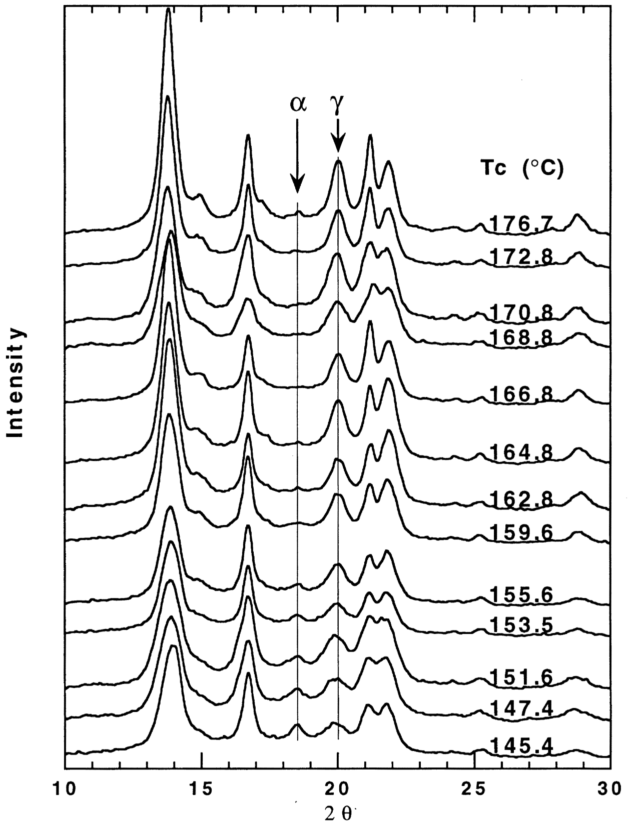

Figure 5 WAXD patterns of samples crystallized isothermally at 125 MPa

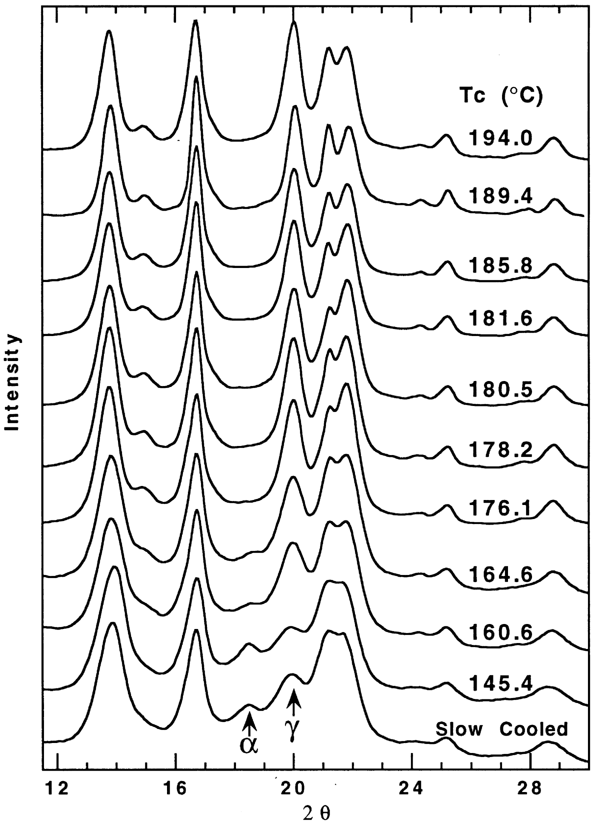

Figure 6 WAXD patterns of samples crystallized isothermally at 200 MPa

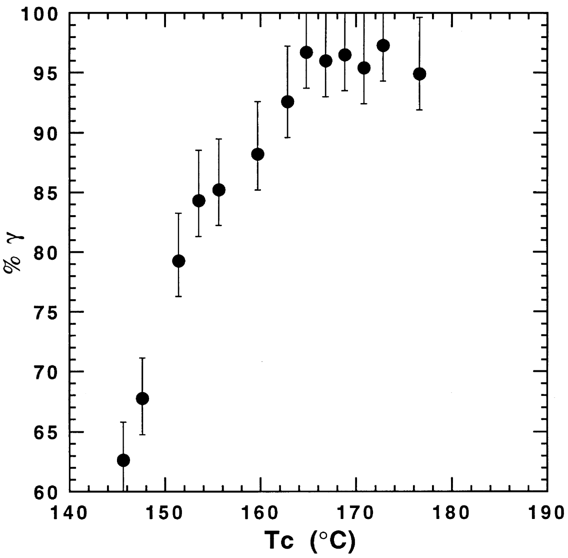

Figure 7 The γ-content at 125 MPa as a function of crystallization temperature

17° to 21°. Furthermore, all SAXS results of the elevated pressure samples exhibit circular shaped 2-D plots, indicating no preferred orientation of the samples[20].

In addition, one sample isothermally crystallized at 185.8°C and 200 MPa was sent to Dr S.V. Meille, at Politecnico de Milano, Italy. The sample was ground to powder at a temperature well below the glass transition temperature of iPP; then the WAXD experiment was conducted on the powder. The results of the WAXD as reported by Dr Meille indicate the presence of pure γ-form in that sample. Moreover, the WAXD of the powder sample is identical to the one reported here. These facts confirm that the γ-contents reported in this study are not due to orientation. Consequently, the variations of the two different intensity peaks in the region 17° to 21° are good indicators of the change in γ-content of the elevated pressure samples. Also, it is worth mentioning that an independent study of the molecular weight of a sample crystallized at 200 MPa for several hours indicated no degradation of that sample[21].

The variation of the γ-content with crystallization temperature is not unique to the crystallization pressure of 125 MPa (1.25 kbar), but is rather a common phenomenon for all pressures studied. Although only representative results are presented here, the WAXD studies of samples prepared at 75, 175, and 200 MPa show similar behaviour. These figures clearly indicate that the γ-form is preferred at low supercoolings at all pressures (125 MPa being one of the lowest pressures considered) and that 100% γ-form is attainable at crystallization pressures lower than 200 MPa, in contrast to the conclusions of the earlier study[10], in which only a constant supercooling of 50°C was considered.

The available data in the literature reveal three facets of the development of the γ-form:

(i) The γ-form is preferred at high pressures. The higher the pressure the higher the amount of the γ-form produced.
(ii) The γ-form can develop in copolymers at atmospheric pressure.
(iii) The γ-form can evolve in a sample where $M_w < 6000$, and where extended chain crystals are possible, if very low cooling rates are used. From this study, with the analyses conducted on high molecular weight iPP at elevated pressures one important parameter is added to the others:
(iv) The γ-form is preferred at low supercoolings (or high crystallization temperatures). The higher the crystallization temperature the higher the amount of the γ-form produced.

The reasons for this behaviour need to be explored. As far as the high molecular weight homopolymer is concerned we are now in a position to begin to resolve the problem.

A basic approach for solving this question is the use of the Gibbs free energy. At constant pressure, the change in Gibbs free energy between the crystalline and amorphous states can be calculated as follows:

$$\Delta G = \Delta H_f - T\Delta S \tag{1}$$

The Gibbs free energies of α- and γ-forms have to be calculated separately and compared at constant pressure. Accordingly, the form that has lower Gibbs free energy has the higher probability for nucleation and growth.

It is clear from equation (1) that two parameters, ΔH_f and ΔS, are required to calculate ΔG as a function of temperature. The change of entropy (ΔS) can be determined from equilibrium, where $\Delta G = 0$ and $T = T_m^o$, as follows:

$$\Delta S = \frac{\Delta H_f}{T_m^o} \tag{2}$$

Consequently, two parameters are needed, ΔH_f and T_m^o.

It is therefore necessary to know the heats of fusion and the equilibrium melting points of both α- and γ-forms. These two parameters are reported in the literature for the α-form with considerable differences in experimental values. However, for the case of the γ-form no values are reported.

The equilibrium melting points of the α-form at atmospheric pressure have already been discussed[17] and the pressure dependence will be discussed in the next section. Consequently, the equilibrium melting points of the γ-form at elevated pressures will be determined from lamellar thickness studies as well as from short time crystallization procedures and the use of the Hoffman Weeks plot.

In order to determine the heat of fusion (ΔH_f) of the γ-form, the Clapeyron equation will be used. Since melting of polymers is a change of state from crystals to melt, the heat of fusion, ΔH_f, can be indirectly estimated from the equilibrium melting temperature change as a function of pressure. The Clapeyron equation has been shown to apply to many polymers[22–32]. In most studies, the equilibrium melting temperature is linearly proportional to the applied pressure. An additional approach is to use a combination of the heat of fusion determined from DSC studies and the crystallinity determined from WAXD studies; however, these measurements have to be made, of necessity, at atmospheric pressure.

The next step is to determine T_m^o of the α-form at different pressures. For this purpose, the Clapeyron equation is used. Once the heat of fusion and the equilibrium melting temperatures of both forms are known the Gibbs free energy can be calculated as a function of temperature at constant pressure. Hence, thermodynamic prediction of the relative stabilities of the α- and γ-forms is possible. Then the prediction can be tested using the experimental data.

Melting at elevated pressures

Similar to the determination of the equilibrium melting point at atmospheric pressure[17], two different extrapolations

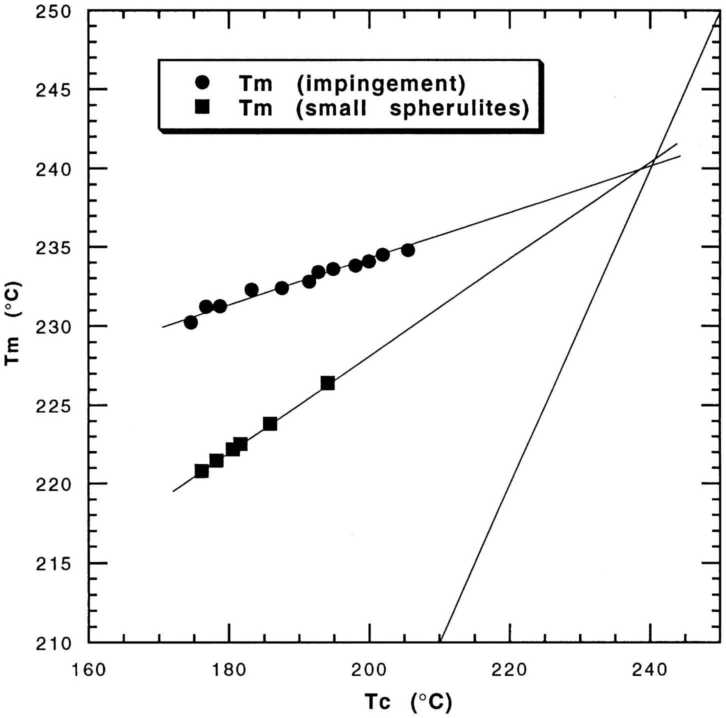

Figure 8 Melting point versus crystallization temperature for samples crystallized at short and at long crystallization times at 200 MPa

were performed (*Figure 8*) at 200 MPa (2.0 kbar). First, specimens were crystallized for long times and at least to impingement and then melted at a rate of 3°C $\min^{-1}$. Second, specimens were crystallized for very short times and then melted at the same rate. The points in *Figure 8*, which represent the melting temperature as a function of isothermal crystallization temperature at 200 MPa, fall reasonably well on the drawn lines, which are best fit with a least squares method. In contrast to the behaviour of the α-phase at atmospheric pressure the extrapolation here leads to a single equilibrium melting point of 241°C. This specimen is known from WAXD studies to be very close to 100% γ-form and the obvious conclusion to be reached is that the α- and γ-forms exhibit quite different thickening behaviour. Accordingly their respective responses in a Hoffman Weeks plot are quite different. As will be shown later in this paper, the validity of the Hoffman Weeks plot for the γ-phase is confirmed by equilibrium melting point values obtained using lamellar thickness extrapolations. It will also be demonstrated in a later publication that extrapolations of inverse lamellar thickness using (a) crystallization temperature, (b) the melting point at short crystallization times and (c) the melting point at long crystallization times, all determined at 200 MPa, give rise to a value of the equilibrium melting point that is within 1°C of that determined from the Hoffman Weeks plot of *Figure 8*.

Melting of the γ-form at atmospheric pressure

Melting of the γ-form at atmospheric pressure was studied using the DSC, and typical melting curves of different samples were shown earlier (*Figure 1*). Most peculiar is the V shape of the Hoffman Weeks plots at all elevated crystallization pressures (*Figure 2*). The behaviour of the specimens containing predominantly γ-phase is conventional, i.e. the melting point increases with increasing crystallization temperature. The α-crystals show a decreasing melting point as supercooling is decreased! It was at first thought that lamellar thickening processes were

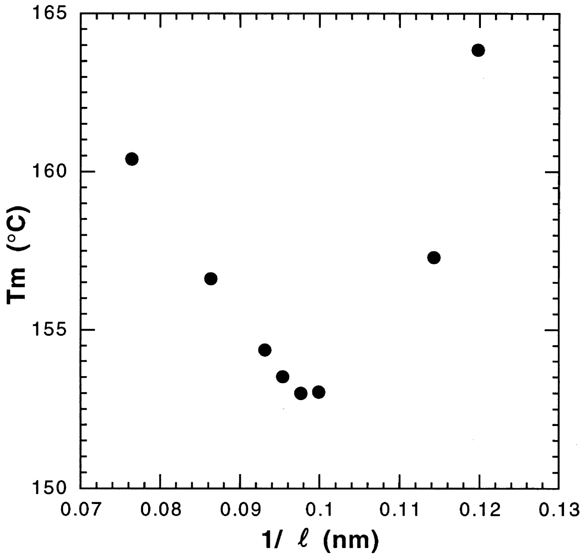

Figure 9 Melting peak temperature versus inverse lamellar thickness for samples prepared at 200 MPa at various crystallization temperatures

being suppressed progressively as γ-formation became more prevalent. However, SAXS studies, to be reported in detail later[20], when processed in the conventional manner allowed the lamellar thicknesses to be estimated. When the melting peak is plotted as a function of lamellar thickness (*Figure 9*) the same peculiar behaviour is observed. It is clear that the melting point decreases with inverse lamellar thickness for the first five points (i.e. the γ-phase region), and then it starts to increase (the α-phase region). All samples were prepared in the same high pressure cell and at the same crystallization pressure (200 Mpa) and then melted under the same conditions at atmospheric pressure. The only difference between these samples is the γ-content. According to the WAXD results the pure (100%) γ-form is developed above the crystallization temperature of 176°C,

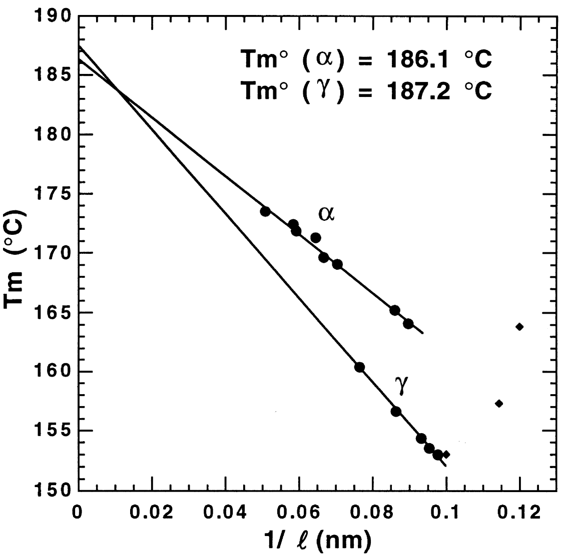

Figure 10 Melting temperatures of the α- and γ-forms as a function of inverse lamellar thickness; all γ-form specimens were prepared at 200 MPa with different crystallization temperatures

Table 1 Differences in thermodynamic parameters between the α- and the γ-forms

Phase	T_m(°C)	ΔH_f(J g^{-1})	ρ(g cm^{-3})	σ_e(erg cm^{-2})
α	186.1	209.0	0.936	52.2
γ	187.2	144.8	0.933	51.7
		150.0		53.6

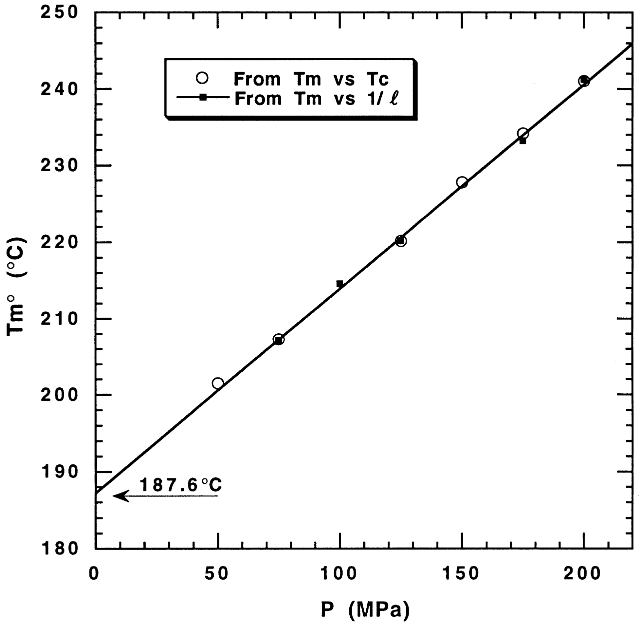

Figure 11 Equilibrium melting temperature of the γ-form as a function of hydrostatic pressure

and below that temperature the α-content starts to increase and does so with increasing supercooling. Comparison of WAXD and DSC results shows that the melting point decreases with increasing lamellar thickness up to the point where 100% γ-form is present. However samples with predominantly α-form have higher melting points than γ-samples, even though their lamellar thicknesses are lower.

This appears to be the first report of a polymeric crystal form in which the melting point decreases with increasing lamellar thickness. This very strange behaviour of the α-phase cannot be explained at the present time. It can, however, be concluded that the higher the α-content the higher also is the melting temperature. This phenomenon occurs at all pressures studied. Since our major concern here is the determination of the equilibrium melting point of the γ-form, only melting points of this form need to be considered. The behaviour is conventional and the plot of melting point at atmospheric pressure versus inverse lamellar thickness is shown in *Figure 10*. Accordingly, typical melting behaviour is observed, and the equilibrium melting point of the γ-form is determined to be 187.2°C, slightly higher than that of the α-form (186.1°C).

When melting of the α-form crystallized and melted at atmospheric pressure and that of the γ-form crystallized at 200 MPa and melted at atmospheric pressure are plotted as a function of lamellar thickness (*Figure 10*) two interesting phenomena are observed. First, for the same lamellar thickness, the melting point of the α-form is considerably higher than the melting point of the γ-form. However, their equilibrium melting points are similar. In addition, the melting points of the three specimens with high α-content, but crystallized at 200 MPa, fall near to the extrapolated α-line, but do not fall on it (diamond symbols).

Table 1 shows different values of the fold surface energies of both crystals as determined from lamellar thickness studies using different values of heat of fusion. The two values of the heat of fusion, ΔH_f, for the α-form are the ones mostly used in the literature, whereas the ones for the γ-form are determined from Clapeyron studies (144.8 J g^{-1}) and from the average of the DSC–WAXD studies (150 J g^{-1}). The results indicate that the γ-form has only a slightly higher fold surface free energy than the α-form. Indeed if the upper value of the heat of fusion of the α-form from the literature is used, the two crystals show the same value of the fold surface free energy.

Clapeyron studies

Clapeyron studies, which involve the variation of the equilibrium melting temperature with applied hydrostatic pressure, are one of the most useful approaches for the estimation of the heat of fusion (ΔH_f). The Clapeyron equation involves the dependence of the melting point on pressure and the change in volume at the melting point. The volume changes from crystalline to amorphous states can be correlated to the density changes, and the Clapeyron equation can be modified to fit the purpose of high pressure melting of polymers as follows:

$$\frac{dT_m^o}{dP} = \frac{T_m^o}{\Delta H_f}\left(\frac{\rho_c - \rho_a}{\rho_c \rho_a}\right) \tag{3}$$

Where ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively. It is important, therefore, that these two quantities be known as a function of both temperature and pressure in order to properly apply the equation.

The equilibrium melting points at different pressures obtained from Hoffman Weeks plots are presented in *Figure 4*. When all the data points applicable to the γ-phase are plotted in *Figure 11*, a linear relationship between the equilibrium melting point and the pressure is observed. The data points obtained from SAXS studies of lamellar thickness, to be reported later in detail[20], are also plotted to demonstrate an excellent correlation between the two approaches. It is quite remarkable that such a high degree of

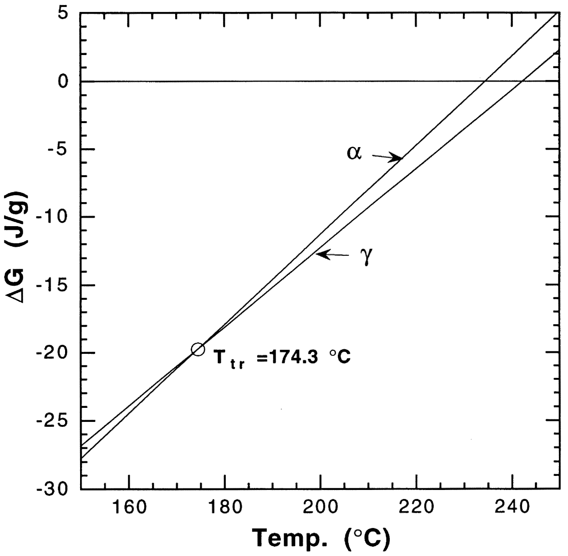

Figure 12 Gibbs free energy as a function of temperature at 200 MPa for the α- and γ-forms

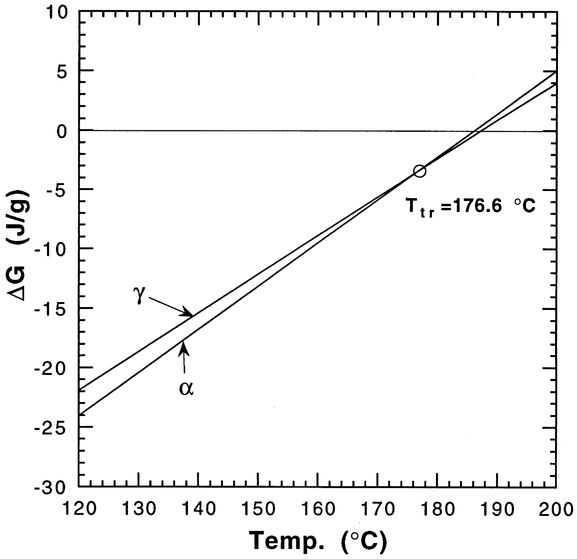

Figure 13 Gibbs free energy as a function of temperature at atmospheric pressure for the α- and γ-forms

correspondence exists. This plot is further confirmation of the lack of abnormal thickening processes in the γ-phase and provides strong evidence for the fundamental validity of the Hoffman Weeks plot in this material.

As a result, the data points of *Figure 11* can be used reliably in conjunction with the Clapeyron equation. The first two points (atmospheric pressure and 25 MPa) of *Figure 4* are not included in the Clapeyron equation because they represent mostly the melting of the α-form. The equilibrium melting point, T_m^o, of the γ-form at atmospheric pressure is the intercept at $\Delta P = 0$ and extrapolates back to 187.6°C at atmospheric pressure. This equilibrium melting point is very close to the one determined from the DSC and lamellar thickness studies as described in the previous section.

The slope of the line is related to the heat of fusion and the volume change. The volume change as a function of temperature and pressure can be determined only from pressure–volume–temperature studies, which are beyond the scope of this research. If the Clapeyron equation is assumed to apply then ΔH_f is constant; therefore, the volume change has to be constant. In order to proceed, it has been assumed that the volume change can be approximated to the density difference between amorphous and crystalline materials. This procedure leads to an estimate of the heat of fusion of the γ-form as 144.8 J g^{-1}. Furthermore, if the heat of fusion of the γ-form, determined from the DSC, is multiplied by the crystallinity from WAXD (both determined at atmospheric pressure), then an average value of all samples is found to be close to 150 J g^{-1}, which is in good agreement with the value of 144.8 J g^{-1} determined from the Clapeyron equation.

An alternative approach is to try to estimate the variation of the volume change with pressure. Pressure–volume–temperature relationships for iPP have been reported by Zoller[33]. Even though the melting curves do not represent the melting of an infinitely large crystal (the definition of T_m^o), the densities of the amorphous and the crystalline materials can be estimated from the figures reported as a function of temperature and pressure, once the crystallinity of the sample is known. However, neither the experimental procedure nor the crystallinity were given for the plots. For this reason, in order to proceed it has been assumed that the fairly common value of 65% crystallinity occurs in all samples. Since the concern here is about density changes not about the melting of either form, in addition to the fact that the crystalline densities of the α- and γ-forms are similar, it does not matter which form is melting in these curves, to a first approximation. However, it is recognized that the assumption of constant 65% crystallinity and lack of knowledge of the crystal types present may be sources of error.

When the density changes are estimated as a function of temperature and pressure, the heat of fusion can be estimated using the Clapeyron equation. In order to generate similar equilibrium melting points to those found experimentally the best value of the heat of fusion is 196 J g^{-1}, considerably larger than that determined from the Clapeyron analysis as well as the combined DSC–WAXD analysis.

There are two values of ΔH_f of the α-form reported in the literature. One value is 167 J g^{-1}, which is close to the value that can be obtained from combined DSC–WAXD studies of the α-form. The higher value of 209 J g^{-1} tends to be the most quoted in the literature. If it is assumed that both crystal forms have similar systematic errors incorporated into the DSC determinations, because of their behaviour during the heating scan, then a simple scaling of 209 J g^{-1}/167 J g^{-1} using the values determined leads to an estimate of the latent heat of fusion of γ-form of 190 J g^{-1}. This value is very close to the one estimated from the Zoller data. Regardless of the exact accuracy of these estimations, the most striking observation is the consistent reduction in the values of the heat of fusion that results in these cases, when the DSC–WAXD method is used.

Thermodynamic prediction of the α- and γ-formation

The Gibbs free energies of α- and γ-forms have to be calculated separately and compared at constant pressure. Accordingly, the form that has lower Gibbs free energy has higher probability of existence. It is clear from equations (1) and (2) that ΔH_f and T_m^o are required to calculate ΔG as a function of temperature. There are two sets of values of ΔH_f for both α- and γ-forms. The first set, which is determined from DSC and WAXD for both forms, and also from our Clapeyron study of the γ-form, has low values of ΔH_f of 150 J g^{-1} and 167 J g^{-1} for the γ- and α-forms, respectively.

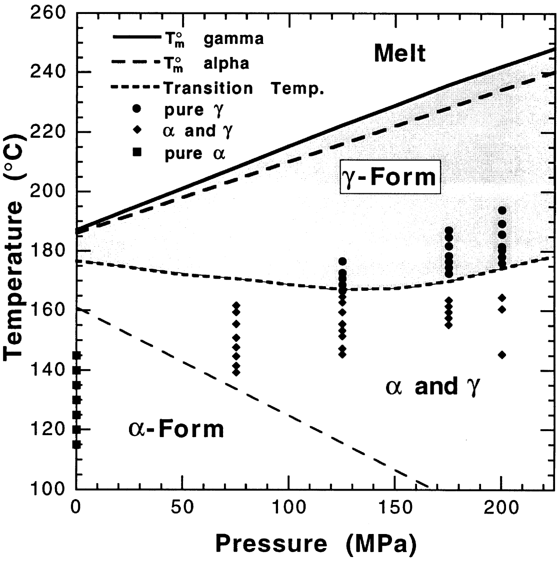

Figure 14 Theoretical prediction of the pure γ-form as a function of temperature and pressure and its comparison with the experimental data

The other set is composed of 190 J g^{-1} and 209 J g^{-1} for the γ- and α-forms, respectively.

The equilibrium melting points of the α-form at any pressure can be estimated using the Clapeyron equation. For example at 200 MPa T^o_m is 235°C. Using the lower set of ΔH_f values, the Gibbs free energies of both forms are generated as a function of temperature at 200 MPa and presented in *Figure 12*. The transition temperature, where Gibbs free energies of both forms are equal, is calculated to be 174°C. This value is in good agreement with the γ-content determined from WAXD at 200 MPa. A similar calculation can be performed for atmospheric pressure (*Figure 13*). In addition, the transition temperatures that are calculated at atmospheric pressure and 200 MPa using the second higher set of ΔH_f values are very close to the ones just quoted for the lower set of values.

The transition temperature, T_{tr}, can be correlated with the equilibrium melting temperatures of the α- and γ-forms, by using the equality of the Gibbs free energies of the two phases, as follows:

$$T_{tr} = \frac{T^o_{m\alpha}T^o_{m\gamma}(\Delta H_{f\alpha} - \Delta H_{f\gamma})}{T^o_{m\gamma}\Delta H_{f\alpha} - T^o_{m\alpha}\Delta H_{f\gamma}} \qquad (4)$$

Therefore, at any pressure if the equilibrium melting temperatures of both forms are known the transition temperature can be calculated and a phase diagram constructed (*Figure 14*). The predicted transition temperature is plotted on the diagram and the experimental data points are in good agreement with the theoretical values. In all cases the experimental points for the presence of pure γ-crystals agree with the predictions. However, for conditions where only the α-form would be expected to occur, both forms are found to be present. This is most likely due to variations of tacticity in the specimen, since it is known that the γ-phase is encouraged by the presence of comonomers, or of heterotactic units. Molecules, or sections of molecules, with higher atacticities than average would be expected to favour the γ-phase under conditions where the average molecule, or section of molecule, would be producing α-crystals.

It is possible to check experimentally the theoretical values at high pressures. However, at low pressures ($P < 100$ MPa) the crystal growth rate is so slow that total impingement of the sample may not be possible for many reasons. One of these reasons is degradation of the sample. In fact, crystallization at 165°C and atmospheric pressure was conducted under nitrogen in the microscope for several days. After 4 days no nucleation had occurred. The sample was then held at, and permitted the opportunity to crystallize at, 155°C for several more days and then was slow cooled to room temperature. The WAXD showed the presence of a small amount of the γ-form in the sample. However, the source of this γ-form was not clear because the colour of the sample when removed was yellow; therefore, it might have been due to low molecular weight degraded material.

Even though the prediction of the regions of existence of the pure γ-form and the pure α-form is successful, the reason for the existence of the mixed phase region of α- and γ-forms at temperatures below the transition temperature is not proven.

CONCLUSIONS

The equilibrium melting points of the γ-form at elevated pressures were determined from lamellar thickness studies as well as from short time crystallization procedures and found to be quite similar. The melting of iPP at high pressures was affected by the amount of γ-phase present. This phenomenon limited to low supercoolings the range of temperatures from which the equilibrium melting point could be determined.

A plot of the equilibrium melting point versus pressure showed a linear relationship. All data points were fitted to a line which was related to the Clapeyron equation. The intercept of this line at atmospheric pressure was 187.6°C, the equilibrium melting point of the γ-form. The heat of fusion of the γ-form was determined from the slope of the line to be 144.8 J g^{-1}. These two values were cross-correlated by melting pure γ-form samples in the DSC. The equilibrium melting point of the γ-form at atmospheric pressure, determined from the DSC and lamellar thickness studies, was 187.2°C. Furthermore, the average value of the ΔH_f of the γ-form, determined from the combined DSC–WAXD studies, was close to 150 J g^{-1}, which is in good agreement with the value of 144.8 J g^{-1} determined from the Clapeyron equation.

When the equilibrium melting point and the heat of fusion values of the α- and γ-forms were available, thermodynamic prediction of the γ-formation was possible using the Gibbs free energy equation. Results showed that the thermodynamic prediction of pure γ-form was in good agreement with experimental values.

When the α-phase is produced at elevated pressures, in competition with the γ-phase, peculiar behaviour is observed in which its melting point is inversely proportional to its lamellar thickness. No explanation of this phenomenon is offered.

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REFERENCES

1. Addink, E. J. and Beintema, J., *Polymer*, 1961, **2**, 185.

2. Turner-Jones, A., Aizlewood, J. M. and Beckett, D. R., *Makrom. Chem.*, 1964, **75**, 134.
3. Binsbergen, F. L. and Lange, B. G. M., *Polymer*, 1968, **9**, 23.
4. Norton, D. R. and Keller, A., *Polymer*, 1985, **26**, 704.
5. Awaya, H., *Polymer*, 1988, **29**, 591.
6. Brückner, S., Meille, S. V., Petraccone, V. and Pirozzi, B., *Prog. Polym. Sci.*, 1991, **16**, 361.
7. Varga, J. J., *Materials Sci.*, 1992, **27**, 2557.
8. Kardos, J.L., Christiansen, J. L. and Baer, E., *J. Polym. Sci.*, 1966, **4**, 777.
9. Turner Jones, A., *Polymer*, 1971, **12**, 487.
10. Campbell, R. A., Phillips, P. J. and Lin, J. S., *Polymer*, 1993, **34**, 4809.
11. Mezghani, K. and Phillips, P. J., *Polymer*, 1995, **36**, 2407.
12. Bruckner, S. and Meille, S. V., *Nature*, 1989, **340**, 455.
13. Meille, S. V., Bruckner, S. and Porzio, W., *Macromolecules*, 1990, **23**, 4114.
14. Meille, S. V., Phillips, P. J., Mezghani, K. and Bruckner, S., *Macromolecules*, 1996, **29**, 795.
15. Mezghani, K. and Phillips, P. J., *Polymer*, 1997, **38**, 5725.
16. Phillips, P. J. and Tseng, H. T., *Macromolecules*, 1989, **22**, 1649.
17. Mezghani, K., Campbell, R. A. and Phillips, P. J., *Macromolecules*, 1994, **27**, 997.
18. Campbell, R. A., Ph.D. Dissertation, University of Tennessee, 1991.
19. Pae, K. D., *J. Polym. Sci.*, 1968, **6**, 657.
20. Mezghani, K. and Phillips, P. J., in preparation.
21. Stehling, F., personal communication.
22. Starkweather, H. W., Zoller, P. and Jones, G. A., *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21**, 295.
23. Zoller, P., Starkweather, H. W. and Jones, G. A., *J. Polym. Sci., Polym. Phys. Ed.*, 1986, **24**, 1451.
24. Starkweather, H. W. and Jones, G. A., *J. Polym. Sci., Polym. Phys. Ed.*, 1986, **24**, 1509.
25. Starkweather, H. W., Zoller, P. and Jones, G. A., *J. Polym. Sci., Polym. Phys. Ed.*, 1984, **22**, 1615.
26. Davidson, T. and Wunderlich, B., *J. Polym. Sci.*, 1969, **7**(A2), 377.
27. Zoller, P., Kehl, T. A., Starkweather, H. W. and Jones, G. A., *J. Polym. Sci., Polym. Phys. Ed.*, 1989, **27**, 93.
28. Tsujita, Y., Nose, T. and Hata, T., *Polymer J.*, 1974, **6**, 51.
29. Ueberreiter, K., Karl, V. H. and Altmeyer, A., *Eur. Polym. J.*, 1978, **14**, 1045.
30. Leute, U. and Dollhopf, W., *Coll. Polym. Sci.*, 1983, **261**, 299.
31. Jones, L. D. and Karasz, F. E., *Polym. Lett.*, 1966, **4**, 803.
32. Starkweather, H. W., Zoller, P., Jones, G. A. and Vega, A. J., *J. Polym. Sci., Polym. Phys. Ed.*, 1982, **20**, 751.
33. Zoller, P., 'The GNOMIX PVT Apparatus', equipment manual, 1991.