

**Morphology, Crystallization and Melting Behavior
of Statistical Copolymers of Propylene
with Ethylene, 1-Butene, 1-Hexene and 1-Octene**

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(ABSTRACT)

In this thesis, the morphology, crystallization and melting behavior of polypropylene copolymers (propylene/ethylene, propylene/1-butene, propylene/1-hexene and propylene/1-octene) has been examined. The multiple melting behavior has been correlated with the presence of α and γ phases and with the occurrence of cross-hatching morphology. The Crystallization and melting behavior of propylene/ethylene and propylene/1-butene are qualitatively similar and compatible with the expectations that the ethylene and butene comonomers are partly included in the propylene lattice. Propylene/1-hexene and propylene/1-octene copolymers exhibit remarkably similar behavior and morphologies consistent with the expectations that the hexene and the octene comonomers are rigorously excluded from the crystal lattice.

The origin and the crystallization time dependence of the multiple melting behavior is very different for these two pairs of copolymers. For PE and PB it is consistent with the melting of parent α -phase lamellae and α or γ -phase daughter lamellae. For PH and PO copolymers it is very similar to that observed for ethylene-octene(EO) and ethylene-styrene(ES) copolymers and compatible with the melting of primary lamellae and secondary mosaic or fringed micellar structures.

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CHAPTER 1

Introduction:

Ziegler and Natta discovered in 1954, the catalysts for the highly stereo-specific polymerization of polypropylene(1). This scientific breakthrough led to the development of processes for extremely high yields of isotactic polypropylene. The ease of manufacturing and the increased stereospecificity led to the commercial exploitation of this product. For this scientific achievement, Ziegler and Natta were awarded the Nobel Prize in Chemistry in 1963.

Polypropylene is considered to be one of the most important commodity thermoplastics. The level of interest in this material may in general be attributed to the following factors(2):

- The low costs for the monomer and for the polymerization techniques, which are highly efficient.
- The ease with which it can be modified by techniques like copolymerization and orientation leading to a wide variety of physical and chemical properties.
- The ease with which it can be processed which enables its use in the most common fabrication techniques.

Since this material is so versatile and also because of its low cost, new applications for polypropylene are continuously being developed. Catalysts for the preparation of polypropylene have resulted from a series of major technological advances. It is the complex system of catalysts, which makes it feasible for polypropylene to be so attractive in terms of its low cost manufacturing and wide commercial application.

Early catalysts possessed low activity and low stereoregularity and the removal of catalytic residues was necessary after polymerization. Then, Solvay developed what are referred to as the Second Generation Catalysts(3) with activities and stereoregularity almost 5 times higher than previous generation catalysts, spurring on the growth of polypropylene products. Then came the Third and Fourth-Generation catalysts, which could control the shape, size, and internal morphologies as well as the types of various phases that might be generated during the polymerization process. This was a major

scientific breakthrough and it further spurred the investment in new plants for the manufacture of Polypropylene and its products.

Another exciting piece of work within the last few years has been in the field of homogeneous catalysts(8,9). These catalysts have sites, which are consistently of one well-characterized type, and hence they produce polymers that are very stereoregular and have narrow molecular weight distributions. Research in this area is being pursued with gusto and numerous patents have already been granted.

In industry, the term polypropylene is generally meant to refer to the following types of compounds:

1. Homopolymers – Polymers of propylene only
2. Random Copolymers – Small quantities of comonomer are inserted randomly in the polymer chain.
3. Impact Copolymers – Also referred to as heterophasic copolymers. Consist of Ethylene Propylene Rubber (EPR) dispersed in the polypropylene matrix.
4. Filled and reinforced versions of all of the above.

Homopolymers vary only in their molecular weights and defect content. Sometimes certain additives are mixed with the polymer to attain desirable properties. Homopolymers are generally injection molded into small items, where low temperature impact strength is not critical(3) such as bottle caps, syringes. These polymers can also be oriented into fibers, ropes etc.

Random copolymers have generally lower melting points, improved optical properties and lower modulus. Because of their improved optical properties, they find use as packaging materials. These copolymers are also used in auto bumpers(4) for their energy absorbing capacity and low density.

Impact copolymers provide impact strength at low temperatures even while having high flexural modulus or melt flow rates. They are prepared by adding a comonomer at a later stage of polymerization, leading to a dispersed phase. Typical applications include interiors of automobiles, luggage, small appliance parts and appliance housings(5).

Because of the development of the Fourth Generation Catalysts, it has become possible to prepare a new family of high alloy copolymers, which include soft copolymers, stiff copolymers and low melting copolymers. These materials show a great

degree of flexibility in terms of degree of crystallinity, comonomer selection and molecular weight(6,7). Soft copolymers are used for the production of industrial sacks, diaper backings and geo-membranes. They are also used as impact modifiers and because of their low melting points they provide low seal initiation temperature in such products.

Stiff copolymers are used for injection-molding applications requiring high heat deflection temperature or great stiffness.

Thus, we see that propylene and related compounds find widespread use in the modern day world from injection molded parts, to fibers and films. The commercial applications of these substances are so numerous that it would be difficult to comprehend life without them.

In terms of the economic impact, polypropylene has evolved from a high growth product in the 1960s to a high volume product with wide applications. The annual growth rate of polypropylene consumption is higher than that of the plastics industry as a whole and sales are much higher (to the tune of 15%) than those of all thermoplastics combined together(1).

By the simple modification of polypropylene molecular structure with comonomer(s), a variety of polymer grades can be produced having an entire array of properties. For every grade of copolymer, several variations are possible. Copolymerization basically leads to modification of polymer crystallinity in a controlled manner introducing ‘irregularities’ in the polymer molecule. These lead to specific changes in the properties like increased toughness reduced stiffness and melting temperature.

The characterization of copolymers is by no means easy because of the multiplicity of structural species present. An in-depth characterization requires knowledge of distribution of molecular weight, crystallinity and composition.

The popularity of polypropylene compounds can, in a large part, be attributed to the development of these substances. But the fact remains that their commercial exploitation has more or less been limited to copolymers of polypropylene and ethylene. This observation provides the motivation for this work.

In this work, copolymers of polypropylene with ethylene, 1-butene, 1-hexene and 1-octene have been studied and an attempt has been made to characterize their

morphology, crystallization and melting behavior. The techniques used include Differential Scanning Calorimetry (DSC), Atomic Force Microscopy (AFM), Polarizing Optical Microscopy (POM) and Wide Angle X-Ray Diffraction (WAXD). The issue of inclusion/exclusion of the comonomer in the polypropylene crystal structure and its effect on the formation of various phases during crystallization has been addressed. The thermal behavior of the copolymers and the phase transitions during heating and cooling have been probed. Also, the kinetics of isothermal melt crystallization have been studied at different temperatures.

In Chapter Two, we present a pertinent literature review. The theory of homopolymer crystallization is briefly discussed followed by theories of copolymer crystallization. Then, we give a selective review of the studies on it-PP and follow by a literature review on related work done on various copolymer systems. Chapter Three contains the experimental details while Chapter Four focuses on the results and discussions. Chapter Five provides the conclusions and suggested future work.

Chapter 2

Literature Review:

2.1. Polymer Crystallization

Crystallization can take place in a variety of ways, depending on conditions such as orientation and composition (pure polymer or mixtures, homopolymer or copolymer) (10) (Fig 2.1). Here we will deal only with homopolymer and copolymer crystallization from the melt state.

2.1.1 Crystallization Process

2.1.1.1 Spherulite Structure

Linear polymer chains crystallize as spherulites from a free unconstrained melt. Spherulites, when fully developed, are spherically symmetrical assemblies of lamellar structures which grow from a central nucleus. The growth of lamellar crystal occurs by a chain folding mechanism. While lamellae grow mainly in the radial direction, they also exhibit branching and splaying, thus leading to the formation of compact spherical objects as shown in Fig 2.2 (11, 12). Typical spherulite diameters range from few micrometers to millimeters, whereas lamellar lengths are of the order of a few tenths of a μm to a few μm . The thickness of the lamellar structure is usually approximately equal to the fold length and is in the range of 5 to 20 nm. As polymers never crystallize fully, spherulites are actually composites of crystalline and amorphous regions. Amorphous regions are mostly located between lamellae and composed of tie chains, loose folds and cilia. Lamellae remain connected to each other by 'Tie Chains' (13). These tie chains impact the mechanical strength of the semicrystalline polymer. They make the crystallites more stable by distributing the stress throughout the material (10,14). The amount of tie chains is a function of the crystallization temperature. The higher the temperature, the lower the amount of tie chains, hence, more brittle the material is and vice-versa.

Morphology of the spherulites can be described as Compact or Open and b) Coarse or Fine (12). a) In a compact morphology, a large portion of the material has already crystallized while an open represents the case where the lamellae are separated by large regions of uncrystallized melt. b) A coarse structure refers to the texture in which bundles

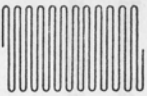
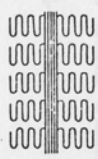
TYPE OF MACROMOLECULE	CONFORMATION	MICROSTRUCTURAL UNIT	CONDITIONS	MACROSTRUCTURE	PATTERN (CROSS-SECTION)
FLEXIBLE MACROMOLECULE IN QUIESCENT CONDITIONS	RANDOM COIL	FOLDED CHAIN LAMELLAE	VERY DILUTE QUIESCENT SOLUTION	SINGLE CRYSTAL	
			MELT	SPHERULITE	
FLEXIBLE MACROMOLECULE IN FIELDS OF FORCE (FLOW)	DEFORMED COIL	CORE OF ALIGNED CRYSTALS (ROW) + LAMELLAR "SIDE PLATES"	DILUTE STIRRED SOLUTION	SHISH-KEBAB	
			EXTRUDED "MELT"	ROW NUCLEATED STRUCTURE	
RIGID MACROMOLECULE	ROD (LIQUID CRYSTAL)	MICRO- FIBRIL (RODLET)	SPINNING FROM SOLUTION WITHOUT SPECIAL PRECAUTIONS	MOZAIC OF RANDOMLY ORIENTED MICROFIBRILS	
			SPINNING WITH MAINTENANCE OF FULL ORIENTATION	HIGHLY AND SYMMETRICALLY ORDERED MICROFIBRILS	

Fig 2.1 Schematic illustration of different types of polymer crystals crystallized from various conditions (from reference 10)

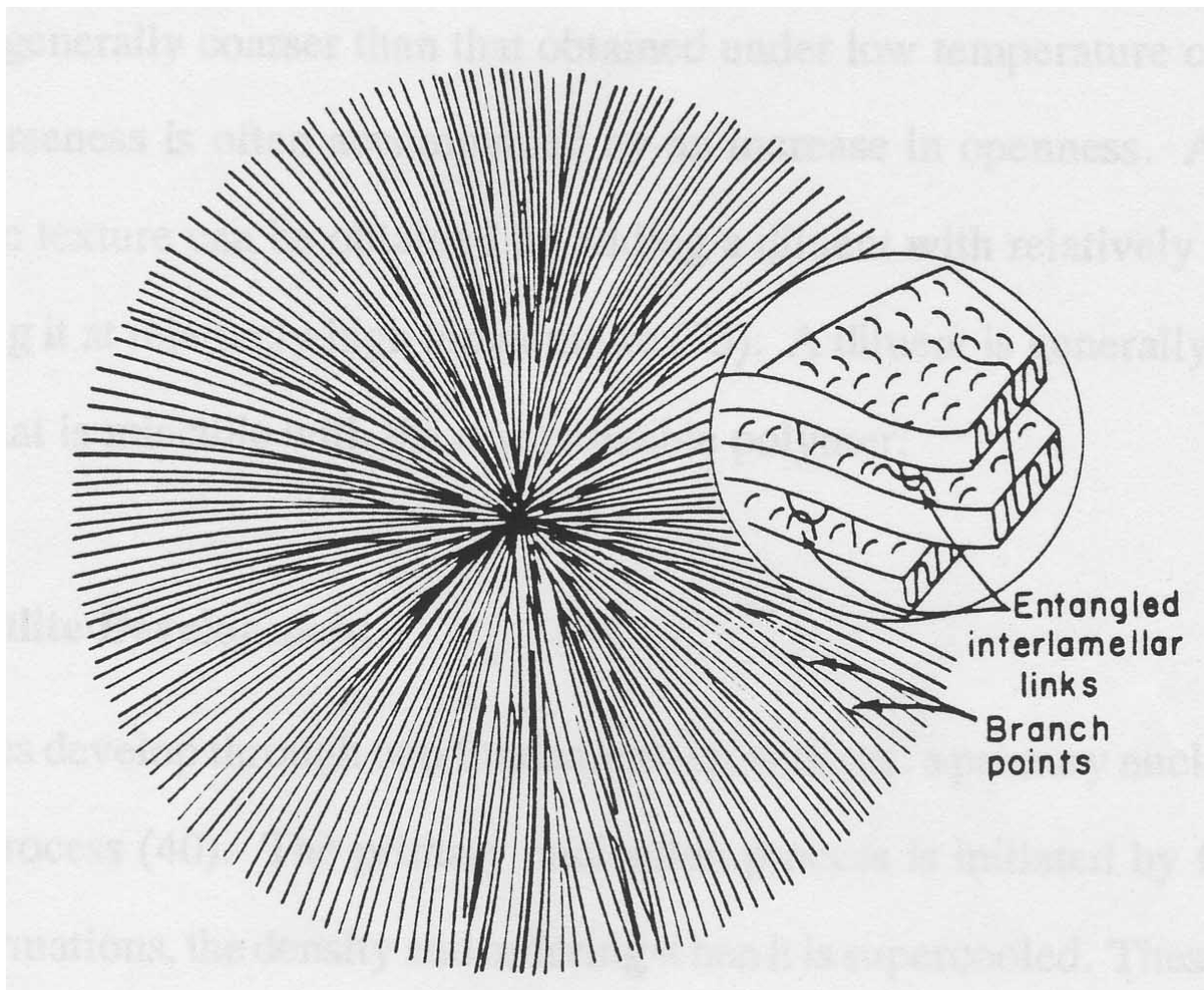


Fig 2.2 Schematic illustration of the structure of polymer spherulite (from reference 11)

of lamellae have relatively large cross-sections while a fine structure has more tenuous radial fibrous units.

2.1.1.2. Spherulite Development

Spherulites are formed as a result of two processes: primary nucleation and lamellar growth. Because of fluctuations in chain conformations, density and ordering due to supercooling, primary nuclei form below the equilibrium melting temperature. The growth process consists of two steps – surface nucleation (secondary nucleation) and substrate completion. Schematic illustration of the lamellar growth mechanism is shown in Fig 2.3.

Once the primary nuclei are formed, they grow by small angle branching growth, wherein the parent lamella splits into two daughter lamellae at the end (12). As a result of this continuous splitting and growth, finally, spherical structures called spherulites are formed. The schematic development of the spherulite is shown in Fig 2.4. These spherulites continue to grow until they impinge upon each other and form the interspherulite boundaries. The lamellar width remains constant throughout the entire process (12). Crystallizable polymers are actually semi-crystalline in nature as they never crystallize completely. There is a non-crystalline (amorphous) phase in between the crystals. Even after the impingement of spherulites, the crystallinity keeps on increasing. This is attributed to the secondary crystallization process that never quite reaches completion (11). This might be attributed to the formation of new crystals between the primary lamellae or to lamellar thickening. Isothermal lamellar thickening is quite common in polymers as the crystallites try to reach a more thermodynamically stable state by decreasing the surface to volume ratio.

Superstructures like spherulites are lost and lamellar growth hindered when a significant concentration of defect is introduced into the polymer backbone. The reason being that crystallization is hindered and sometimes prohibited by the presence of these non-crystallizable defects. This issue will be more thoroughly addressed in section 2.2.

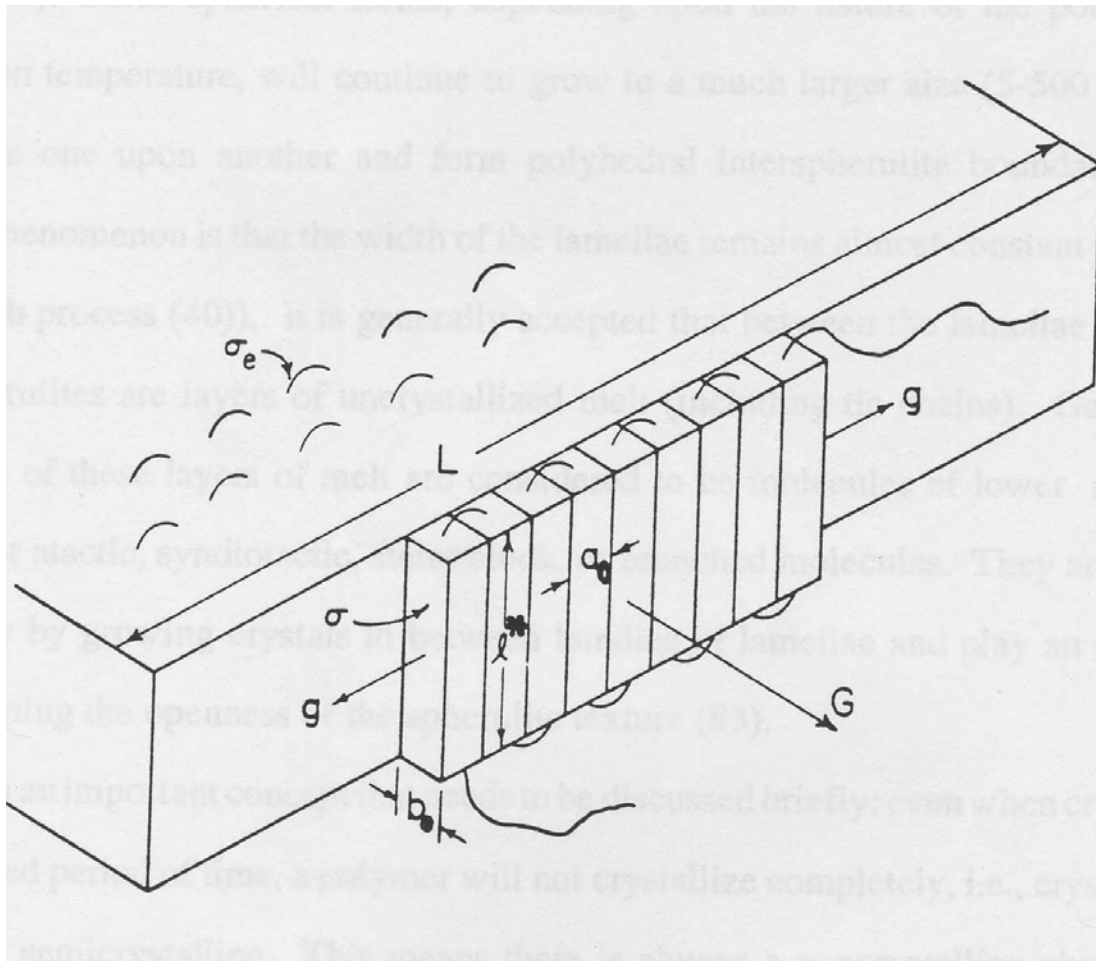


Fig 2.3 Schematic illustration of the lamellar growth mechanism (from reference 17)

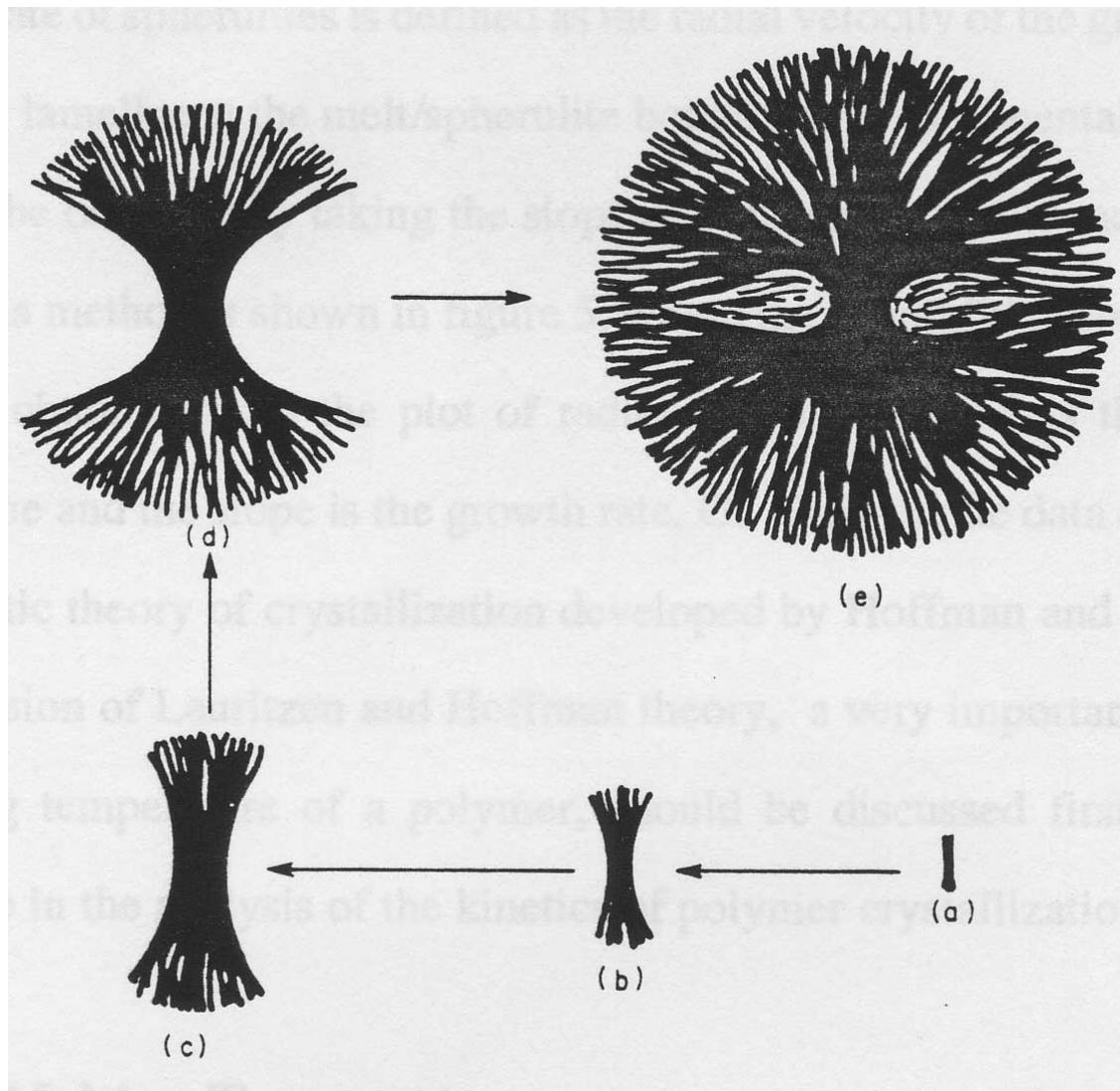


Fig 2.4 Schematic illustration of the development of a polymer spherulite (from reference 18)

2.1.1.3 Homopolymer Crystal Growth Theory

Various theories have been proposed to describe the kinetics of homopolymer crystallization. These include Sadler's rough surface model (15, 16) and the Lauritzen-Hoffman (LH) secondary nucleation theory (17,18). A brief review is included here.

The LH theory suggests that the lamellar growth process comprises of two elementary steps: 1) the deposition of a first stem onto a fresh lamellar growth front which occurs at a rate denoted by 'i' and 2) the substrate completion or the lateral growth occurring by a chain folding process occurring at a rate denoted by 'g'. This theory predicts that crystal growth can be categorized into three regimes. As shown in Fig 2.5, let us assume that the growth face can be described as a substrate of length 'L' and lamellar thickness 'l'. At high crystallization temperature 'g' is much larger than 'i'. Thus, once the nucleus is deposited, it continues to grow laterally to complete the crystalline layer on the substrate before the next nucleation event. Growth proceeds at a rate G in the direction normal to the substrate. In this case G is given by $G = b_0 i L$, where b_0 is the thickness of one crystalline layer. This is described as the Regime I. As the crystallization temperature decreases, 'i' and 'g' become comparable, which is Regime II. In this case, several nucleation events take place and the nuclei grow laterally but compete with each other to give rise to a new crystalline layer. Growth in this region is given by $G = b_0 (2ig)^{1/2}$. Further decrease in the crystallization temperature results in a much larger i as compared to g. This is Regime III and in this regime secondary nucleation becomes rate determining, as there is no time for the nuclei to grow laterally. The growth rate is given by $G = b_0 i L'$ where L' is the average distance between niches, which is about 2-3 times the width of a stem.

For all three regimes, the overall growth rate 'G' is expressed in the LH theory (19) as follows:

$$G = G_0 \exp [- U^*/R(T_x - T_\infty)] \exp [-K_g/T_x \Delta T] \quad (2.1)$$

Where G_0 is a pre-exponential factor that depends on the regime, U^* is the activation energy for transport of crystallizable segments from the interface to the site of crystallization. T_∞ is the temperature at which segmental transport vanishes (akin to T_K , the Kauzmann temperature or T_z , the thermodynamic glass transition temperature). It is

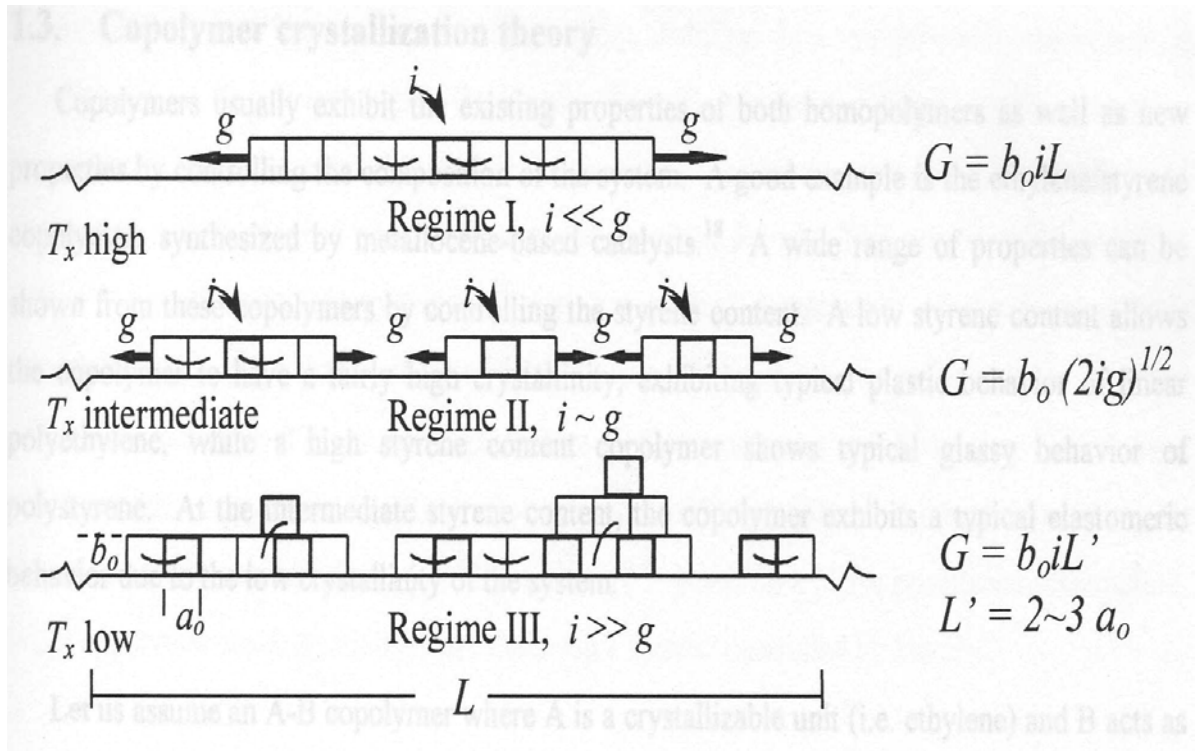


Fig 2.5 Schematic of the crystal growth in different regimes according to the LH theory (from reference 25)

generally taken to be $T_{\infty} = T_g - 30^{\circ}\text{C}$ where T_g is the glass transition temperature. K_g is the secondary nucleation constant for a given regime and is given by

$$K_{gj} = j b_0 \sigma \sigma_e T_m / \Delta H_f \quad (2.2)$$

Where σ and σ_e are lateral and fold surface free energy respectively. ΔH_f is the theoretical heat of fusion and k is the Boltzmann constant. $j = 4$ in regime I and III and $j = 2$ in regime II.

Thus, the LH theory predicts that a plot of $\log G + U^*/R(T_x - T_{\infty})$ versus $1/T_x \Delta T$ yields K_{gj} as the slope and G_0 as the intercept for each regime. Furthermore, the theory predicts that $K_{gI} / K_{gII} = K_{gIII} / K_{gII} = 2$.

2.2 Random Copolymer Crystallization Theory

Copolymers show a wide range of properties starting from those of the homopolymer to several new properties which can be controlled by varying the composition and more important by the distribution of comonomers along the chain. There are several theories regarding the crystallization of copolymers. In this section we will discuss a few of these theories.

Flory (19) proposed a thermodynamic model for the crystallization of copolymer systems in which the comonomer was excluded from the lattice of monomer A. He contended that the temperature at which the crystallites melt or at which the last traces of crystallinity disappear (T_m) depends on the melting point of homopolymer A (T_m^0), the heat of fusion of homopolymer A and the sequence propagation probability which is a characteristic of the copolymer. At temperatures just below T_m , only very thick crystallites can exist in stable equilibrium with the melt. As the temperature decreases further, thinner crystals become stable, thus shorter sequences of crystallizable units can participate in the crystallization process. Hence the crystallinity remains very low in an appreciable temperature range below the melting point but it increases with a further decrease in temperature.

While homopolymers melt over a very short temperature interval, random copolymers with excluded comonomers display a very large melting temperature range. The fact that copolymers melt over a wide temperature range may be attributed to the presence of excluded units present along the otherwise crystallizable backbone. And the breadth of melting region results from the variations in crystallite thickness, thus from

variations in sequence lengths of crystallizable units. The thicker the crystallite, the greater the melting temperature. Since longest sequences are very rare, it is not surprising that the ultimate melting point of such random copolymer is poorly defined(20,21).

Consider a polymer with crystallizable units (A) and co-units (B) which are excluded from the lattice of A. Flory (19,22,23) predicted the melting temperature and the crystallinity of the copolymer system as a function of temperature and sequence length distribution, based on a phase equilibrium theory. The theory predicts that there is a minimum stable crystallite thickness, therefore a minimum sequence length for a stable crystal ζ , which is determined by the crystallization temperature T_x . At a given temperature only those crystals with crystallizable sequence length ζ longer than ζ^* will be stable, while other with A blocks smaller than ζ will be unstable. ζ^* increases with increasing T_x . At temperatures just below T_m , ζ^* is very large, hence, only extremely long crystallites can form. As T_x is further decreased, ζ^* decreases, leading to the formation of thinner crystallites with shorter crystallizable sequence length.

The melting temperature depression for the copolymer system is predicted as:

$$1/T_m - 1/T_m^0 = -(R/\Delta H_u) \ln p \quad (2.3)$$

where T_m is the melting temperature of the copolymer, T_m^0 is the equilibrium melting temperature of homopolymer A, R is the gas constant, ΔH_u is the heat of fusion per repeat unit of homopolymer A and p is the sequence propagation probability for repeat unit A. For random copolymers $p = 1 - X_B$, where X_B is the content of B unit.

Flory's theory is based on the assumption that B units are never included in the crystal and hence the copolymer melting temperature and crystallinity would not depend on their chemical nature. Quantitative comparison of this theory with experimental results isn't totally satisfying(24). Flory's theory is usually only used as a guide. The lack of quantitative agreement between the theory and experiments on random copolymers with excluded comonomers is the consequence of the fact that kinetic effects are usually very important for crystallization processes. Since a thermodynamic equilibrium is never reached during crystallization, the maximum crystallite dimensions are never achieved and both melting point and degree of crystallinity are below the values predicted by the theory.

Helfand and Lauritzen proposed a theory of copolymer crystallization for cases when the B units may be incorporated in the crystal of A units (25,26). They however said that copolymers do not achieve equilibrium concentration, rather kinetic considerations determine the fraction of 'B' in the crystal. Kinetic considerations mean that crystals are not in an equilibrium state and comonomer concentrations are determined by the kinetics of their attachment to the crystal and that of their detachment.

Data obtained for isoprene systems (27) seem appropriate for this theory. Trans isomers are the impurities in a predominantly cis polymer for such a system. Lauritzen and Helfand insist that the inclusion of copolymers occurs for all systems, the difference being the degree of inclusion.

Sanchez and Eby (28) dealt with the crystallization of copolymers in a manner similar to Lauritzen et al. and different from Flory et al.. They contemplated that the crystallization process is kinetically determined and the concentrations of comonomers in the crystal and melt are fixed by kinetic considerations, rather than equilibrium conditions. The crystalline state of a random copolymer must lie between two extreme conditions. The first one being that, all B units are excluded from the crystal and the crystallites are in metastable equilibrium with the amorphous phase comprising of both A and B units. The other extreme condition considers the uniform inclusion of B units in the crystal, and the concentrations of B in the crystal and the melt phases. These two extreme conditions are shown in Fig 2.6

The bulk free energy difference between the crystalline phase and the melt as given by the authors (28) is

$$\Delta G = \Delta G^0 - RT \{ \epsilon X_C / (RT) + (1 - X_C) \ln [(1 - X_C) / (1 - X)] + X_C \ln [X_C / X] \} \quad (2.5)$$

where ΔG^0 is the same as that for the homopolymers and the first term in the braces accounts for the enthalpic effect and the latter two account for the entropic effect. The above equation can be easily reduced to the case of the exclusion model (29) and that of uniform inclusion model (30,31) simply by putting $X_C = 0$ and $X_C = X$ respectively.

where, X_C = actual concentration of B co-units in the crystal

and X = mole fraction of B.

Melting temperature of an infinitely large crystal can be determined by putting $\Delta G = 0$.

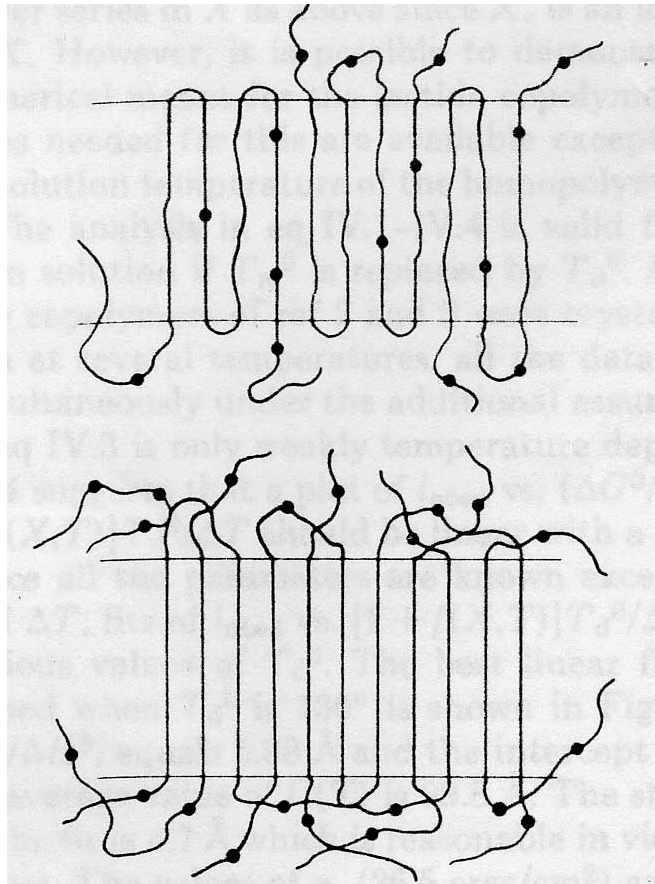


Fig 2.6 Schematic drawing showing the extreme states of crystalline random copolymers. The one on top represents complete inclusion while the one at bottom, complete exclusion (from reference 30)

It has also been shown that lamellar thickness increases with increasing comonomer concentration (30). The authors found it to be valid for all concentrations of B units from complete exclusion to intermediate concentrations to complete inclusion.

The equations proposed were found to be consistent with the experimental data on L- and DL- lactides (32,33).

The inclusion or exclusion of comonomer units in the crystal is determined by their size. Methyl branches can be included in polyethylene crystals (34). Thus the ethylene/propylene copolymers can be described by Sanchez and Eby's model.

However for higher ethylene/ α -olefin copolymers, melting temperature and crystallinity do not depend on the chemical nature of the comonomer but they depend only on the comonomer content (35, 36) which suggests that Flory's exclusion model is more appropriate in this case. A similar behavior has been observed for ethylene/styrene copolymers in recent studies from our laboratory(24).

2.3 Polypropylene: Isomerism and Polymorphism

2.3.1 Isomerism of Poly(propylene)

The chemical structure of polypropylene is shown in Fig 2.7. It shows two types of isomerism: positional and stereo isomerism.

Positional isomerism is also referred to as regio-isomerism or orienticity. It refers to the orientation of the repeat unit in a growing polymer chain. This, in turn, depends strongly on the catalyst system in use. The orienticity in a polymer chain may be head-to-head, head-to-tail or tail-to-tail. A polymer chain is said to be regio-regular when its repeat units are in the head-to-tail arrangement. Positional and stereodefects cause a decrease in crystallinity because of interruptions in the regular monomer sequence in the polymer chain. Isotactic poly(propylene) and syndiotactic propylene/ethylene copolymers are highly regio-regular (35,36). At the same time, syndiotactic propylene/ethylene copolymers (obtained from vanadium catalysts) have head-to-head and tail-to-tail defects (37,38).

Stereo-isomerism can be seen in Fig 2.8. For polypropylene the side group R is a methyl. The different configurations are referred to as tacticities. When the side groups are on the same side of the fully extended carbon backbone, the configuration is called 'isotactic' (Fig 2.8a). When the position of the side group alternates, it is called

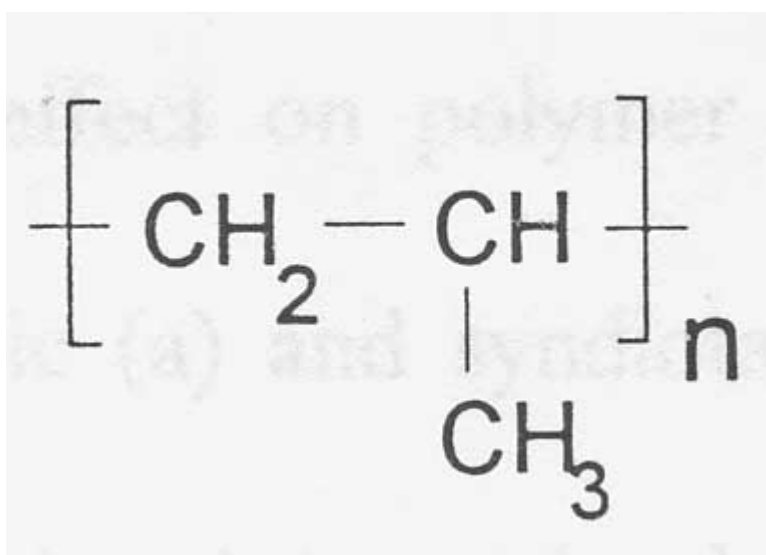


Fig 2.7 Chemical structure of Polypropylene

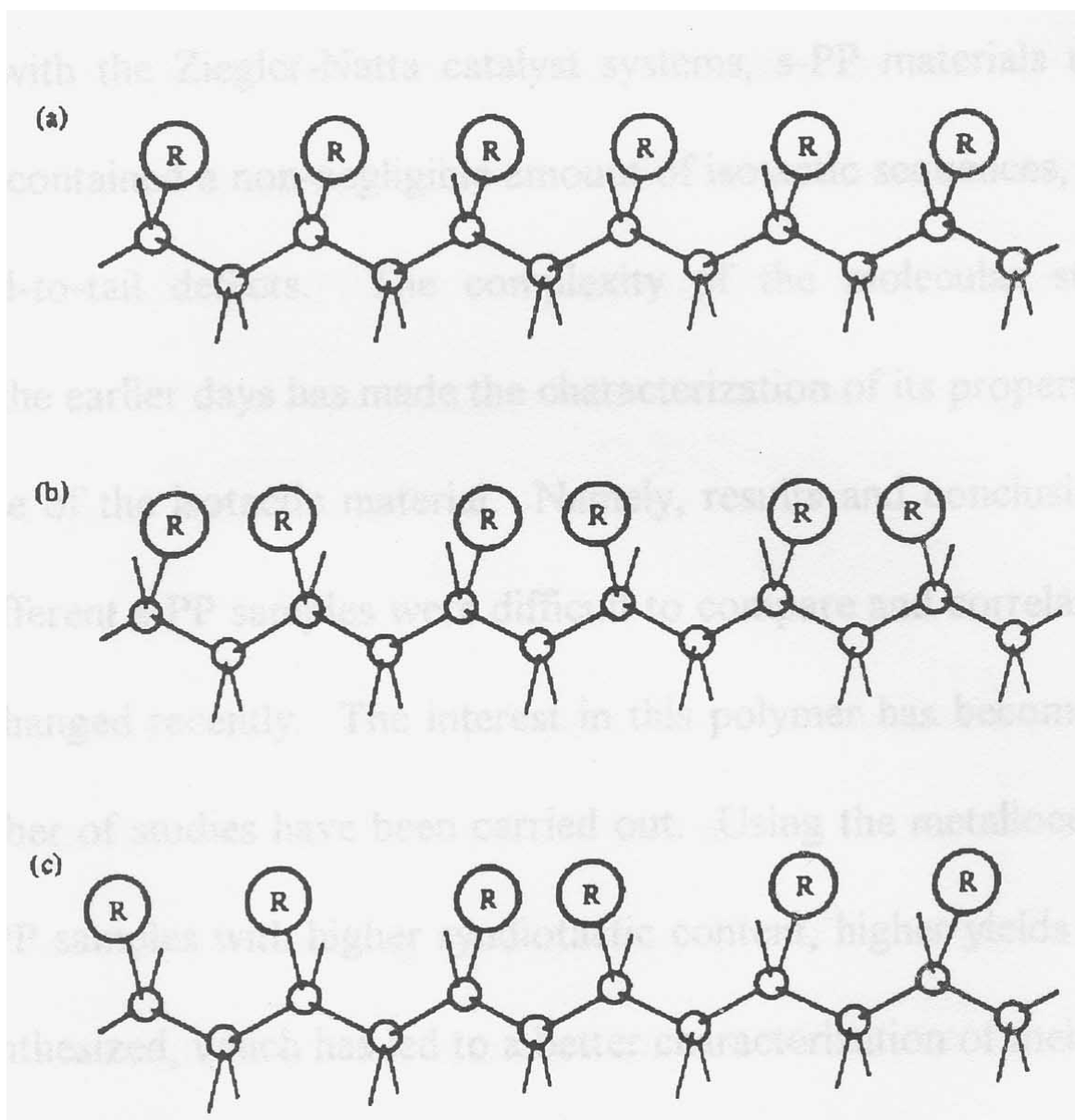


Fig 2.8 Different tacticities: a) isotactic b) syndiotactic c) atactic (from reference 34)

'syndiotactic' (Fig 2.8b). When the position of the side group follows a random sequence, the configuration is called 'atactic' (Fig 2.8c). The polymer can either be isotactic, syndiotactic or atactic. Tacticity significantly affects the crystallization behavior and other polymeric properties.

For example, isotactic and syndiotactic polypropylene show a wide range of properties, which are very different from one another. Isotactic and syndiotactic polypropylene are semi-crystalline material while atactic polypropylene is amorphous. Moreover the crystal structure, melting behavior and physical properties for polymers of different tacticities are very different.

While polypropylene has been traditionally made by Ziegler-Natta catalysts it is also being made nowadays using the metallocene catalysts (39-46), also referred to as single site catalysts. Ziegler-Natta polypropylene is usually a polymer exhibiting a very broad molar mass distribution with the higher molar mass chains exhibiting higher tacticity. Most of the atactic component of Ziegler-Natta PP is confined to the lower molar mass fractions. Ziegler-Natta PP usually exhibit no or very low regio defects. Metallocene PP on the other hand exhibit much narrower molar mass distribution ($M_w/M_n \sim 2-3$) and variable regio defect and stereodeflect contents depending on polymerization temperature and catalyst type.

It-PP also shows polymorphism, which is significantly affected by the nature of the defects and will be discussed in the next section.

2.3.2 Polymorphism in Isotactic Polypropylene

The structure and morphology of isotactic polypropylene have provided for fascinating studies and have reached a stage where the understanding is almost near completion. It-PP shows 4 different crystal phases: α , β , γ and smectic. α may be further subdivided into two phases namely α_1 and α_2 . The β and γ phases were discovered (49,50) as long as 30 years ago but were solved as recently as 1995 and 1989 respectively (51).

It-PP crystallizes with the trans-gauche [(TG⁺)₃ and (G-T)₃] conformation that forms a 3/1 helix with a period of 6.5Å (47-48). The various subdivisions of the aforementioned conformation are shown in Fig 2.9. As shown, the 3/1 helical

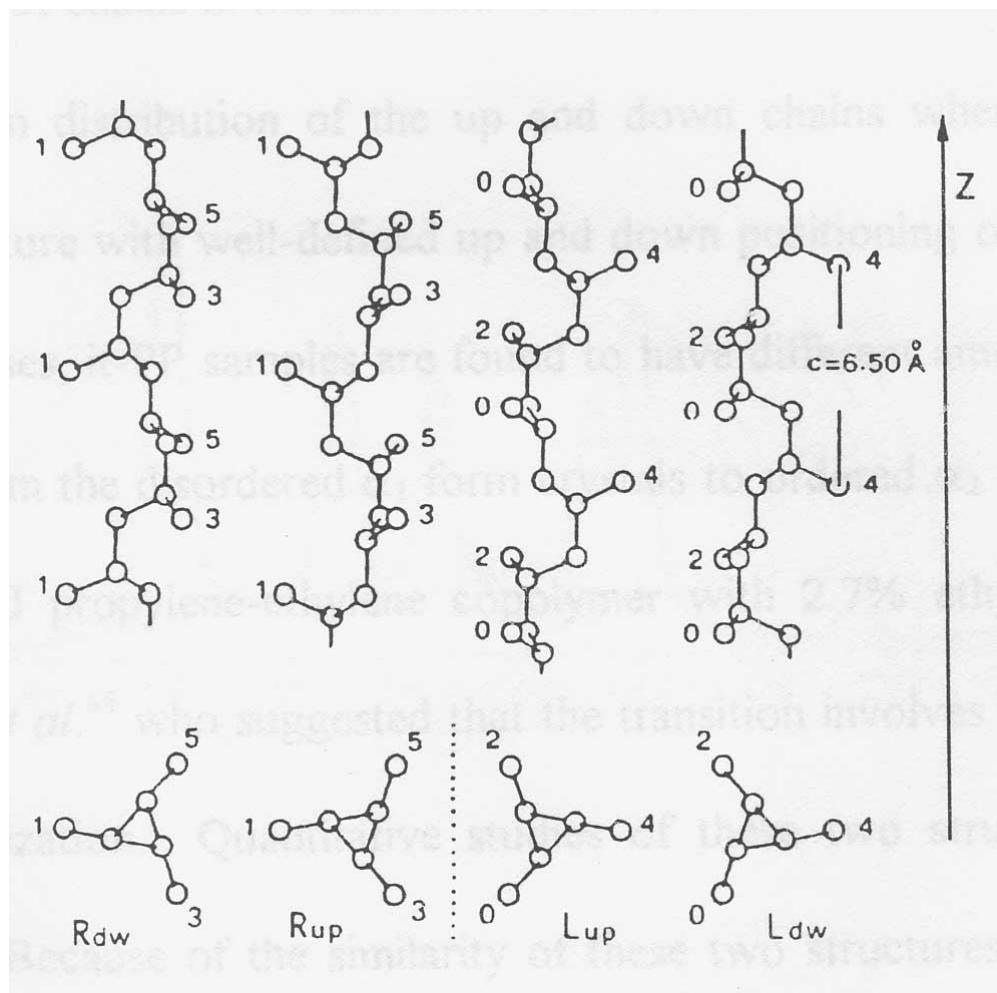


Fig 2.9 Right (R) and left handed (L) conformations of it-PP with the up and down orientation w.r.t. the reference z-axis (from reference 50)

conformation depicts not only right and left-handed but also up and down orientations, for a given reference axis.

2.3.2.1 α -phase Structure

Natta and Corradini (52) first established the crystal structure of α -phase. Subsequent studies (53,54) since then have confirmed the same with minor variations. The geometry for this phase is monoclinic with the parameters being: $a = 6.65\text{\AA}$, $b = 20.96\text{\AA}$, $c = 6.5\text{\AA}$ and $\beta = 99^\circ 80'$ (55). Fig 2.10 shows the WAXD pattern for the same. α phase can be further subdivided into two different phases namely α_1 and α_2 . These differ in the randomness of the up and down positioning of chains. While α_1 has random distribution for the orientation of chains, α_2 displays an ordered orientation. Because of their similarity, it is very difficult to analyze these phases quantitatively. They can only be distinguished using the two higher order Bragg peaks in the 34° and 38° 2θ range (56). The authors have suggested that the transition between these two phases involves partial melting and recrystallization. The transition from α_1 (low temperature) to α_2 (high temperature) has been studied in PP-homopolymers and propylene/ethylene copolymers (57).

The α -phase of *it*-PP exhibits unique lamellar branching (leading to cross-hatching morphology), which is manifested under a variety of crystallization conditions (51). The branching can be seen in thin films, in fibers, and after crystallization from solution ('quadrites') (58-62). The spherulites corresponding to this phase may show positive optical character as a result of radial and tangential orientation of lamellae during their growth. It is only at extreme temperatures ($>160^\circ\text{C}$ (63) and $< 30^\circ\text{C}$ (64)) that the branching effect (cross-hatching) disappears. The lamellar branching is however observed between 150 and 155°C and increases in frequency with the lowering of crystallization temperature. This was in accordance with the earlier findings by Norton and Keller (64), who studied the relationship between lamellar branching and birefringence change in the α form polypropylene spherulites. It has been established that branching takes place whenever two successive ac layers are made up of chains of the same hand (65). In the spherulite the angle between mother and daughter lamellae are either 100° or 80° (51) (Fig 2.11).

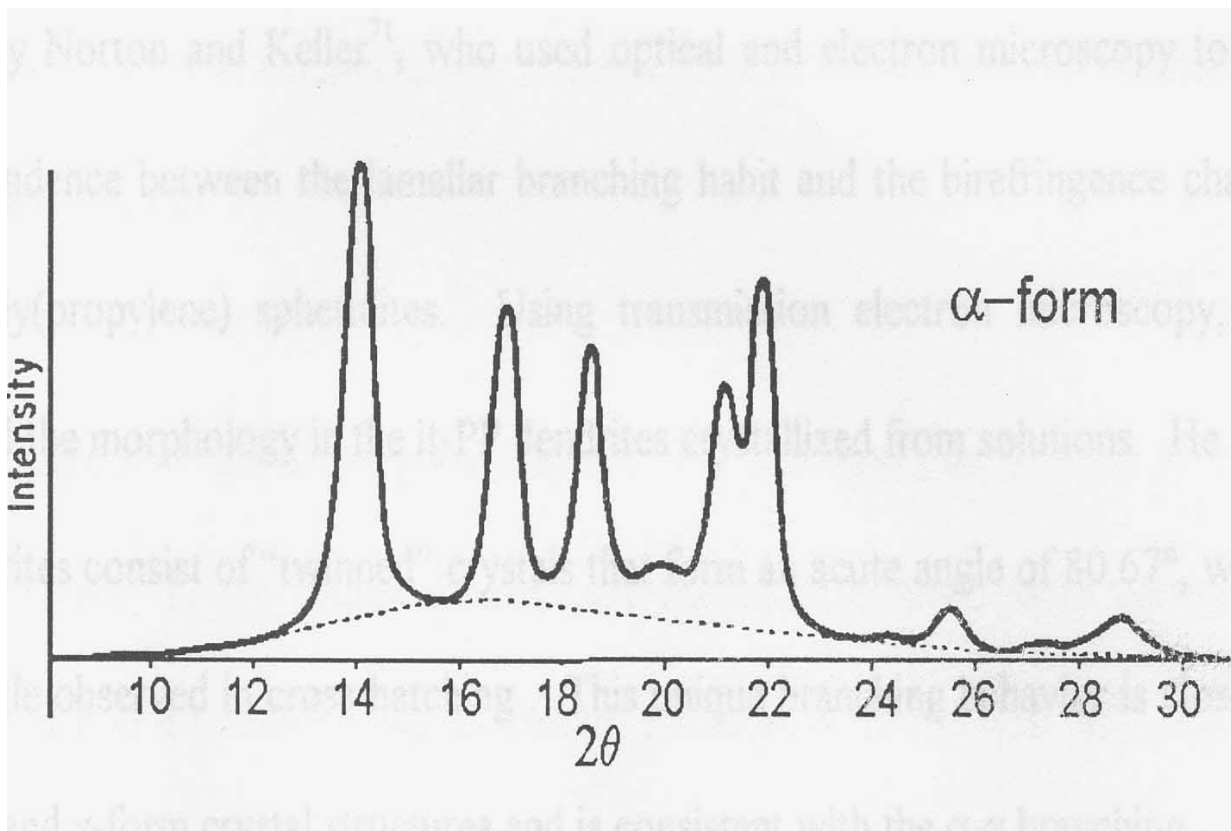


Fig 2.10 Powder X-Ray diffractogram for an α -form it-PP bulk sample (from reference 49)

2.3.2.2 γ -phase Structure

Since this phase coexists with the α -phase, it has remained elusive over the years. First discovered in 1961 (50), it was finally understood in 1989 (66). Meanwhile, a greater interest in developing a better understanding of this phase structure, has been fuelled by the development of well-developed *it*-PP copolymers using metallocene catalysts (67). Several factors can promote the formation of γ -phase crystals: low molecular weight (50,68), slow cooling from melt (47), crystallization under high pressure (69) and defects in the polypropylene backbone such as ethylene, butene comonomers (70).

Electron microscopy studies indicated that the γ -phase crystallizes on the lateral *ac* phases of α -*it*-PP (51). Thus, it had been long suspected that there was a structural similarity or compatibility with the α -phase, which was finally understood from a paper by Bruckner et al. (69). While it was thought earlier that the structure was triclinic (47), Bruckner et al. (69) convincingly showed that it is a face centered orthorhombic cell with unit parameters: $a = 8.54\text{\AA}$, $b = 9.93\text{\AA}$, $c = 42.41\text{\AA}$. The diffraction pattern for the γ -form is shown in the Fig 2.12.

Bruckner et al. proposed that the chain axes were not parallel in this case. The structure, in fact, is made up of a succession of bilayers tilted 80° or 100° with respect to each other (51). This structure, though revolutionary, answers a lot of nagging questions that were troubling scientists early on (51). The γ -phase lamellae actually branch at 40° to that of the α -phase and the chains in this phase are tilted at an angle of 40° to the normal to the lamellae (72).

Another important point to be noted is that, so far spherulites of γ -phase have shown positive birefringence. Lotz et al (73), obtained γ -form single crystals and showed that non-parallel chains in the γ -form unit cell and the specific branching angle of 80.67° in the α -form spherulite were indeed consistent.

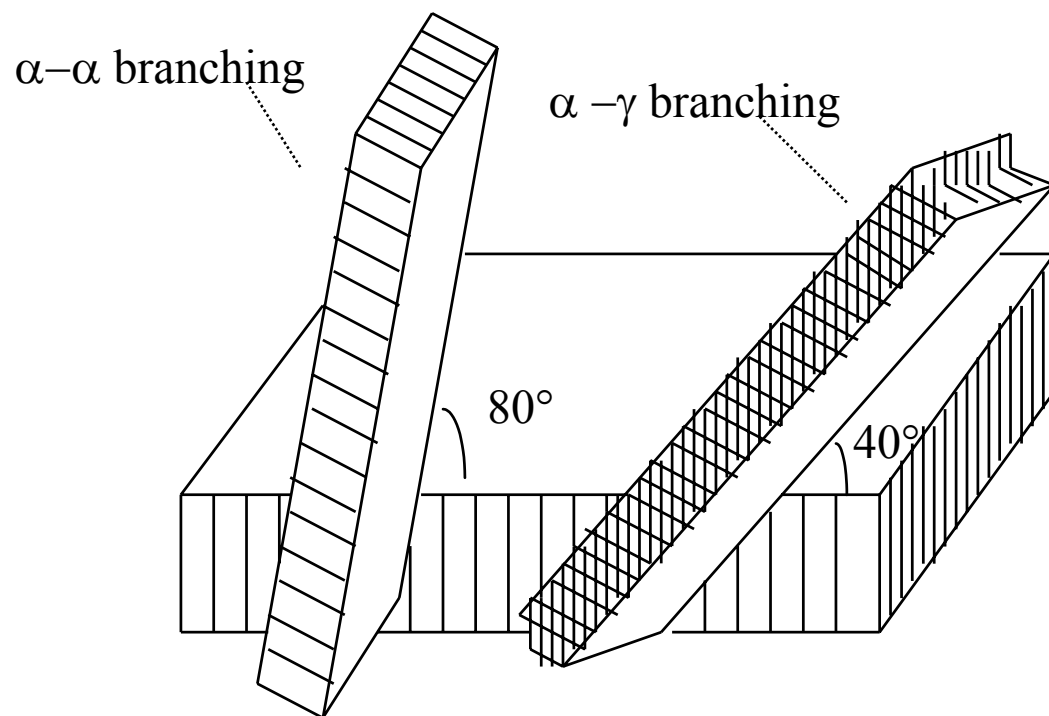


Fig 2.11 Figure showing the branching of lamellae (adapted from ref 51)

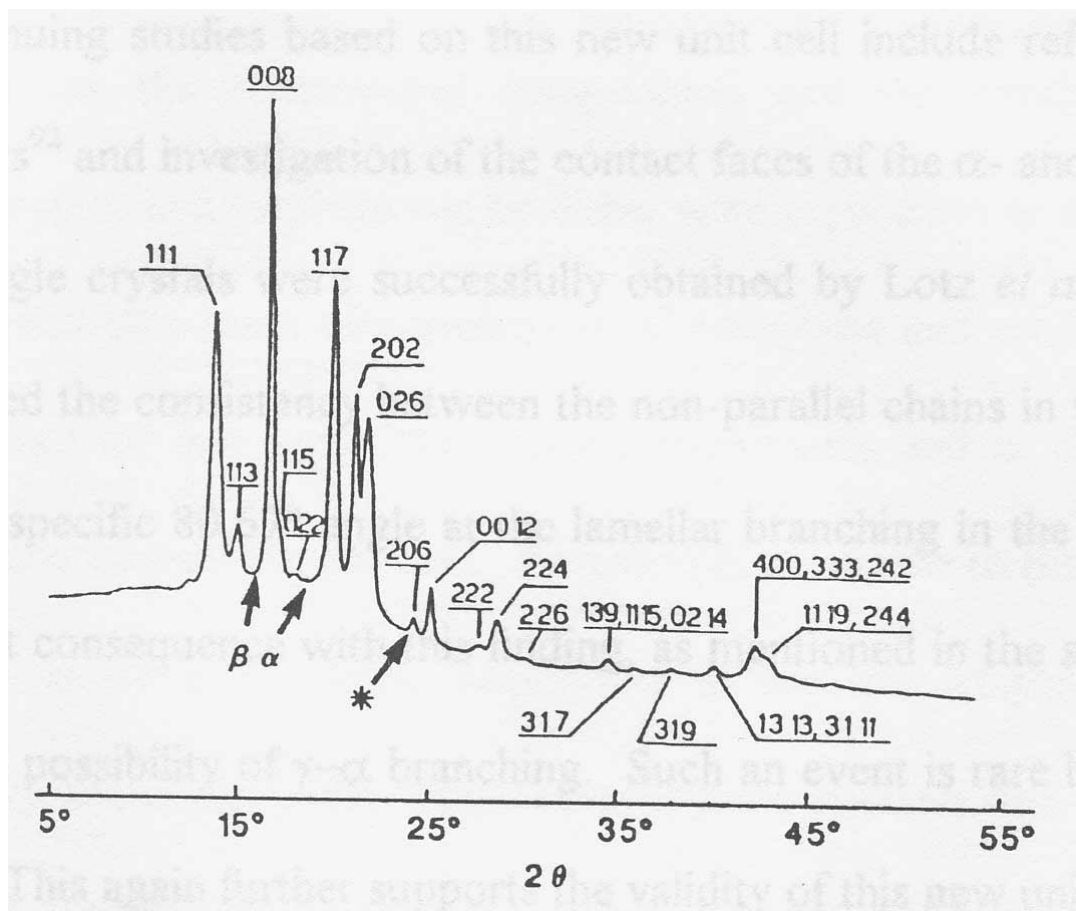


Fig 2.12 Powder X-ray diffractogram for a γ -form it-PP bulk sample (34)

2.3.2.3 β -phase Structure

β -form it-PP has a hexagonal unit cell. Several conditions promote the formation of the β -phase. These include shear-induced crystallization, crystallization from an oriented melt, use of specific nucleating agents and crystallization under temperature gradients (74-76). The WAXD pattern for this phase is shown in Fig 2.13. The β -form can transform into the α -form (66,77-81). The spherulites for this form do not exhibit any cross-hatching, instead lamellae just radiate outwards from the center of the spherulites.

2.3.2.4 Smectic-Phase

This form is also referred to as the mesomorphic or liquid crystal-like form. It is unstable in nature. When the material is heated or if left above its T_g for long times, the smectic form transforms into the α -form. The smectic form is obtained by quenching it-PP samples from the melt to below room temperature. It is formed by chains in the 3/1 helical conformations with less lateral packing order than in the α -phase. Also the WAXD pattern has less defined peaks (82-84) for this form of it-PP.

2.4. Propylene Based Copolymers

Propylene can form copolymers with various olefins: ethylene, 1-butene (85), even octene and hexene (86).

When ethylene is copolymerized with propylene, it acts as a structural or chemical defect along the polymer backbone. It has also been observed that on the introduction of such groups, crystallinity, crystal thickness and related properties like melting temperature, tensile modulus and opacity decrease with increasing comonomer content (87,88).

Commercial propylene-based copolymers often contain 1-7 mol% of ethylene units. The copolymers show lower stiffness because of the insertion of ethylene repeat units. The interruption of propylene sequence leads to other properties like lower crystallinity and higher impact resistance. A wide range of properties can be obtained from different

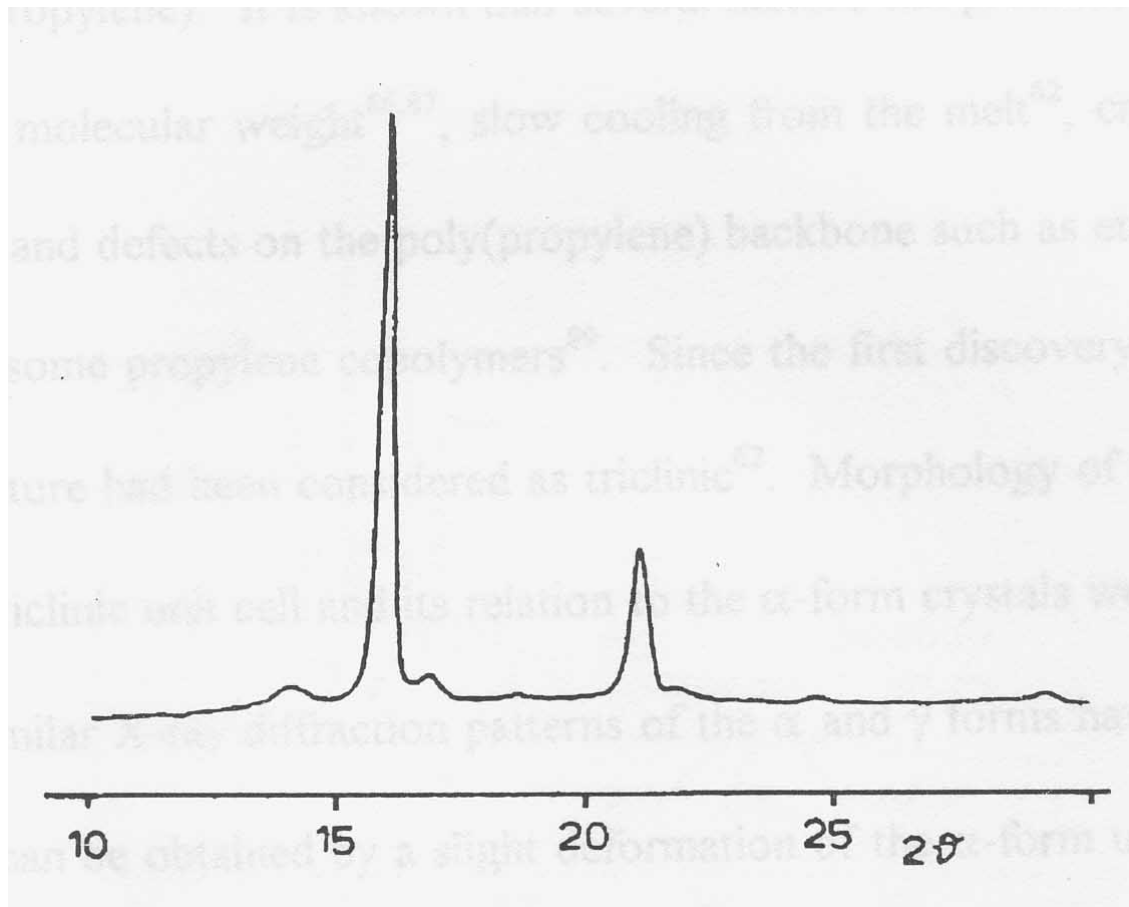


Fig 2.13 Powder X-Ray diffractogram of a β -form it-PP bulk sample (34)

grades of materials with different compositions, different molecular weights and different composition distribution. Also crystallographic properties like unit cell volume or surface free energy of the chain fold can change with increasing comonomer content (99-100).

It has been observed that the crystal structure of propylene/ethylene copolymers vary between two extremes. For low ethylene contents, the crystal structure is similar to that of polypropylene, while for higher content it is similar to that of polyethylene. Similar behavior has been observed for polypropylene/1-butene copolymers (89).

One of the most important questions to answer when dealing with such copolymer systems is whether the comonomeric units are incorporated into the crystalline phase or rejected into the amorphous interlamellar region (87,90-94). The extent to which these comonomers are included or excluded depends upon their size, thus on the free energy change associated with vacancies or with the steric repulsions they create in the lattice structure. The exclusion of comonomeric units into the amorphous region deeply affects the mechanical properties of copolymers.(95-98).

It has been shown that the inclusion of ethylene comonomer units in the polypropylene chain may have an influence on the regularity of the molecular structure (72-74,76,78). Turner-Jones (70) showed in the early 70's that a small amount of comonomer units in the polypropylene backbone could promote the formation of the γ -crystal phase.

Superstructures like spherulites are generally lost when comonomer defects introduced in high enough concentrations into the polymer backbone are rejected from the crystal lattice. Presence of non-crystallizable defects impedes crystallization by chain folding (11,17,18). It has been shown for ethylene/1-octene copolymers (17,18), that morphologies vary from spherulites with thick lamellae to isolated thin lamellae to bundle-like crystals with increasing 1-octene content. The degree of crystallinity continues to increase even after primary crystallization. This may be either be attributed to lamellar thickening and increase in crystal perfection (101,102) or to the formation of small lamellar structure between primary lamellae or in the inter-fibrillar region (103). In recent publications (104,105) it has been postulated that secondary crystallization may be associated with the formation of fringed micellar structure at high undercooling and block

like crystals at lower undercooling. Similar work carried out on random copolymers of ethylene with 1-butene, 1-pentene, 1-hexene (106) and styrene (24) have resulted in identical conclusions. The behavior of these copolymers is characteristic of copolymers where the minor comonomer is rejected from the crystal lattice of the major monomer. This behavior is very different from that exhibited by ethylene/propylene copolymers.

It would therefore be really interesting to compare and contrast the behavior of propylene based copolymers with different comonomer units, namely ethylene, 1-butene, 1-octene and 1-hexene. The crystallization and melting behavior, as well the mechanism of crystallization of these copolymers will be discussed. Much of the work reported will focus on propylene-based copolymers containing approximately 3mol% comonomer for which a number of studies convincingly show that the propylene unit can be included in the polyethylene crystal lattice.

Before going into the results and discussions, let's summarize some of the salient features concerning the properties of polypropylene and its copolymers. The present study is based on the understanding of the following features.

2.4.1 Existence of Multiple Crystal Phases

It has been known for some time now that *it*-PP is a polymorphic material with a number of crystal modifications, including the monoclinic(α) and the orthorhombic(γ). A detailed discussion of their structures and of the conditions which favor their formation has been provided in Section 2.3. The formation of these phases depends upon the conditions of preparation and also the presence of defects in the sample. These defects can be of three types: stereo defects, regio and chemical defects. In the crystallization of *it*-PP, essentially, α -phase modification is formed. But it has been amply demonstrated in the literature that the introduction of defects (regio or chemical), aids in the formation of the γ -phase. When the gamma phase is present in propylene based materials it is usually observed to coexist with the alpha-phase(51). The γ -phase was initially associated with the presence of heterogeneity in the polypropylene chain caused by atacticity or by copolymerization (70). Recent studies have demonstrated that it is also formed at high pressures (112). Turner Jones (70) considered that the presence of comonomer enhanced the formation of γ -phase. But, the polymers available at that time contained highly atactic material and hence the effects of atacticity couldn't really be separated from that of the

presence of comonomers. However with the advent of Ziegler-Natta and metallocene catalysts, high tacticity samples can be obtained and hence the effect of comonomer presence can really be considered.

2.4.2 Cross-hatching of Lamellae

As discussed in sections 2.3, the *it*-PP exhibits, lamellar branching that is unique among all crystallizable polymers and is manifested under a variety of crystallization conditions. The lamellar branching of α -*it*PP, in fact serves as a molecular marker which helps us get insight into the molecular structure which has no equivalent for any other crystalline polymer (51). The filiation between mother and daughter lamellae has been assigned to epitaxial interactions by Keith and Padden (113). The daughter lamellae in α branch at an angle of 100° or 80° to the parent lamellae.

As mentioned earlier, the γ phase is usually observed to coexist with the α -phase. Bruckner et. al. (66) first provided the real breakthrough in understanding the crystal structure for this phase. As mentioned in section 2.3.2.2, spherulites of γ -phase have shown positive birefringence like α -phase (67) which indicates that the γ -phase lamella branch on radiating α -phase (51).

2.4.3 Inclusion and Exclusion of Comonomers

There is disagreement in the literature regarding the inclusion or exclusion of comonomers. As discussed earlier, crystallization theories based on either inclusion or exclusion have been developed.

Zimmermann (86) for instance concluded structure on the basis of X-ray diffraction and DSC data that ethylene units are completely rejected from the PP crystal. His contention was that the heat of fusions normalized by the degree of crystallinity and the electron density difference between the amorphous and the crystalline phase do not change with increasing ethylene content. He also reported that the cell dimensions of the α -form is independent of the ethylene content. Other authors like Busico et. al (114) also found that the unit cells for both crystal forms are independent of copolymer concentration suggesting exclusion. They however suggested that the observed crystallinities for such materials were much higher than predicted by the exclusion model, thus suggesting inclusion of the comonomer in the crystal lattice. Avella et al (115) reported a systematic contraction in unit cell dimensions with increase in ethylene

content for α -form crystal providing support for the inclusion model. Gedde et al. (117,118) suggested that the ethylene units are also included in the PP crystal phase based on the changes in the unit cell parameters. Starkweather et al. (119) support the inclusion model on the basis of molecular mechanics calculations on model compounds. They suggest that such copolymers with low ethylene/propylene ratio are equivalent to it-PP from which a few methyl side groups have been removed. This allows the incorporation of ethylene units into the PP 3/1 helix. Thus, we see that the idea of inclusion or exclusion of the comonomer unit is very controversial. The changes in the lattice parameters cannot really account for the inclusion or exclusion of the comonomers since this can also happen as a result of changes in lamellar thickness changes (116). More recently, NMR studies of these copolymers to investigate the partitioning of the comonomer units in the crystal and amorphous phases (120). This study suggests that the ethylene comonomer is indeed included in the PP crystal phase. Further studies by Alamo et al. (126) suggest that although ethylene and butene units are included in the crystal structure, hexene and octene are not because of their larger sizes. These NMR studies indicate that branches longer than two ethylene units like the hexyl and the butyl are rejected into the interlamellar region as cannot be accommodated in the PP helix. These authors also noted a marked difference in crystallinity and melting points between PE, PH and PO, PE being much higher than the other two.

2.4.4 Multiple Melting Behavior

A survey of literature reveals that it-PP and its copolymers exhibit multiple melting behavior (24,89,117,121-125). This behavior has been attributed to a variety of factors from the melting of different phases, to melting-recrystallization-remelting effects to the melting of thick and thin lamellae. Multiple melting behavior has also been observed in our laboratory for Ethylene/Octene (104) and Ethylene/Styrene (24) copolymers.

Chapter 3

Experimental:

3.1 Introduction

In this chapter, the materials used throughout this study, are listed. Also, the way these materials have been prepared for the specific experiments are elaborated upon. The experimental details for the procedures used in characterizing the copolymers are described, including the equipment details.

3.2 Materials

The materials used for this study were provided by the Dow Chemical Company in Freeport, TX. The materials included the polypropylene homopolymer and propylene copolymers with ethylene, 1-butene, 1-hexene and 1-octene. The samples were provided in two sets. All materials were polymerized using single site catalysts. The chemical composition of these copolymers and their physical properties have been enumerated in the tables below.

First set of Propylene copolymer samples:

Sample	Comonomer	mole%	M _w (kg/mol)	M _w /M _n	T _m (°C)	ΔH _f (J/g)	Notes
67-A	None	0	371	3.23	154.6	116	1
67-C	Ethylene	2.63	245	2.49	141.3	91.4	2
67-D	Ethylene	7.2	135	~2.2	114.3	72.1	3
67-E	Ethylene	14.6	131	2.60	87.8	42.8	4
67-F	Ethylene	27.9	89	2.50	55.3	20.0	4
67-G	1-Butene	4.92	321	2.45	140.8	88.8	2
67-H	1-Butene	9.73	247	2.49	122.5	71.1	2
67-I	1-Butene	15.3	279	2.30	108.7	60.2	4
67-J	1-Hexene	4.84	249	2.26	109.0	54.8	1
67-K	1-Hexene	9.61	207	2.03	71.8	28.5	1
67-L	1-Hexene	13.5	168	2.10	40.2	18.4	4

67-M	1-Octene	3.43	134	~2.2	120.7	59.4	3
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Notes: (1)melt blended masterbatch, with stabilizer package; (2) dry blended masterbatch, no stabilizer; (3)single lot, with stabilizer; (4) single lot, no stabilizer.

Second set of propylene copolymer samples:

Databook#	Co-unit	Mole% target	NMR Data	T_m (°C)	ΔH_f (J/g)
199900847-55B	Ethylene	2	5.3	133.1	88.8
199900847-55A	Ethylene	5	5.8	121.7	69.7
199900847-55	Ethylene	10	10.1	101.6	62.6
199900847-55C	Ethylene	15	12.2	90.2	46.7
199900847-55D	Ethylene	25	20.6	52.1	20.5
199900847-50B	1-Butene	2	0.39	151.4	112.6
199900847-50A	1-Butene	5	3.28	142.6	102.8
199900847-47	1-Butene	10	7.58	129.8	85.5
199900847-52	1-Butene	25	11.2	78.8	40.2
199900847-53B	1-Hexene	2	3.05	119.6	73.7
199900847-53A	1-Hexene	5	9.70	72.6	26.5
199900847-45	1-Hexene	10	13.86	40.4	20.9
199900847-57	1-Octene	5	10.4	65.7	26.2
199900847-46	1-Octene	10	12.6	36.9	23.0

N.B.: The copolymer composition data presented above were provided by the Dow Chemical Company. The T_m and ΔH_f data were obtained upon heating at 10°C/min after quenching from melt. They are also presented in Fig 4.16 and Fig 4.14, respectively

Henceforth in this study, we refer to these samples using the following code: The first letter in the code would be P, for polypropylene, the second letter stands for the comonomer type and the numerical value following that represents the amount (mole %) of comonomer in the sample. For example a copolymer of Propylene with Ethylene

containing 2 mole % ethylene would be represented as PE-2. The homopolymer is simply represented as PP.

These samples were either in the form of small pellets or in powder form. To be able to run the various experiments to be described below, we first needed to prepare thin films of these materials. The thin films were prepared by melt pressing in a Carver laboratory press. The melt-pressing process first involves melting the material at 200°C for 2 minutes. The material was kept between two teflon sheets to avoid contamination, which in turn were placed between two metal sheets. After melting, the load applied to the material was cycled between 10,000 pounds and zero for a minute, to remove potential air bubbles. The material was then kept under constant load of 10,000 pounds for another minute, before releasing the pressure. The entire operation was carried out under a nitrogen atmosphere to minimize oxidative degradation. After releasing the pressure, the material was quenched in an water/ice mixture. Thin films obtained in such a way were approximately 100 μm thick.

3.3 Differential Scanning Calorimetry

Differential Scanning Calorimetric experiments were carried out on 100 μm thick samples in a Perkin Elmer DSC Pyris 1 operated under dry nitrogen purge with a ice-water bath as an heat sink. Sample and reference pans were carefully chosen to ensure that they had similar mass to simplify the thermal lag corrections. Sample masses were kept small (~ 3 mg) to further minimize thermal lag effects. Samples were encased in aluminum pans. Prior to crystallization, all samples were kept in the molten state for 2 minutes at 200°C. The specific details for each type of DSC experiment are included in the next chapter, where we report the results. The temperature calibration for cooling rate studies in the DSC was conducted by monitoring the isotropic to nematic transition of p-azoxyanisole which takes place at 136°C. The temperature calibrations during heating were done using an indium sandwich sample, where a small piece of indium was sandwiched between two pieces of the polymer sample. This was done to account for differences in thermal conductivity between polymers and metals. Appropriate baseline corrections were done for each run by running a scan using an empty pan instead of a sample pan and using that run as the baseline. Heat capacities in this study are not absolute heat capacities. These apparent heat capacities can however be used to follow

the evolution of crystallinity during cooling and heating. The heat flow rates for each calorimetric run is calculated and presented as a pseudo-heat capacity. The calculation is carried out as follows:

$$dq/dt = mC_p(dT/dt) \quad 3.1$$

where dq/dt represents the heat flow rate (mJ/s), m is the sample mass (mg), dT/dt is the heating scan rate ($^{\circ}\text{C}/\text{min}$). Thus we can get, C_p (specific heat) in J/gK. This however doesn't represent the true specific heat as we have not done a rigorous calibration for heat flow rates. Such calibration should be done using a sapphire standard and comparing the experimental heat capacity with those available in the literature. Such calibration, however does not significantly affect the inferred degree of crystallinity as the above procedure allowed a good match between the experimental and theoretical values for the heat of fusion of indium. Once we have the pseudo-heat capacity data, we choose an appropriate baseline and subtract the baseline from it, to get the final values for the heat capacities ($C(T)$ J/gK). The degree of crystallinity can then be calculated as a function of temperature using the following relation:

$$X_c(T) = -\Delta H_c(T) / \Delta H_f^0 \quad 3.2$$

where, ΔH_f^0 represents the theoretical heat of fusion of the fully crystalline polypropylene at the equilibrium melting temperature. $\Delta H_c(T)$ represents the area under the heat capacity curve and is obtained by integrating the curve over the temperature range from 200°C to the temperature T in $^{\circ}\text{C}$.

$$\Delta H_c(T) = - \int_{200}^T C(T) dT \quad 3.3$$

For ΔH_f^0 , we have used the value reported in the literature for the α -monoclinic form of it-PP (207 J/g)(110). The degree of crystallinity obtained in this fashion should be viewed as an approximate degree of crystallinity for a number of reasons: First, the heat capacity values used in the calculations are not absolute. Second, the heat of fusion for the copolymer crystals may be slightly different from the heat of fusion of α -phase it-PP. Finally, we have neglected the temperature dependence of the theoretical heat of fusion. Since all the estimations have been carried out using the same procedure, the

results presented here for different copolymers, although not absolute, can however be compared on a relative basis.

3.4 Atomic Force Microscopy

Sample morphologies were obtained in an Atomic Force Microscope, NanoScope III SPM instrument (Digital Instrument, Dimension 3000), operated in a tapping mode at room temperature using nanosensor TESP (tapping etched silicon probe) type single beam cantilevers. To minimize potential artifacts from tip broadening, the tip was replaced whenever the images were not reproducible. The thin films were melted with a free surface and then recrystallized from the melt in a Linkham heating stage, using iced water as a coolant. Details as to the various sample thermal histories are given in the next chapter.

3.5 Wide Angle X-ray Diffraction (WAXD)

Thicker samples were prepared for wide angle X-ray diffraction by molding. Once, the original samples were put in the mold, they were taken through the same cycle as for the thin films, in the melt press. After obtaining the desired thickness (~ 18 mm), the samples were melted at 200°C in an oven and then crystallized by extremely slow cooling in a nitrogen atmosphere. The optimum thickness, chosen to minimize absorption and maximize scattering of the X-rays was estimated from the sample density and mass absorption coefficients for carbon and hydrogen (122). The diffraction patterns were collected in the $\theta/2\theta$ mode at room temperature with a Scintag XDS 2000 with the nickel filtered Cu K α radiation of an X-ray source operated at 45kV and 25 mA. The details of the X-ray scan are given in the next chapter.

3.6 Optical Microscopy

The spherulitic structure of PB-3.28 has been examined during crystallization and subsequent heating by polarized light optical microscopy (Zeiss, Axioplan) using a Linkham heating stage with a temperature controller and a photographic camera. Samples prepared earlier as thin films were used. A retardation plate was used in the microscope to determine the sign of the birefringence of the spherulites.

Chapter 4

Results and Discussions:

4.1 Results

In this section we provide the results of all the experiments conducted on the various propylene copolymer samples. The experiments were of four types: Differential Scanning Calorimetry (DSC), Wide Angle X-Ray Diffraction (WAXD), Optical Microscopy and Atomic Force Microscopy (AFM). The underlying goal of these studies was to characterize the extent and the kinetics of development of crystallinity during cooling, the melting behavior, the morphology and the crystal structure of materials crystallized under specific conditions. Using these experimental results, a detailed comparison of these various copolymers can be carried out.

4.1.1 Differential Scanning Calorimetry

This section outlines the results obtained from the various DSC experiments conducted on the copolymer samples. The behavior of these samples was analyzed in three broad categories: In studies described below as 'Cooling rate studies', the melt crystallization behavior is monitored as a function of temperature during cooling at a specific rate. The subsequent melting behavior was then recorded at a rate of 10°C/min. The second set of experiments 'Isothermal Studies', is concerned with the time dependence of isothermal melt crystallization at various temperatures. The last set of experiments 'Heating rate studies', focuses on the effect of heating rate on the melting traces of various copolymers.

4.1.1.1 Cooling Rate Studies

To erase previous thermo-mechanical history, each sample was first kept in the melt state at 200°C for 2 minutes. They were then cooled at various rates (1, 2.5, 5, 10 and 20°C/min) to 20°C. Heat flow rates (apparent heat capacities) were monitored during each cooling scan. Subsequent to cooling to 20°C, each sample was heated at 10°C/min to the melt state.

The heat flow rate is plotted against temperature for PP-homopolymer (Fig 4.1), PE-2.63, PE-10.1 and PE-20.6 mol% (Fig 4.2), after baseline and thermal lag corrections. Cooling traces for PE-20.6 are only shown at 1°C/min, since negligible crystallinity

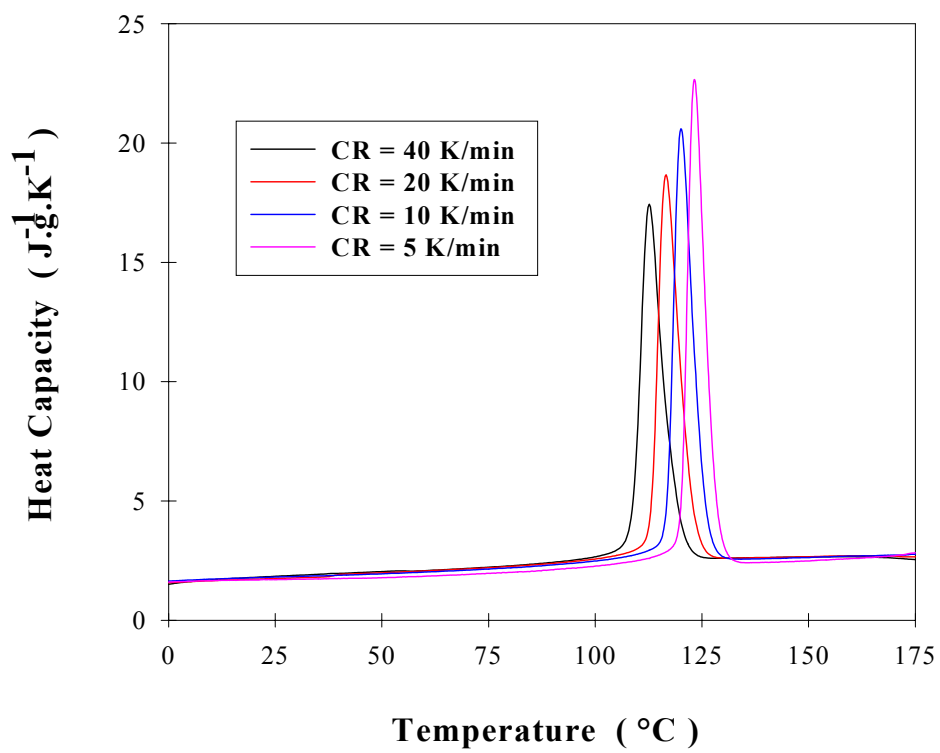


Fig 4.1 Heat flow rate versus temperature during cooling at various rates for pp-homopolymer (Dr. Xu's data)

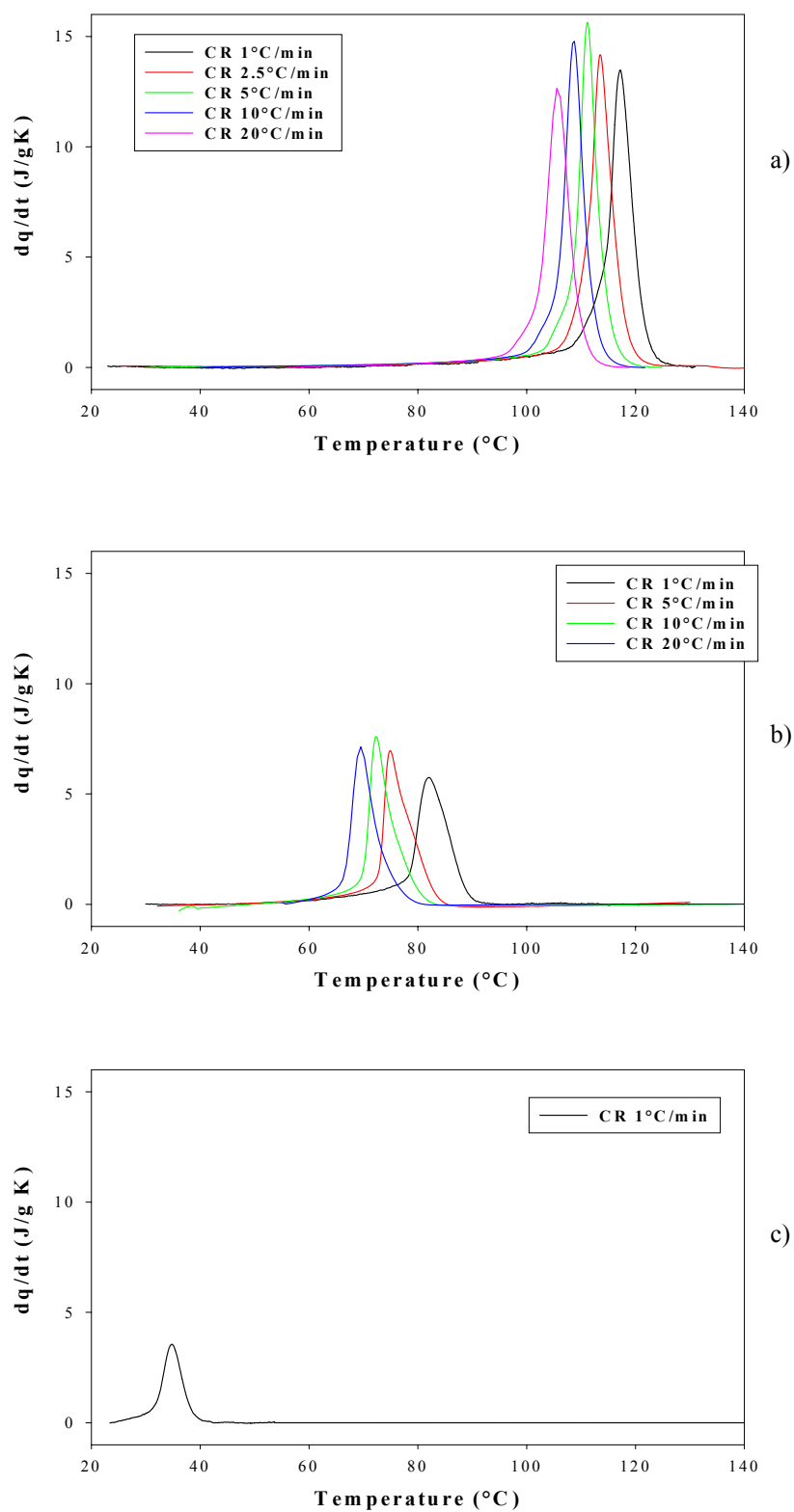


Fig 4.2 Heat flow rate versus temperature during cooling at various rates for a) PE-2.63%, b) PE-10.1% and c) PE-20.6%

developed during cooling at higher rates. Propylene/1-ethylene copolymers are observed to crystallize over a narrow temperature range and exhibit a single exotherm. The peak crystallization temperature or the temperature at maximum crystallization rate decreases as the cooling rate is increased. Furthermore, the peak crystallization temperature decreases significantly as the ethylene content, in the copolymer, increases.

The crystallization behavior of Propylene/1-butene copolymers under cooling at different rates is shown in Fig 4.3. The crystallization behavior for these copolymers appears to be very similar to that of the PE-copolymers. They also crystallize over a narrow temperature range and show strong cooling rate and copolymer composition dependencies.

For Propylene/1-hexene and Propylene/1-octene copolymers, the evolution of crystallinity during cooling is depicted in Fig 4.4. These copolymers show a very different behavior from the PE and PB copolymers. Specifically they exhibit a much broader crystallization exotherm which tails off to much lower temperatures.

The crystallization process in these copolymers takes place over a wide range of temperature. Upon cooling from the melt, the crystallization process is characterized by a sharp high temperature exotherm and a very broad low temperature exotherm. The crystallization process is far from complete in the temperature range shown. Again, we note that the peak crystallization temperature is very strongly cooling rate dependent and shifts dramatically towards lower values as the comonomer content is increased.

We then carried out DSC experiments wherein samples were heated at a rate of 10°C/min, subsequent to cooling at different rates. Subsequent heating rate data for PP-homopolymer is presented in Fig 4.5. For the subsequent heating of PE and PB samples (Fig 4.6 and Fig 4.7) (at 10°C/min), we see a sharp melting peak at high temperatures and a shoulder at lower temperatures. This shoulder is clearly manifested as a distinct peak for the slowest cooling rate and it gradually disappears as the cooling rate is increased. The melting temperatures decrease with increase in comonomer content. While PE and PB exhibit qualitatively the same behavior, the lower peak is observed much more clearly in the case of PB-copolymers than for PE copolymers. For both series of copolymers, the melting temperature decreases with increasing comonomer content.

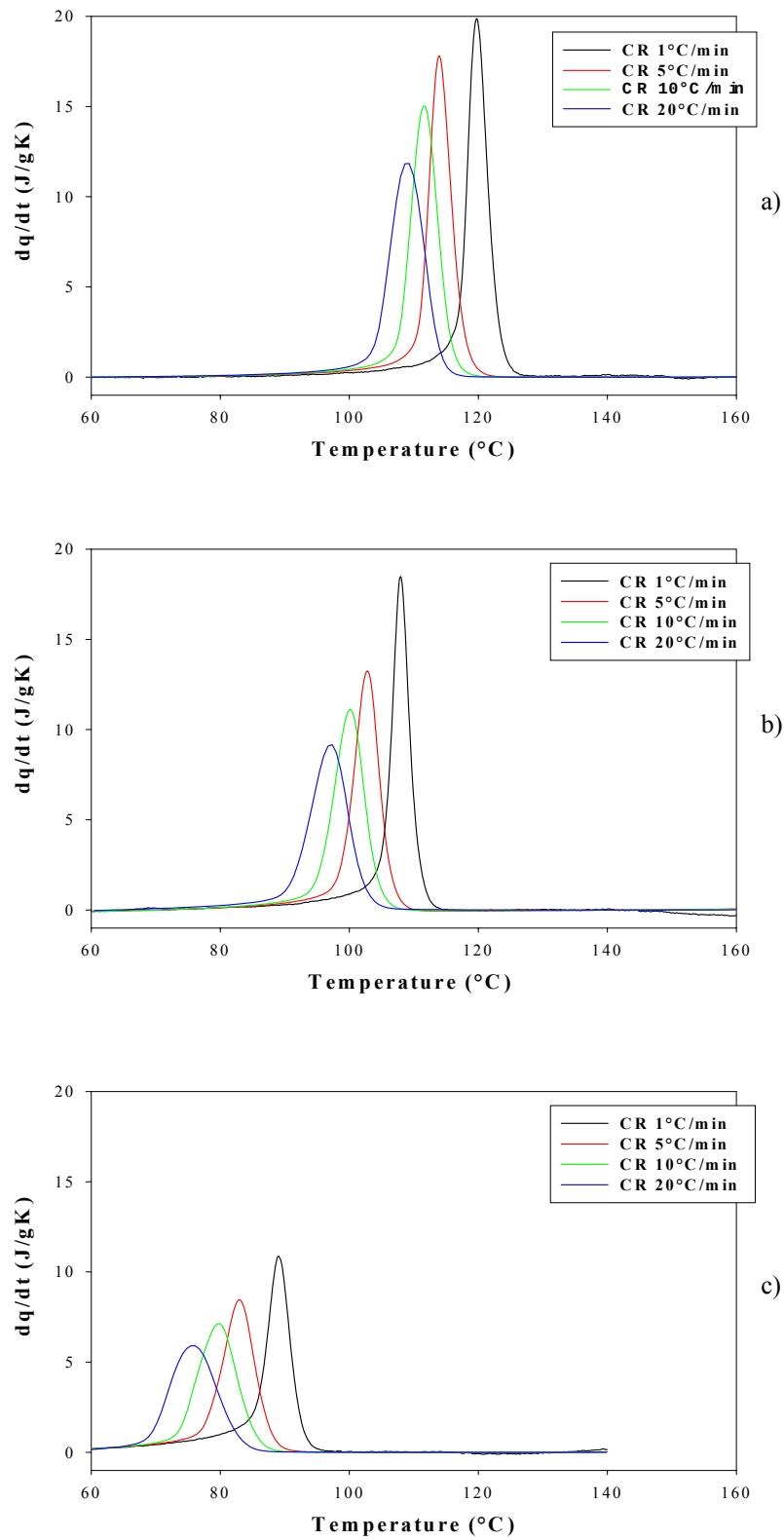


Fig 4.3 Heat flow rate versus temperature during cooling at various rates for a) PB-3.28%, b) PB-7.58% and c) PB-15.3%

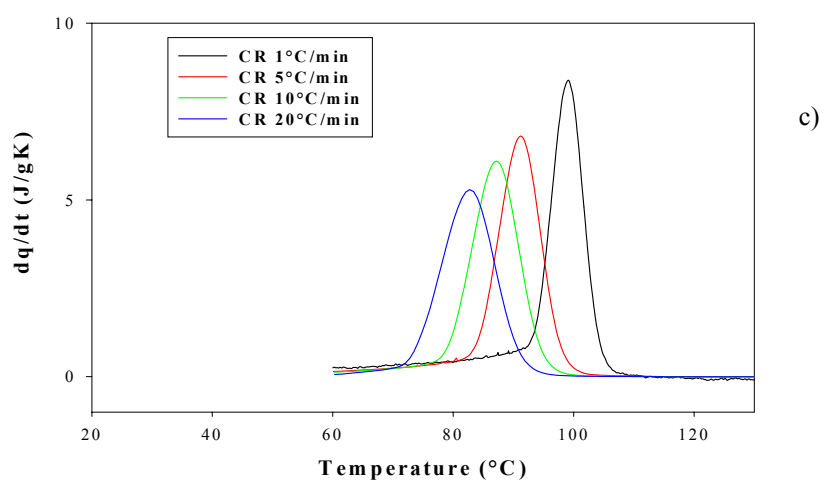
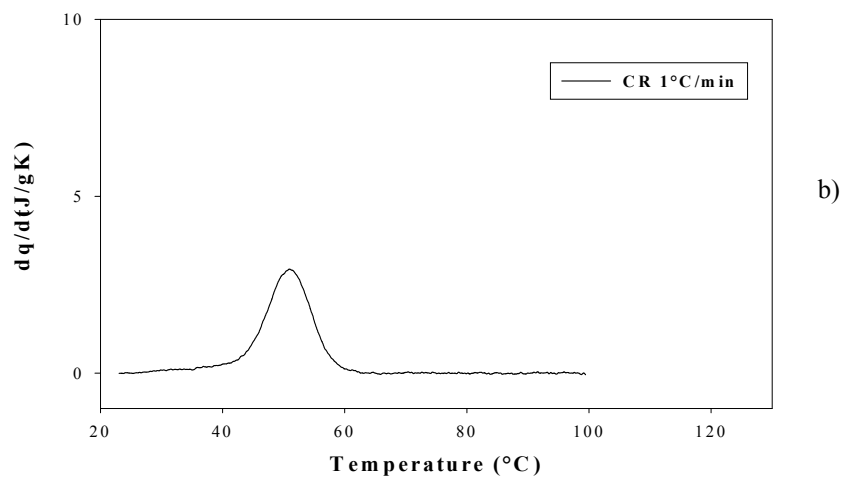
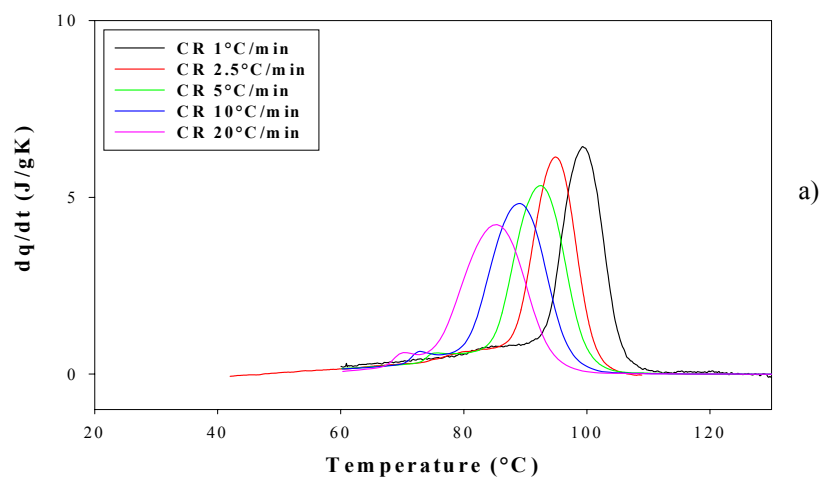


Fig 4.4 Heat flow rate versus temperature during cooling at various rates for a) PH-3.05%, b) PH-9.70% and c) PO-3.43%

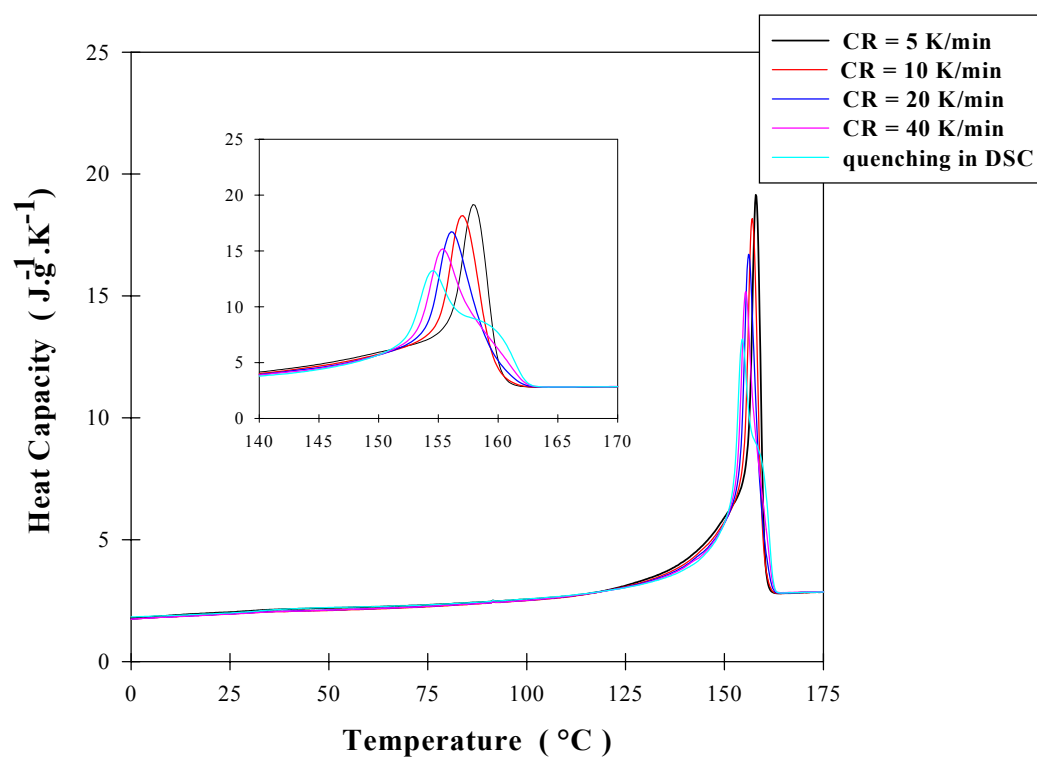


Fig 4.5 PP-homopolymer, cooled at different rates and then heated at 10°C/min till melting (Dr. Xu's data)

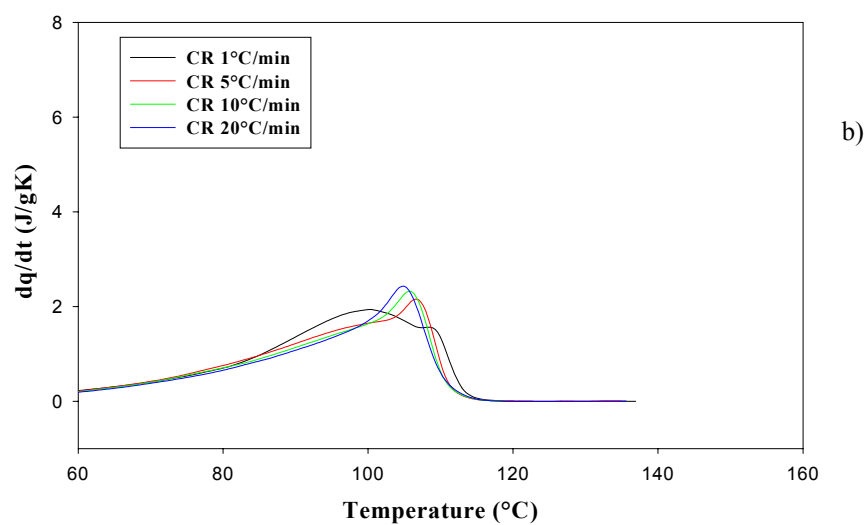
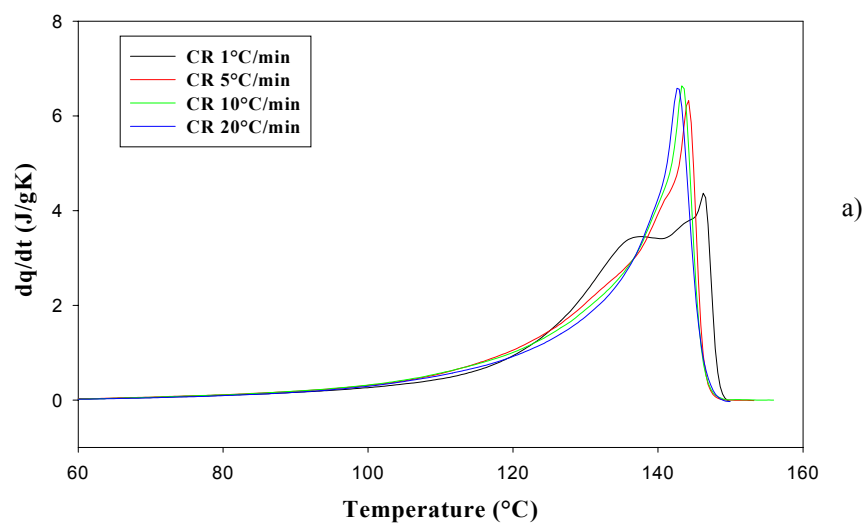


Fig 4.6 Heating traces recorded at 10°C/min after cooling from the melt at various rates for a) PE-2.63 and b) PE-10.1 mol %

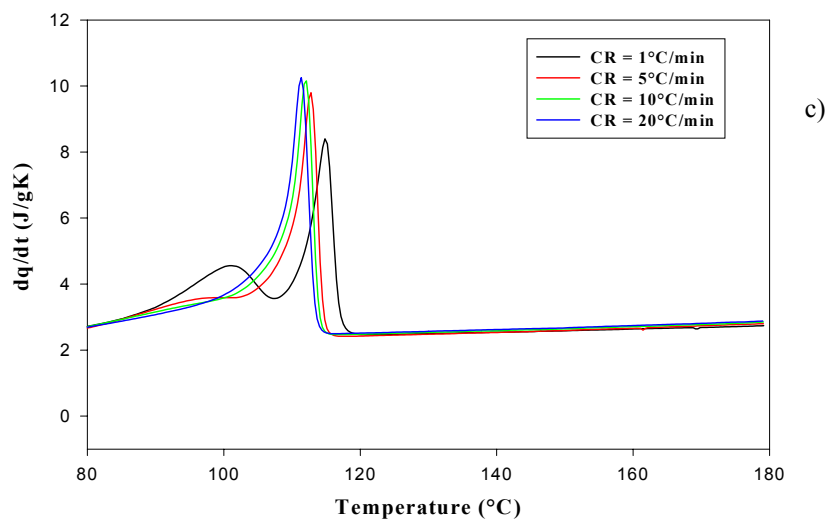
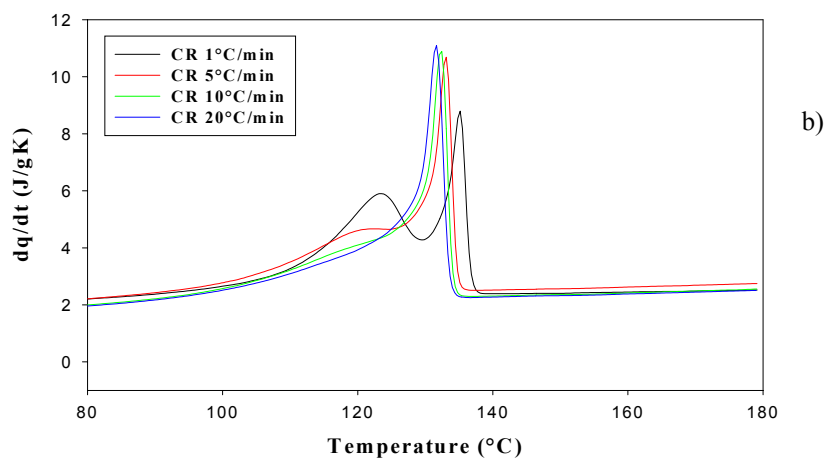
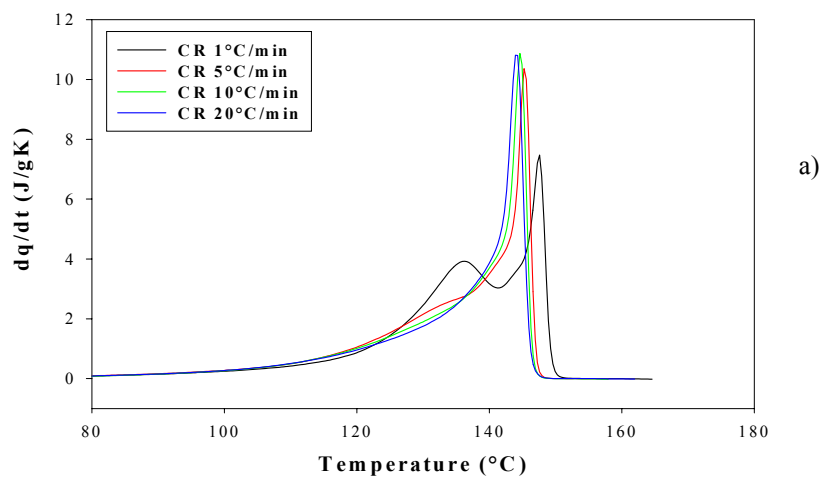


Fig 4.7 Heating traces recorded at 10°C/min after cooling from the melt at various rates for a) PB-3.28, b) PB-7.58 and c) PB-15.3 mol %

Results from similar experiments conducted on PH and PO copolymers are presented in Fig 4.8. A slightly different behavior is observed for this set of copolymers. The cooling rate dependence of the melting temperature is much less than that of the PB and PE copolymers. No distinct low temperature endothermic peak is observed for samples cooled at slow rates.

Figures 4.10, 4.11 and 4.12 show the development of the degree of crystallinity for the copolymer samples during cooling from the melt at different rates. The curves also show the decrease in crystallinity during subsequent heating after cooling at a specific rate. Examination of Fig. 4.10 and Fig. 4.11 reveals that the degree of crystallinity of PE copolymers reaches a plateau during cooling beyond a certain temperature. This temperature decreases steadily as the ethylene content increases. The same holds true for copolymers of propylene and butene. At similar comonomer concentrations, the crystallinity for PE is slightly lower than that of PB copolymers. For PH and PO, however we observe a different behavior (Fig. 4.12). The crystallinity for these copolymers continues to increase with a decrease in temperature and unlike the PE and PB copolymers we do not see a plateau region. We have also calculated change in crystallinity during heating for it-PP and for these copolymers (Fig 4.9, Fig 4.10, Fig 4.11 and Fig 4.12) to probe more thoroughly the crystallization mechanism. While we see that there is a hysteresis loop for each copolymer between the cooling and the heating traces, we also note that PH and PO copolymers, in contrast with PE and PB copolymers and it-PP, exhibit a reversible melting and crystallization region at low temperatures. The heating curve matches the cooling curve at low temperatures while at high temperatures it deviates appreciably.

In Fig 4.13 and 4.14, we show the heat of fusion for a heating rate of 10°C/min after different cooling rates and after quenching from the melt, respectively. The heat of fusion for PB is higher than for PE at all compositions. These in turn are considerably higher than those for PH and PO, which are very similar to each other. We also observe that the heat of fusion decreases with increasing comonomer content for all copolymers. Similar trends are observed for the peak melting temperatures (Fig 4.15 and Fig 4.16). Again, we observe a decrease in the melting temperature with an increase in comonomer content. As for the evolution of the melting peaks with comonomer content and type, the

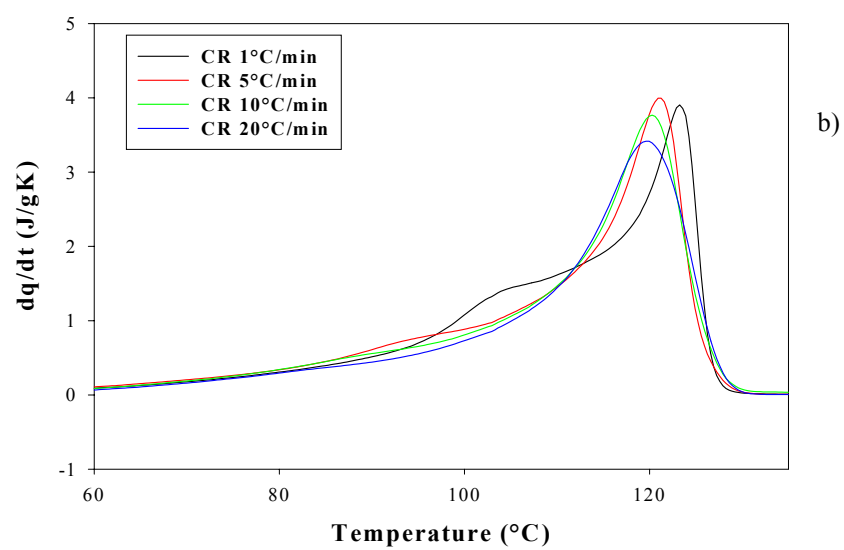
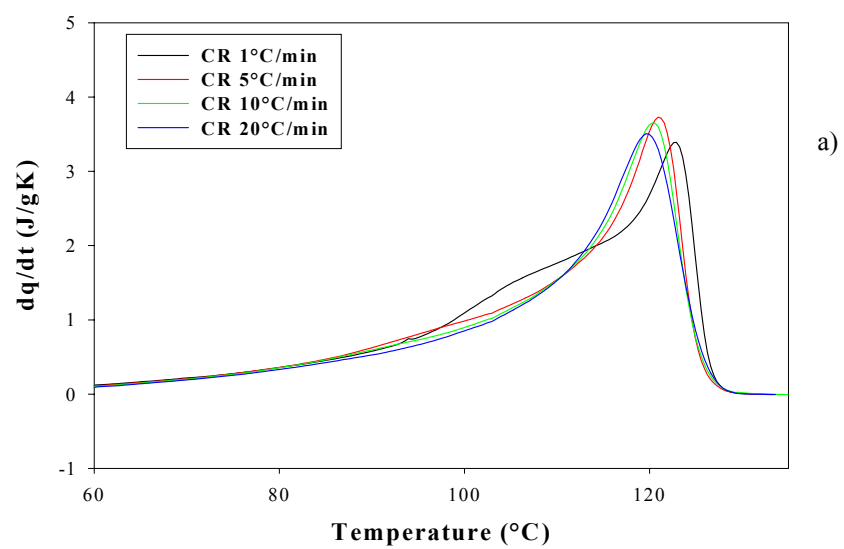


Fig 4.8 Heating traces recorded at 10°C/min after cooling from the melt at various rates for a) PH-3.05 and b) PO-3.43 mol %

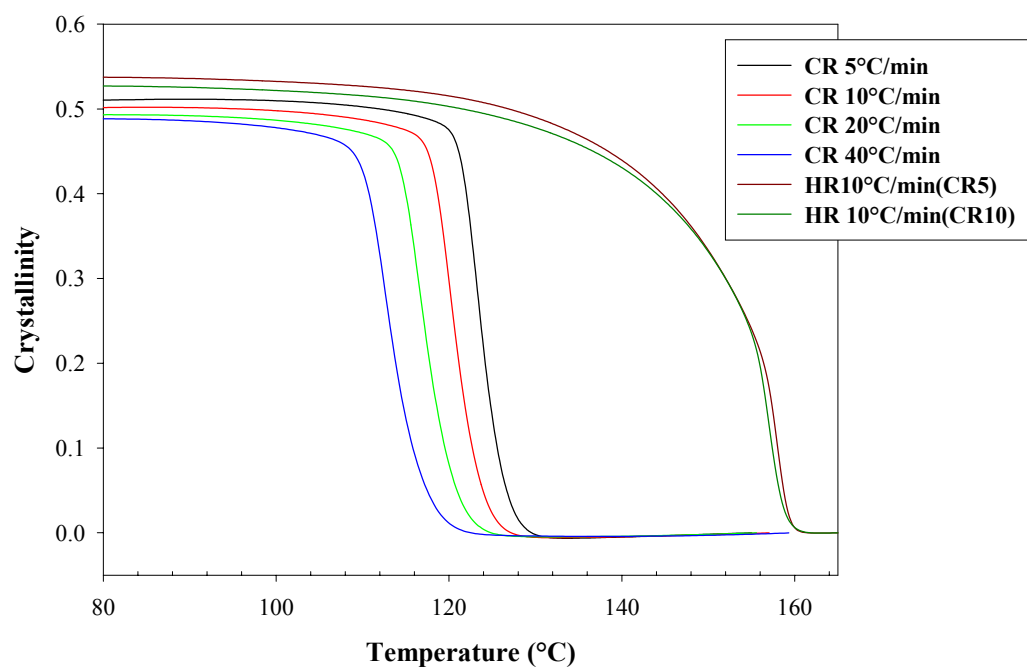


Fig 4.9 Degree of crystallinity as a function of temperature during cooling and subsequent heating for isotactic polypropylene homopolymer

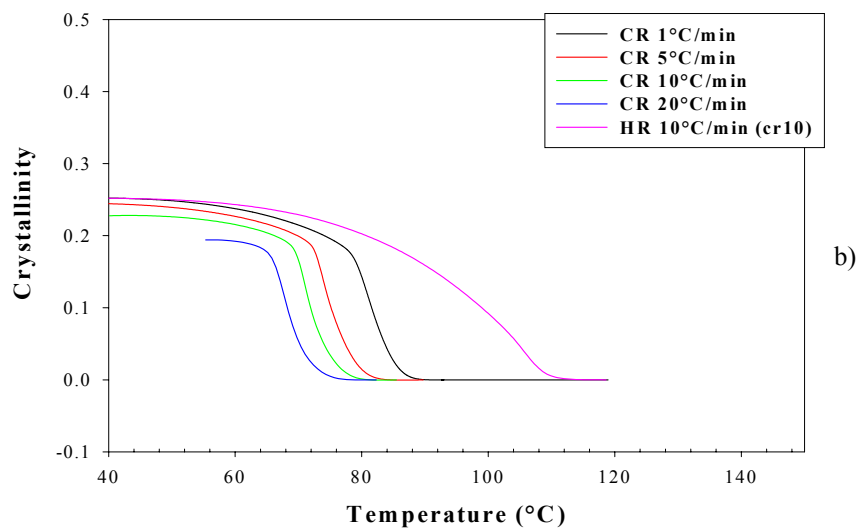
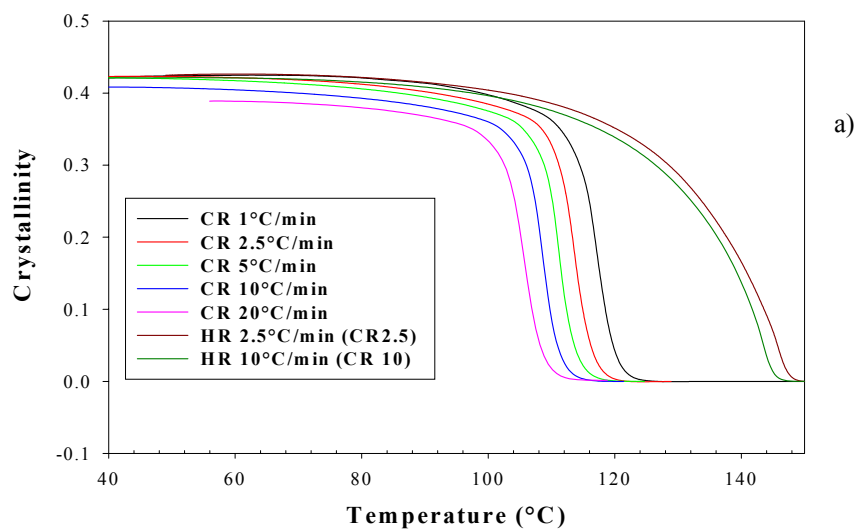


Fig 4.10 Degree of crystallinity as a function of temperature during cooling and subsequent heating for a) PE-2.63 and b) PE-10.1 mol%

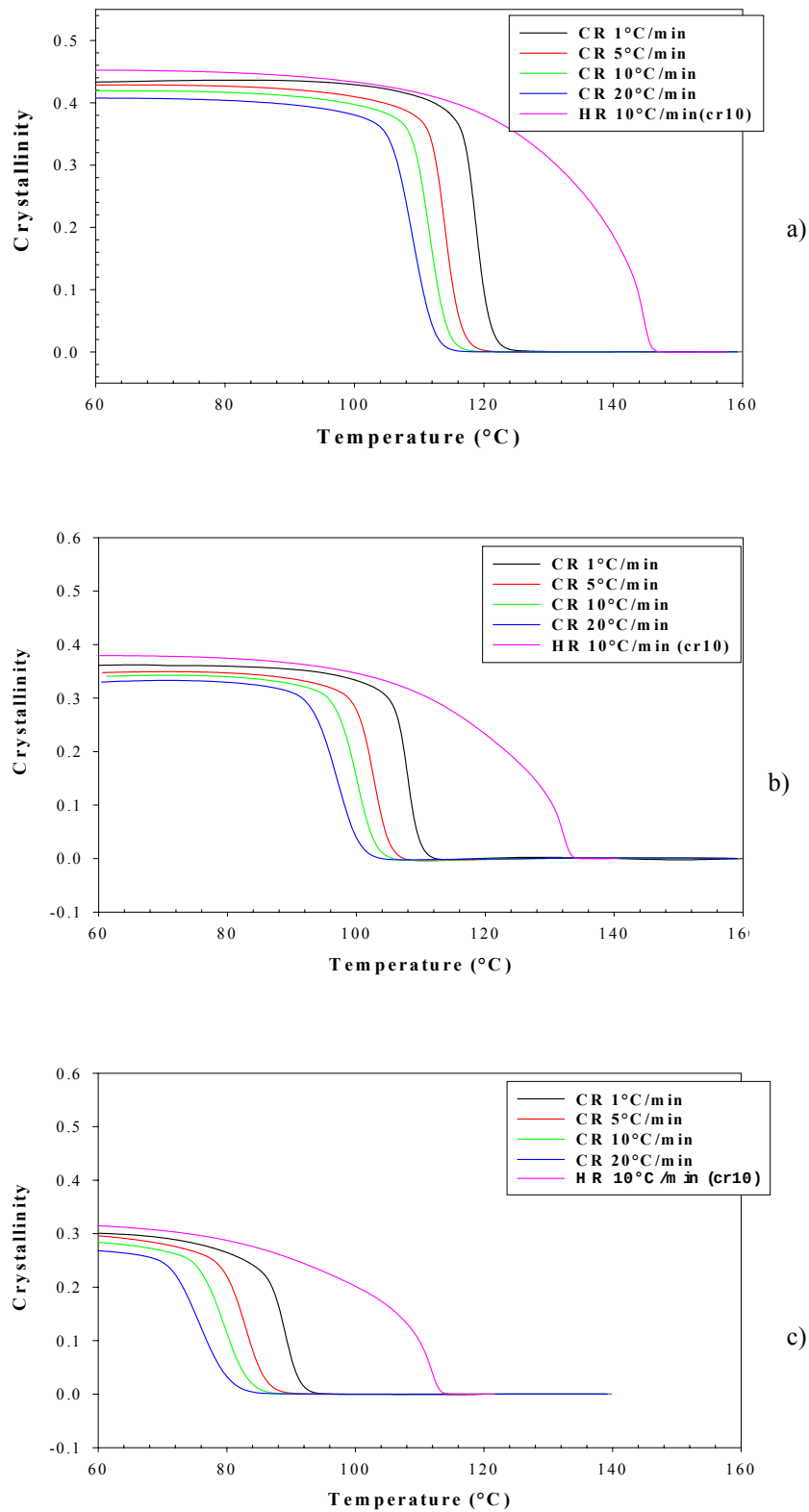


Fig 4.11 Degree of crystallinity as a function of temperature during cooling and subsequent heating for a) PB-3.28, b) PB-7.58 and c) PB-15.3 mol%

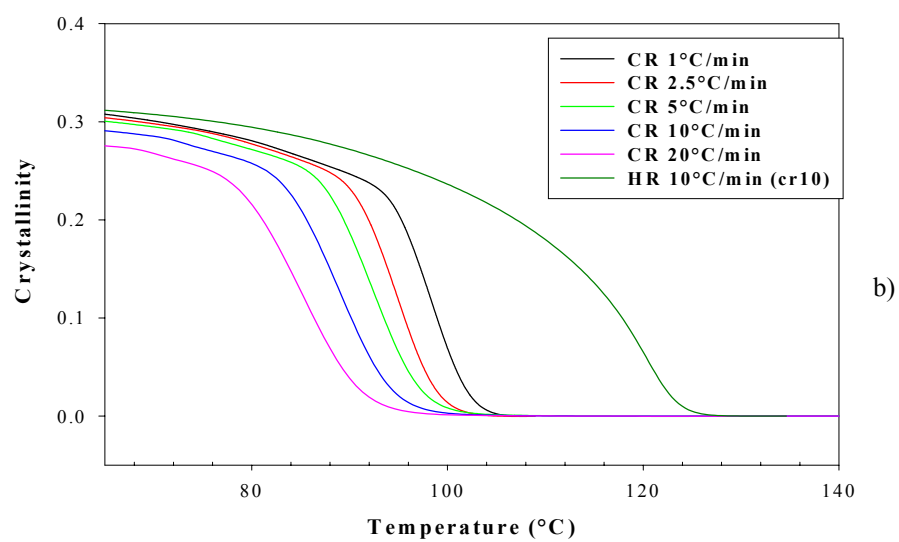
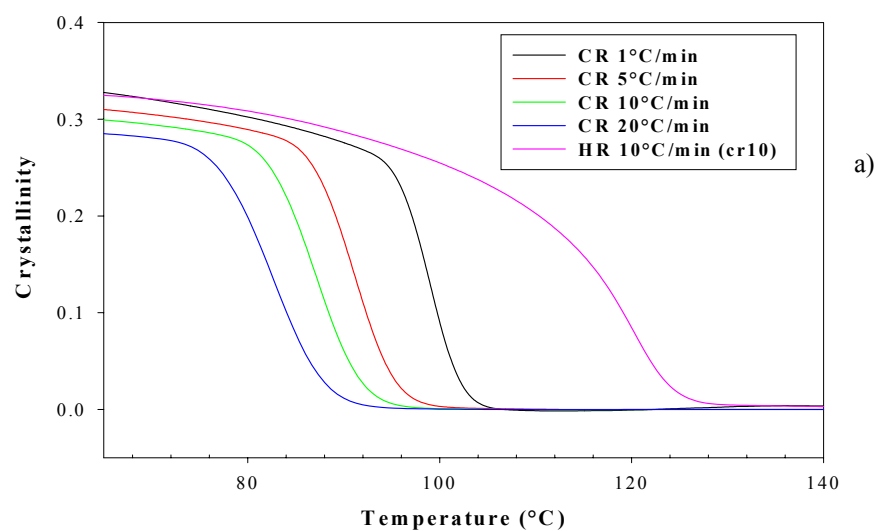


Fig 4.12 Degree of crystallinity as a function of temperature during cooling for a) PH-3.05 and b) PO-3.43 mol%

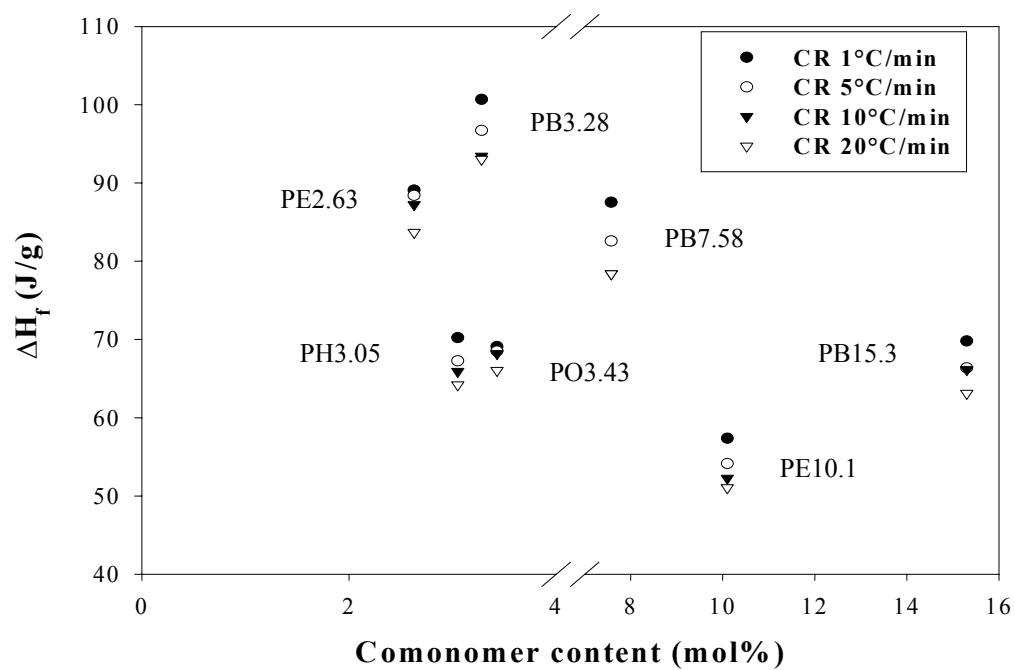


Fig 4.13 Heat of fusion at 10°C/min after cooling at different rates

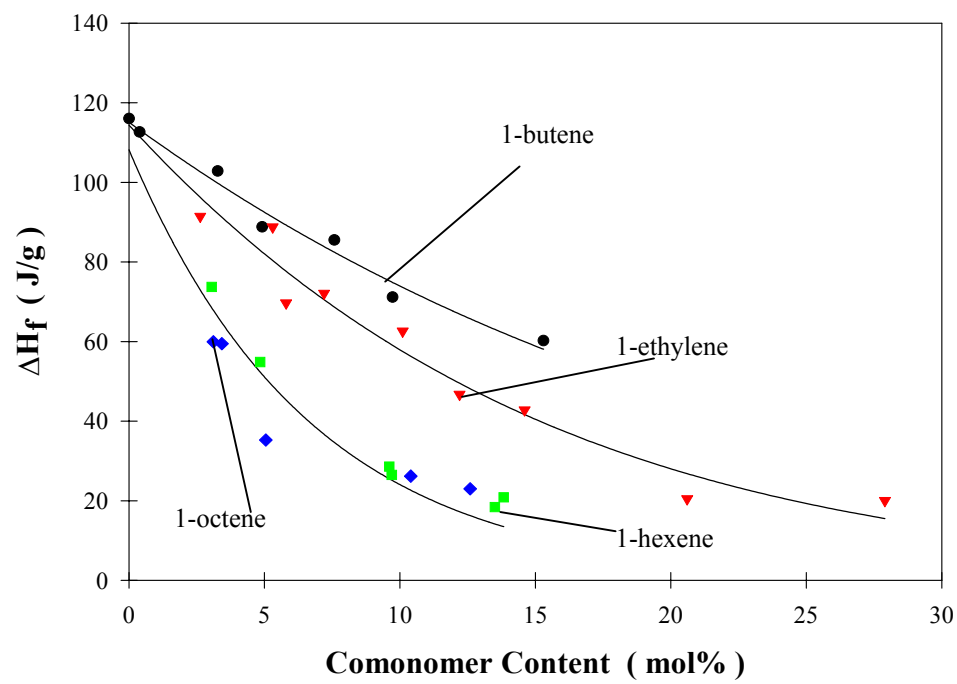


Fig 4.14 Heat of fusion at 10°C/min after quenching from the melt (data obtained by Dr. Xu.)

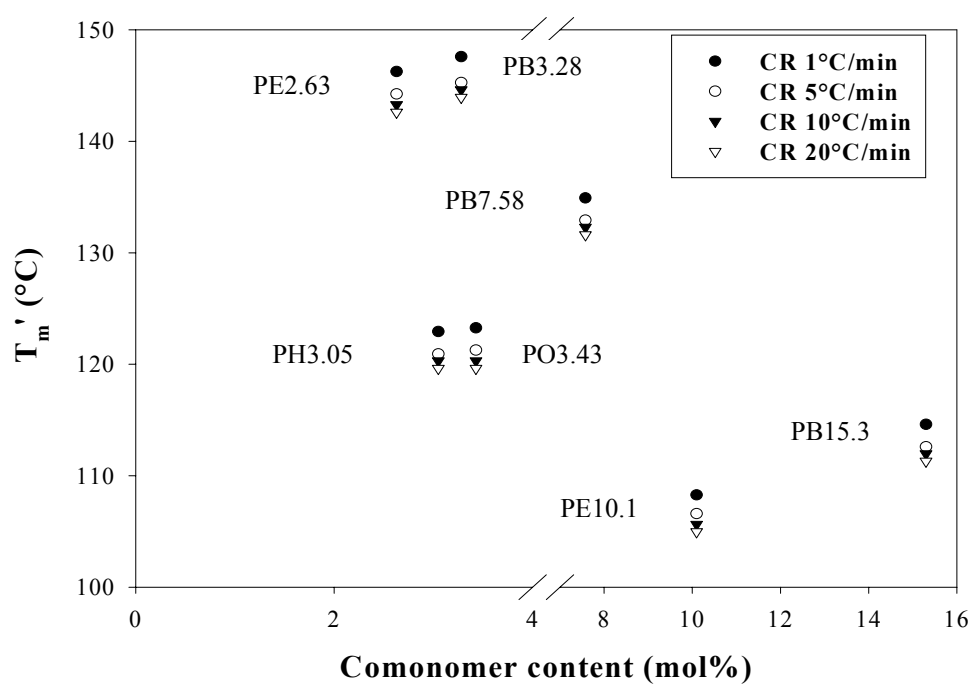


Fig 4.15 Melting temperature recorded during heating (10°C/min) after cooling at different rates

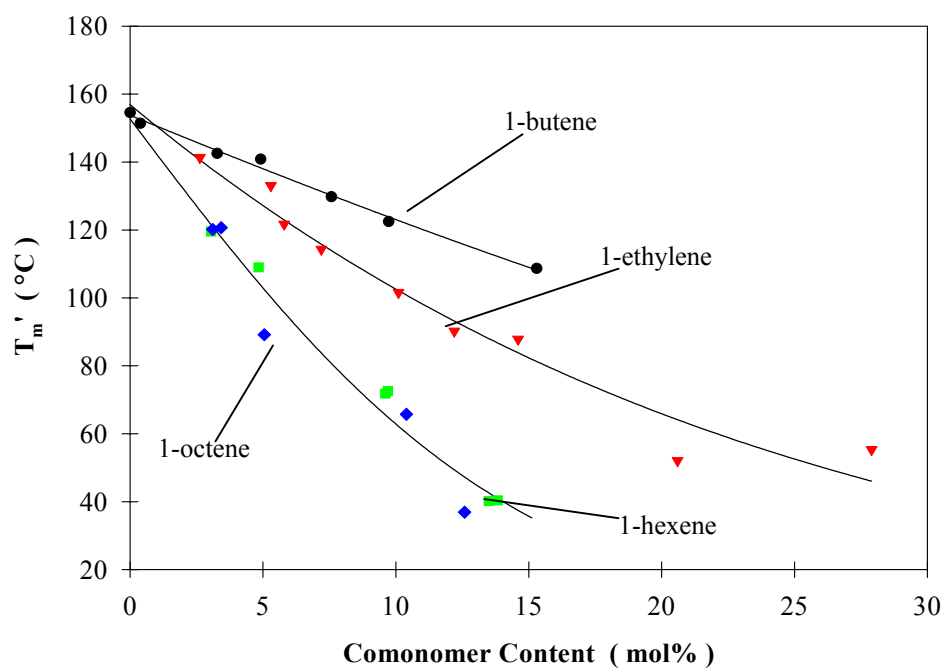
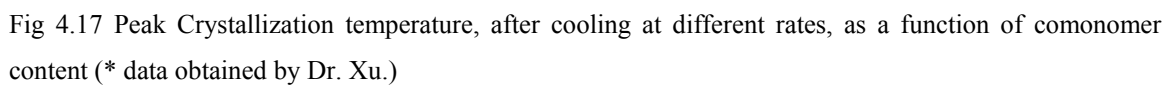


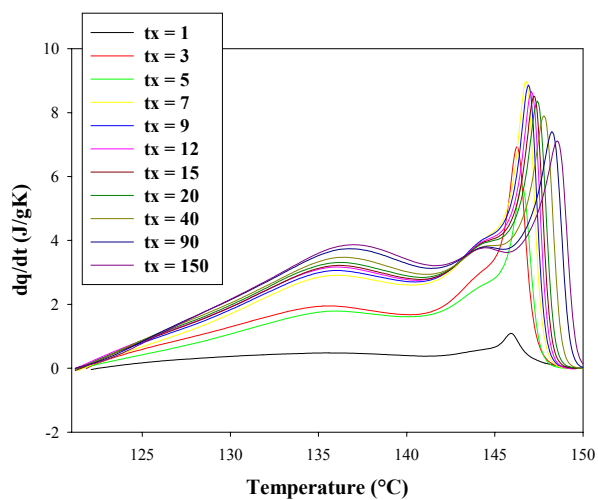
Fig 4.16 Melting temperature recorded during heating (10°C/min) after quenching from the melt (data obtained by Dr. Xu.)

melting temperature depression increases in the order $PB < PE \ll PH \sim PO$. The peak crystallization temperature (Fig 4.17) shows a trend very similar to that of the melting peaks. While PE and PB copolymers crystallize at slightly lower temperature than pure PP, PH and PO copolymers crystallized at much lower temperatures. Again, the increase in comonomer content results in a decrease in the peak crystallization temperature.

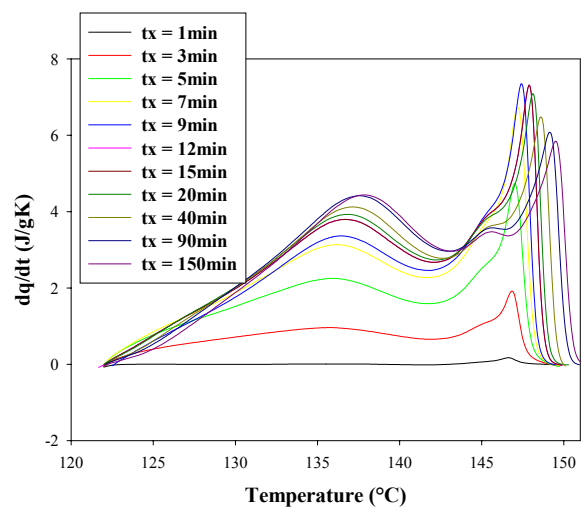
4.1.1.2 Isothermal Crystallization and Subsequent Melting Behavior

In this section, the crystallization kinetics will be investigated under isothermal conditions in temperature ranges determined from the cooling rate studies. The temperature range for isothermal crystallization is chosen so that no crystallinity develops during cooling and crystallization proceeds isothermally over a practical time scale (i.e. less than 1000 minutes). The samples are first melted by keeping them at 200°C for 2 minutes. They are then quenched (40°C/min) to the crystallization temperature (T_x °C). The samples are kept at this temperature for different times (t_x min) and then heated up to the melt state, at a rate of 10°C/min. Heating traces are thus recorded for various crystallization times and temperatures for the four copolymers. Such heating traces are shown for various crystallization temperatures and times for PE-2.63 (Fig 4.18), PB-3.28 (Fig 4.19), PH-3.05 (Fig 4.21) and PO-3.43 (Fig 4.22). For PE-2.63 and PB-3.28, we observe two distinct endothermic peaks. The lower endotherm is barely distinct at the lowest crystallization temperature but becomes prominent as the crystallization is carried out at higher temperature. In fact at higher temperatures, the lower endotherm becomes much larger than the higher endotherm. Both endotherms appear to shift to higher temperature as the residence time at a given crystallization temperature (T_x °C) increases. As expected, in all cases, an increase in crystallization temperature leads to a shift of the melting endotherms to higher temperatures. From examination of Fig 4.18 and 4.19, one concludes that both PB and PE copolymers behave in a very similar fashion. For PH-3.05 and PO-3.43, the behavior is very different from that shown by PB and PE copolymers. The melting endotherms for PH and PO copolymers are again observed at much lower temperatures. The upward shift in the case of PB and PE copolymers with time is not observed for PH and PO copolymers. The low endotherm becomes more prominent for higher crystallization temperatures and longer times.

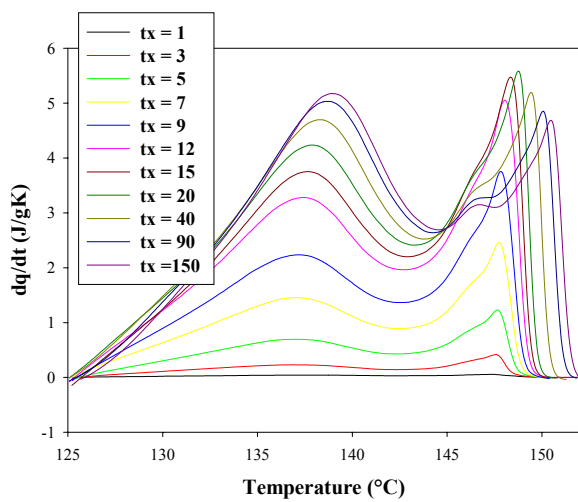




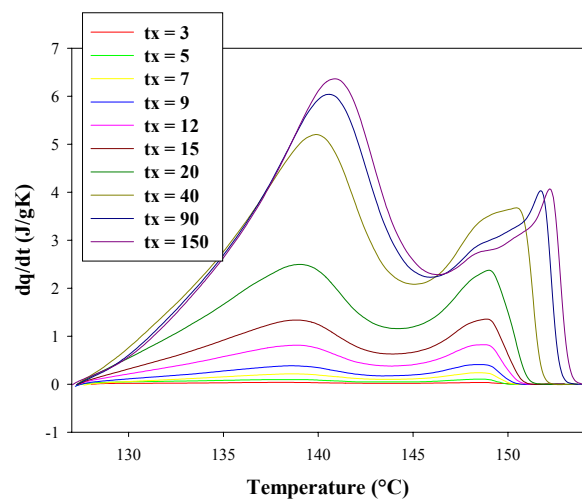
a)



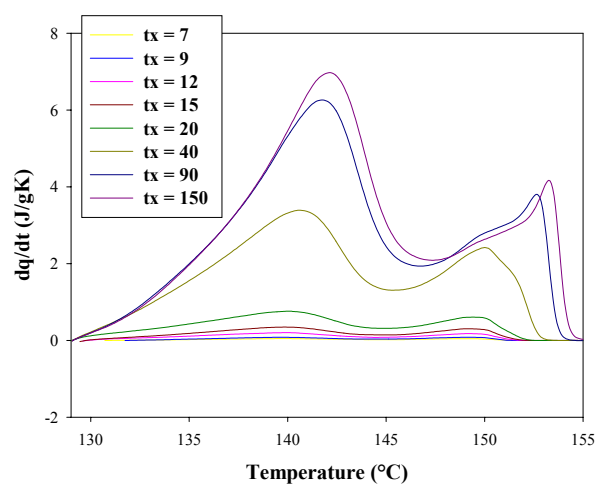
b)



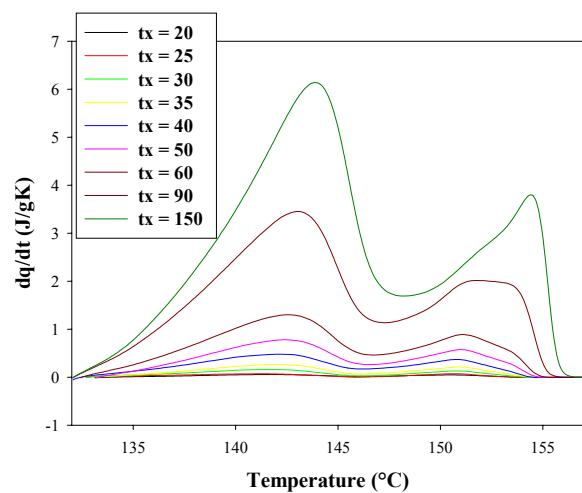
c)



d)

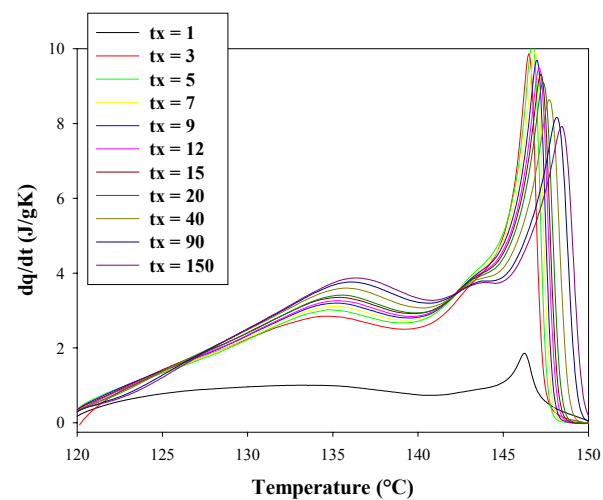


e)

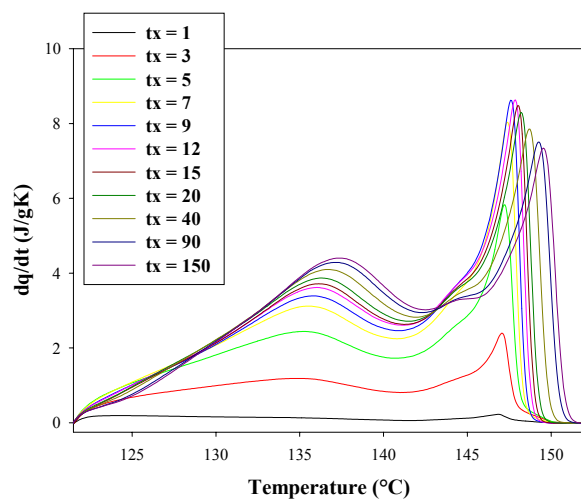


f)

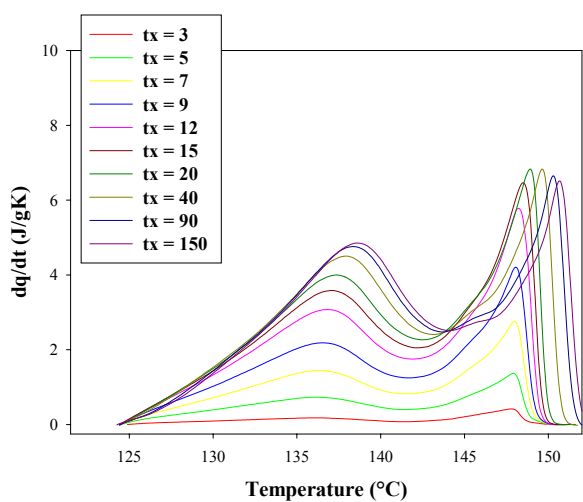
Fig 4.18 PE-2.63%, Heating traces after isothermal crystallization at a) 118, b) 120, c) 122, d) 125, e) 127 and f) 130°C for different times (in minutes)



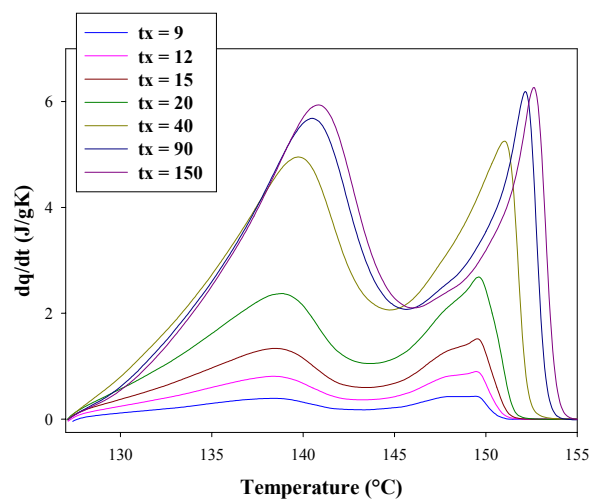
a)



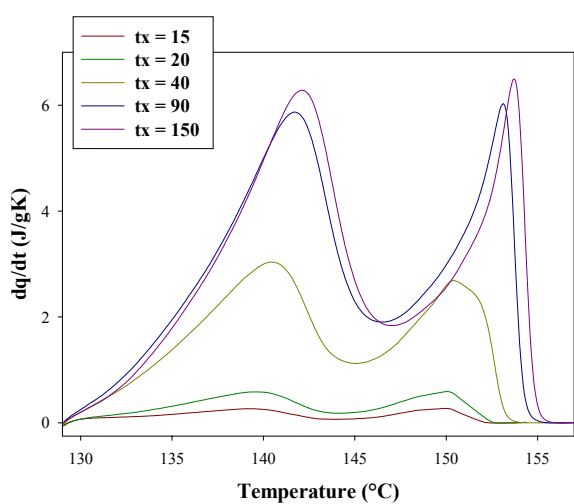
b)



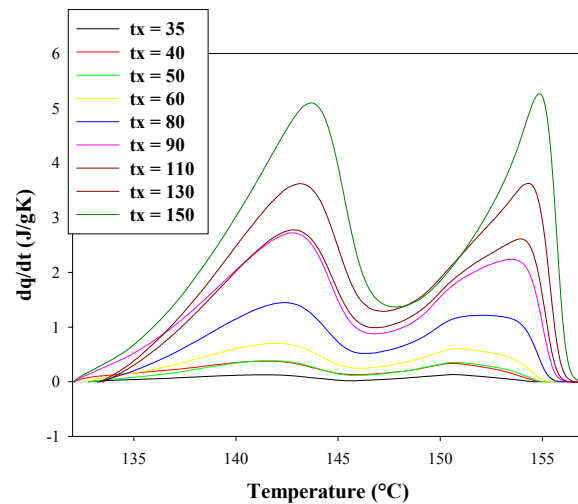
c)



d)



e)



f)

Fig 4.19 PB-3, 28%, Heating traces after isothermal crystallization at a) 118, b) 120, c) 122, d) 125, e) 127 and f) 130°C for different times (in minutes)

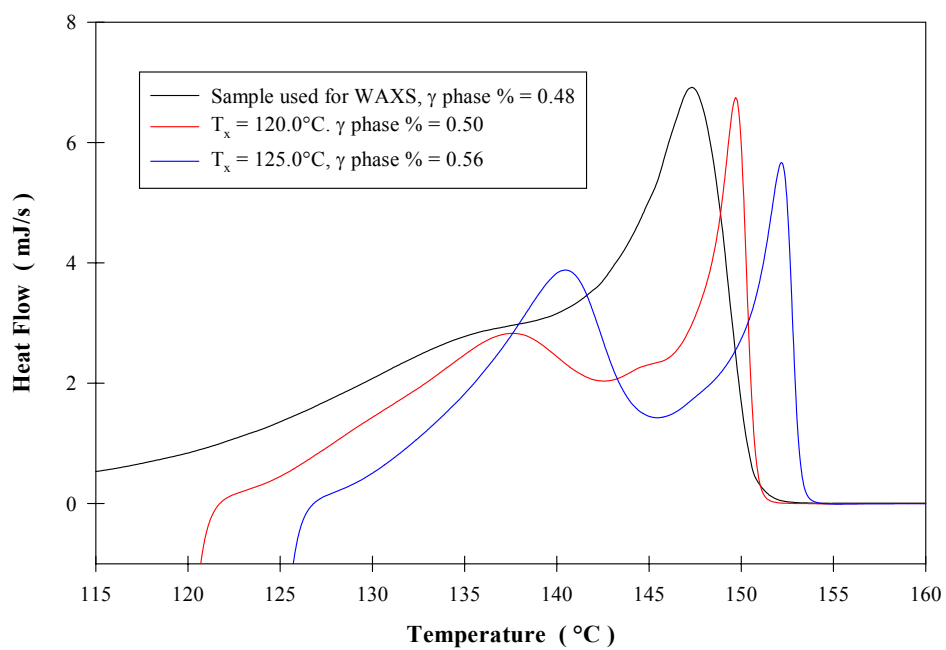


Fig 4.20 Heating scan at $10^\circ\text{C}/\text{min}$ after isothermal crystallization at T_x for PB-3.28 (data obtained by Dr. Xu)

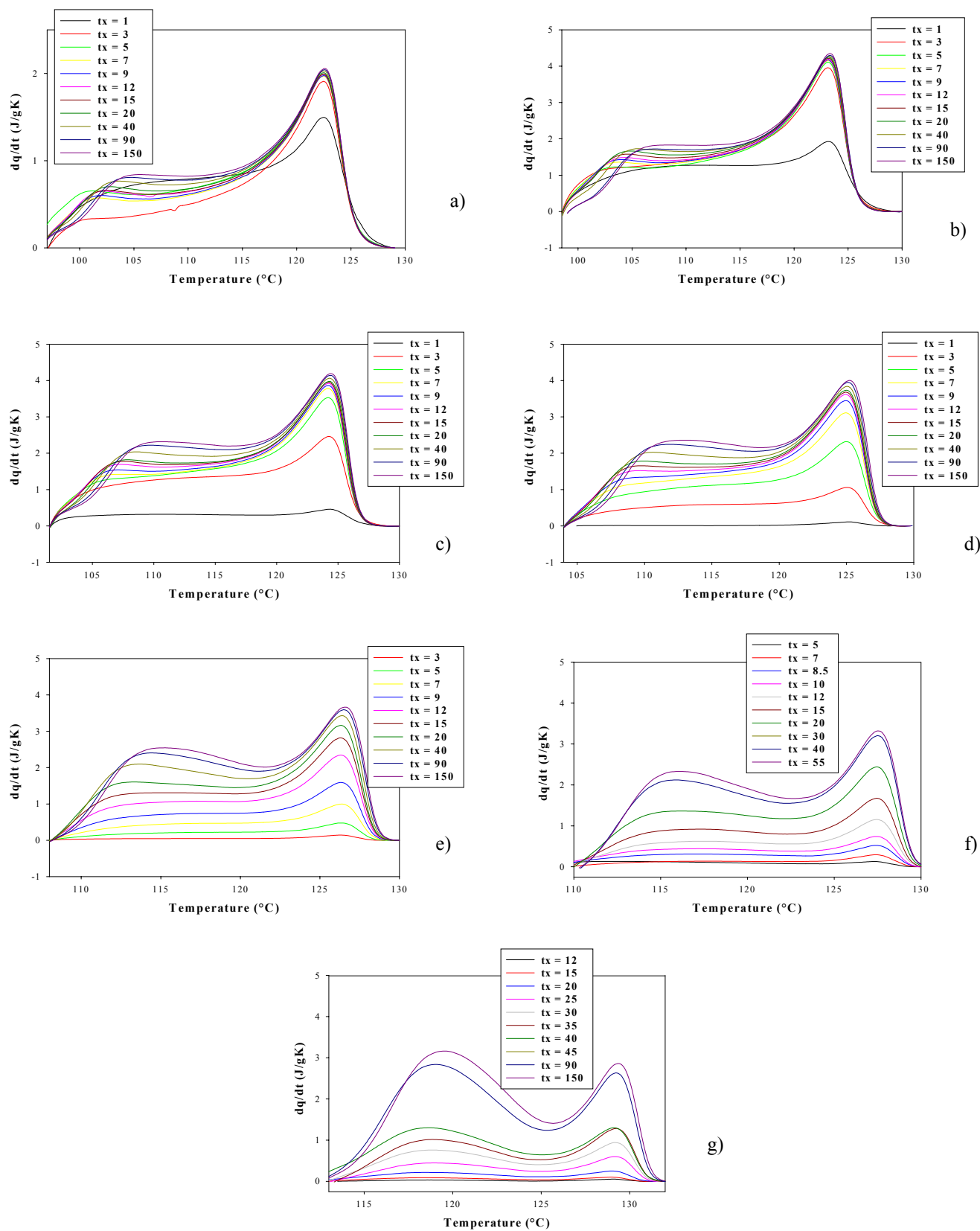


Fig 4.21 PH-3.05%, heating traces after isothermal crystallization at a) 95, b) 97, c) 100, d) 102, e) 105, f) 107 and g) 110 $^{\circ}\text{C}$ for different times (in minutes)

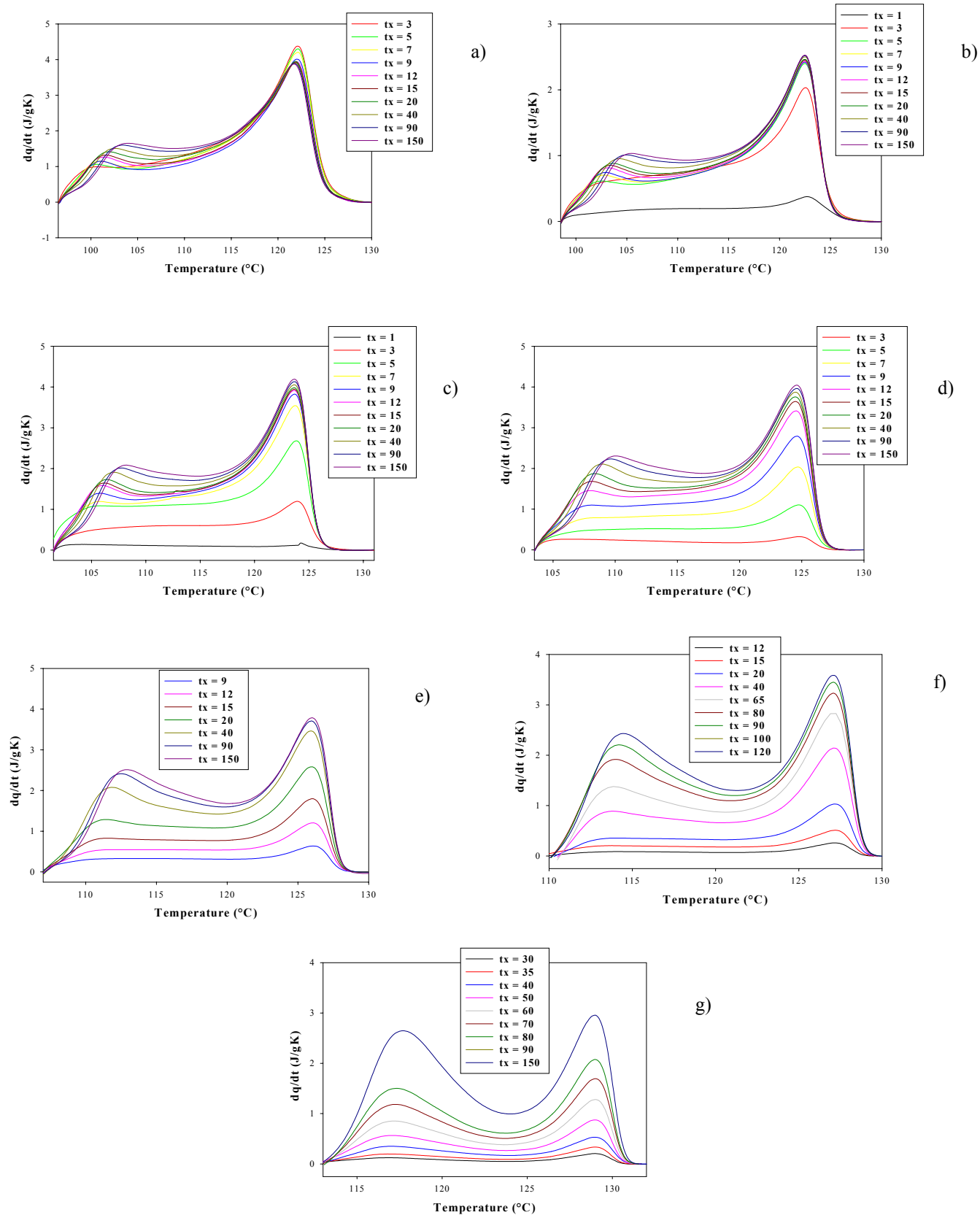


Fig 4.22 PO-3.43%, heating traces after isothermal crystallization at a) 95, b) 97, c) 100, d) 102, e) 105, f) 107 and g) 110 $^{\circ}\text{C}$ for different times (in minutes)

The low endotherms also show a shift towards higher temperature with an increase in crystallization time. A small hump or a third endotherm develops for PE and PB copolymers as the residence time increases for a particular crystallization temperature. This behavior is not shown by PH and PO copolymers.

In order to give a more quantitative characterization of these behaviors and to gain further insights in the mechanism of crystallization, one needs to obtain a mathematical representation of the above data for each of these four copolymers. For example, one can calculate the Avrami Exponent for each of the isothermal crystallization experiments.

The Avrami equation for short times or low degrees of crystallinity can be written as follows :

$$\Delta H_f = kt_x^n \quad 4.1$$

where ΔH_f is the enthalpy of fusion of crystals formed at T_x within the time t_x , k is the crystallization rate constant at that temperature and n is the Avrami exponent, which describes the geometry and the mechanism of crystal growth. The Avrami exponent, thus can be obtained by plotting the logarithm of ΔH_f against the logarithm of time (Avrami plot). The slope would thus represent the value of the exponent. On Fig 4.23 the Avrami plot for ΔH_f (the total enthalpy of fusion under both endotherms) is shown. In order to determine, whether the same crystallization mechanism applies for crystals melting at the low and high endotherms, we have 'deconvoluted' the peaks and obtained the heat of fusion associated with the individual endotherms. The 'deconvolution' has been done very crudely by drawing a vertical line from the minimum between the two endotherms to the baseline and evaluating the areas of individual peaks (Fig 4.24). Fig 4.25 shows the evaluation of the enthalpy of fusion associated with each endotherm for PB-3.28 crystallized at 125°C for different times.

To quantify the shift of the melting temperature with time, we fit the experimental data to the following relation:

$$T_m' = A(T_x) + B(T_x) \cdot \log(t_x) \quad 4.2$$

where $B(T_x)$ can be obtained from the slope of the T_m' versus $\log(t_x)$ plot (Fig 4.26).

The Avrami exponent and the quantity $B(T_x)$ are then plotted versus the crystallization temperature for the different copolymers.

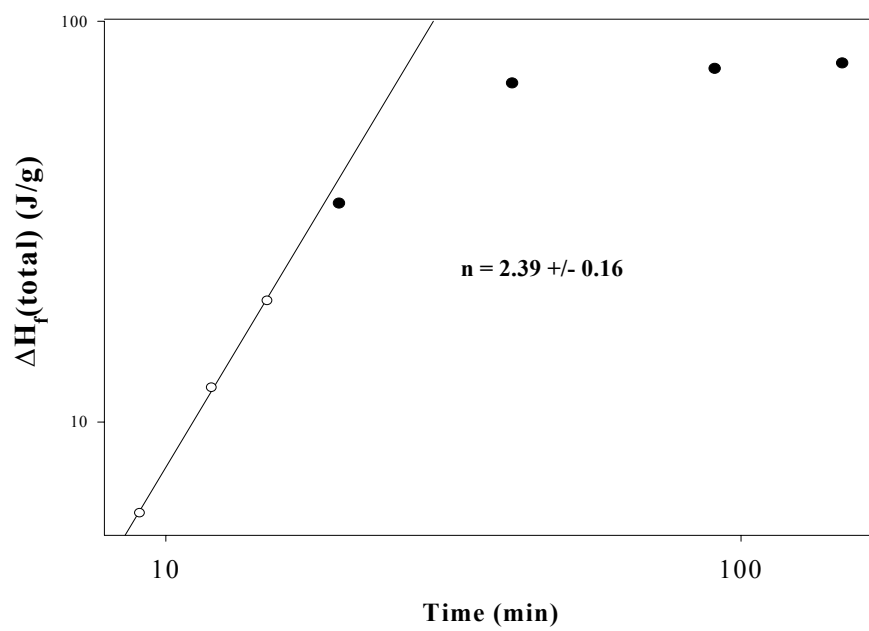


Fig 4.23 Heat of fusion (total) versus time for PB-3.28% crystallized at 125°C for different times

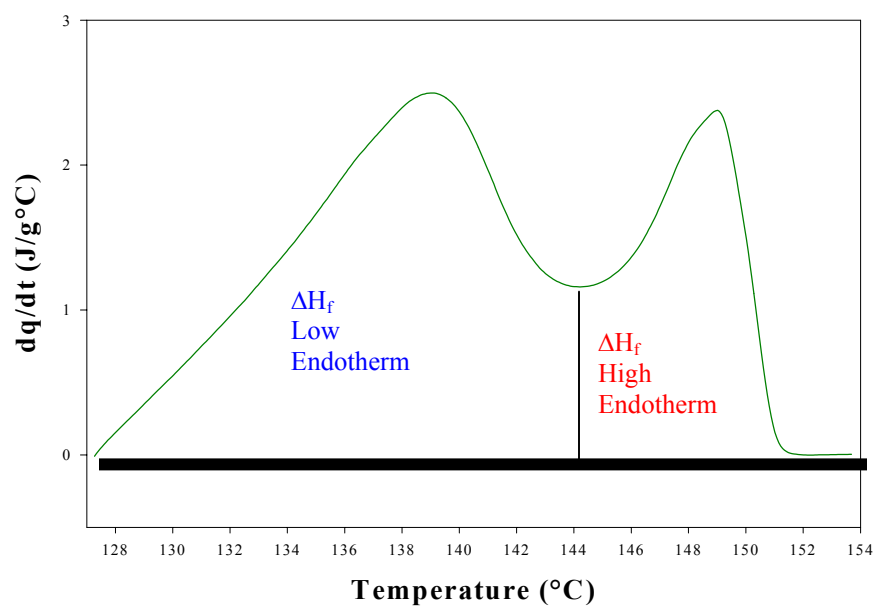


Fig 4.24 Deconvoluting into low and high endotherms

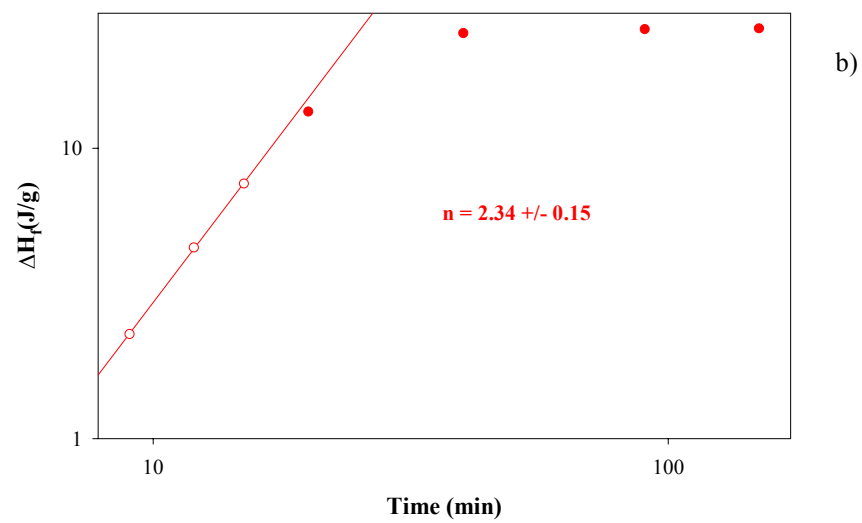
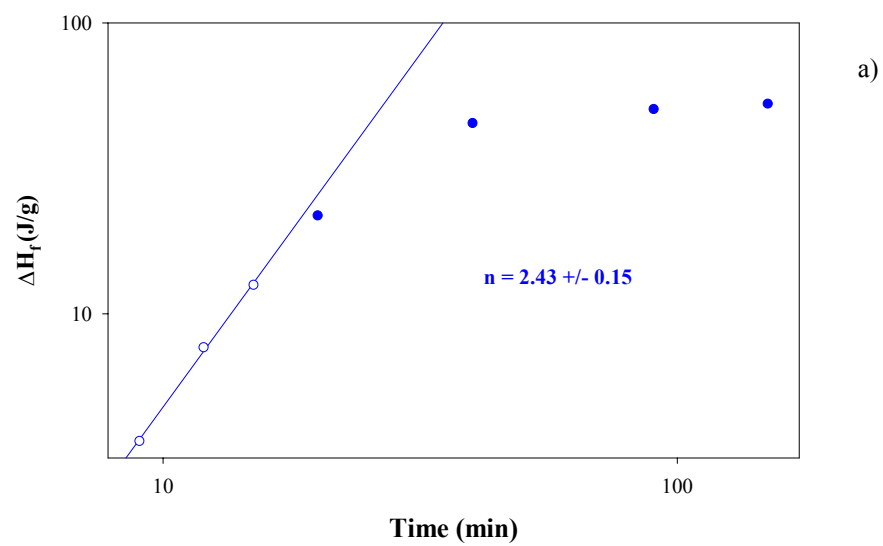


Fig 4.25 Heat of fusion versus time for PB-3.28 crystallized at 125°C for different times a) low endotherm
b) high endotherm

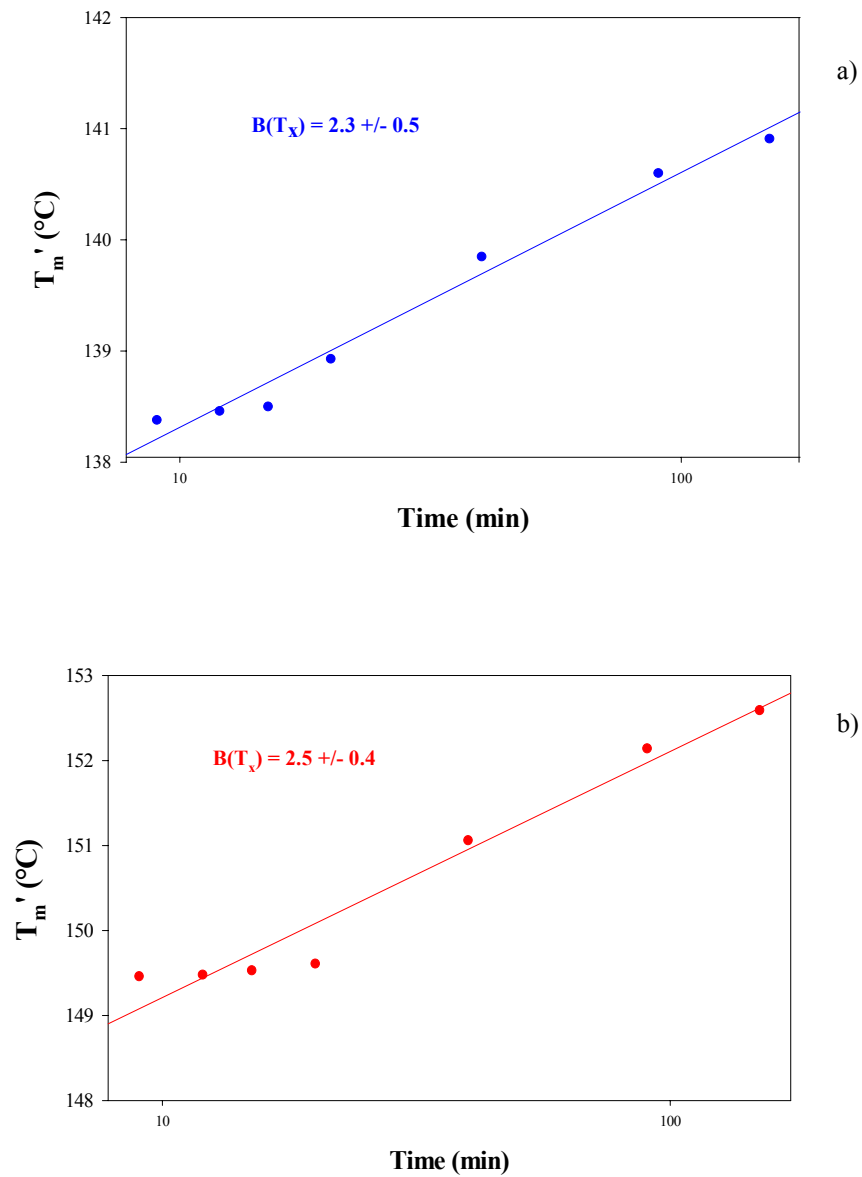


Fig 4.26 Melting temperature versus time for PB-3.28 isothermally crystallized at 125°C for different times
a) low endotherm b) high endotherm

Appropriate error bars are introduced to account for the statistical and observational errors incurred in figuring out the best fits for the $B(T_x)$ values and also in deconvoluting the two endotherms. Even within these uncertainties, the data still show definite trends.

The trends observed for various copolymers are basically of two types. While PE-2.63% and PB-3.28% show identical behavior, so do PH-3.05% and PO-3.43% but these patterns are extremely different from each other. For PE (Fig 4.28) and PB (Fig 4.27) the $B(T_x)$ values lie anywhere between 1-7 . Also, it increases steadily as the crystallization temperature increases. This behavior is seen for both the low as well the high endotherms for both PE and PB copolymers. The Avrami exponent lies between 2-3 and also shows an increase with increasing crystallization temperature. We also observe that upon deconvolution of the peaks, the Avrami exponent for each follows almost the same path, indicating that the mechanism of crystallization for crystals melting at the low and high endotherms may be similar. Because crystallization occurs very rapidly at 118 and 120°C, the error involved in getting the Avrami exponents would have been too large and hence are omitted.

For PH-3.05% (Fig 4.29) and PO-3.43% (Fig 4.30), the quantity $B(T_x)$ exhibits an extremely interesting temperature dependence. The quantity $B(T_x)$ for the lower endotherm is approximately constant at low temperatures and decreases with temperature at higher temperatures. $B(T_x)$ values for the higher endotherm are very small and show only a slight increase as the crystallization temperature increases. In the case of PO-3.43%, the initial $B(T_x)$ values for the higher endotherm are slightly negative, suggesting that the melting temperature decreases with an increase in crystallization time. The deconvolution into low/high endotherms for this sample was much more difficult especially at low crystallization temperature since the endothermic peaks were not very well defined and were broader and flatter. As negative values of $B(T_x)$ are not physically meaningful, it is safe to assume that at low temperature $B(T_x)$ is zero for crystals melting at the high endotherm. The Avrami exponent is then calculated for the entire endotherm and separately for the low and high endotherms and plotted versus crystallization temperature. Again we see that the magnitude of n for PH-3.05% lies between 2 and 3 while that for PO-3.43% lies between 1 and 2. Again it is seen for both PH and PO

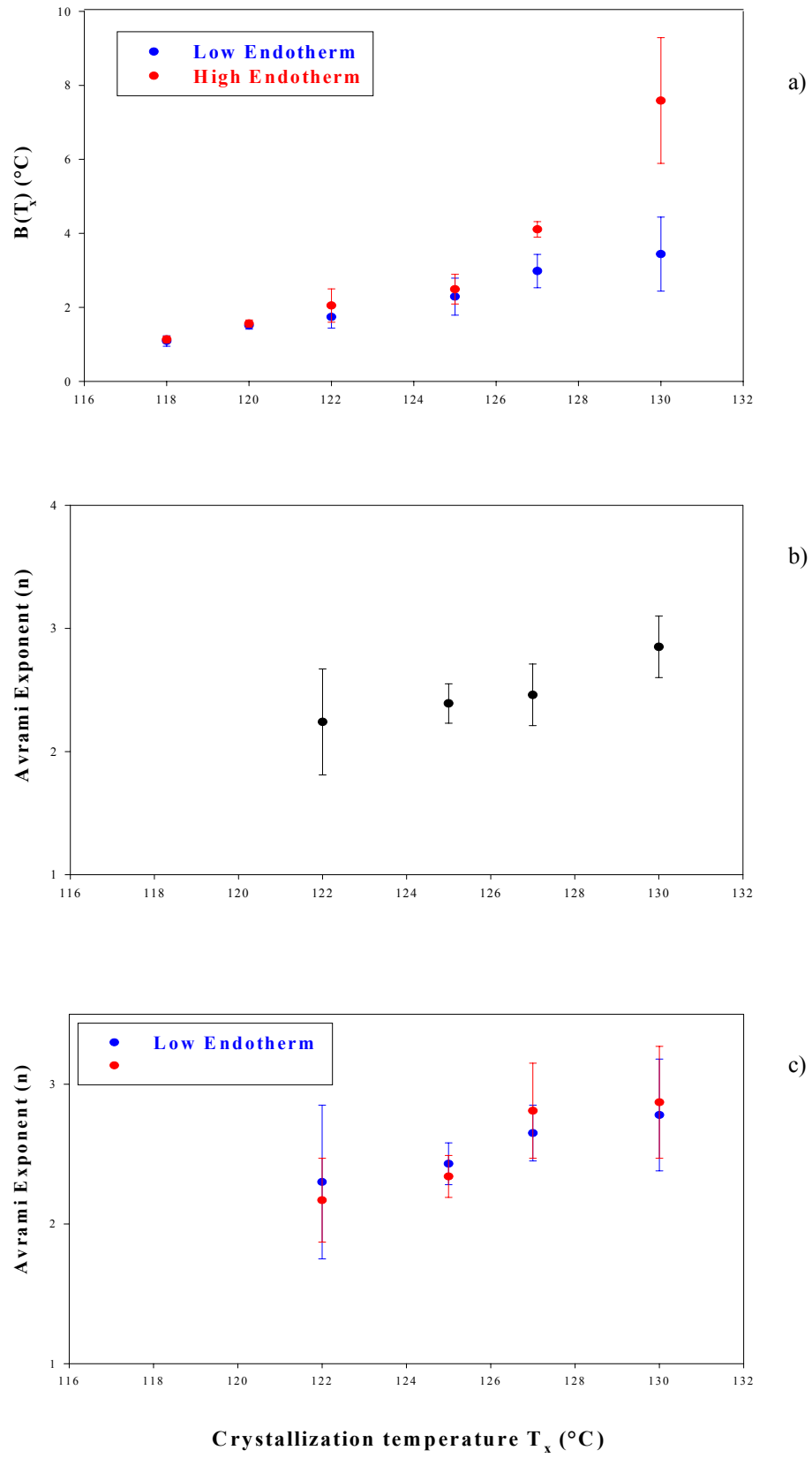


Fig 4.27 PB-3.28%, isothermal crystallization at different temperatures for different times a) $B(T_x)$, b) $n(T_x)$, c) $n_{\text{low}}(T_x)$, $n_{\text{high}}(T_x)$

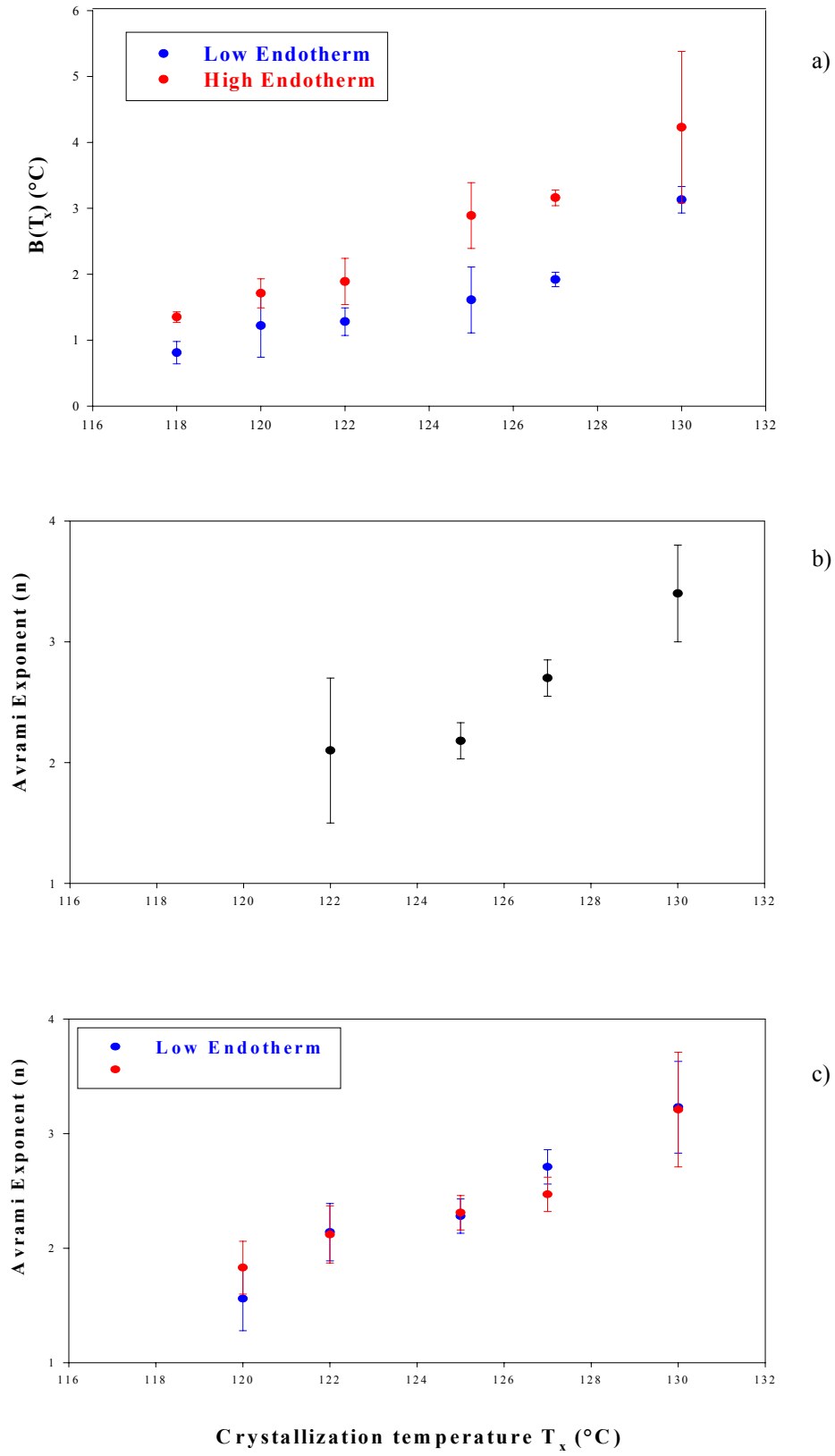


Fig 4.28 PE-2.63%, isothermal crystallization at different temperatures for different times a) $B(T_x)$, b) $n(T_x)$, c) $n_{\text{low}}(T_x)$, $n_{\text{high}}(T_x)$

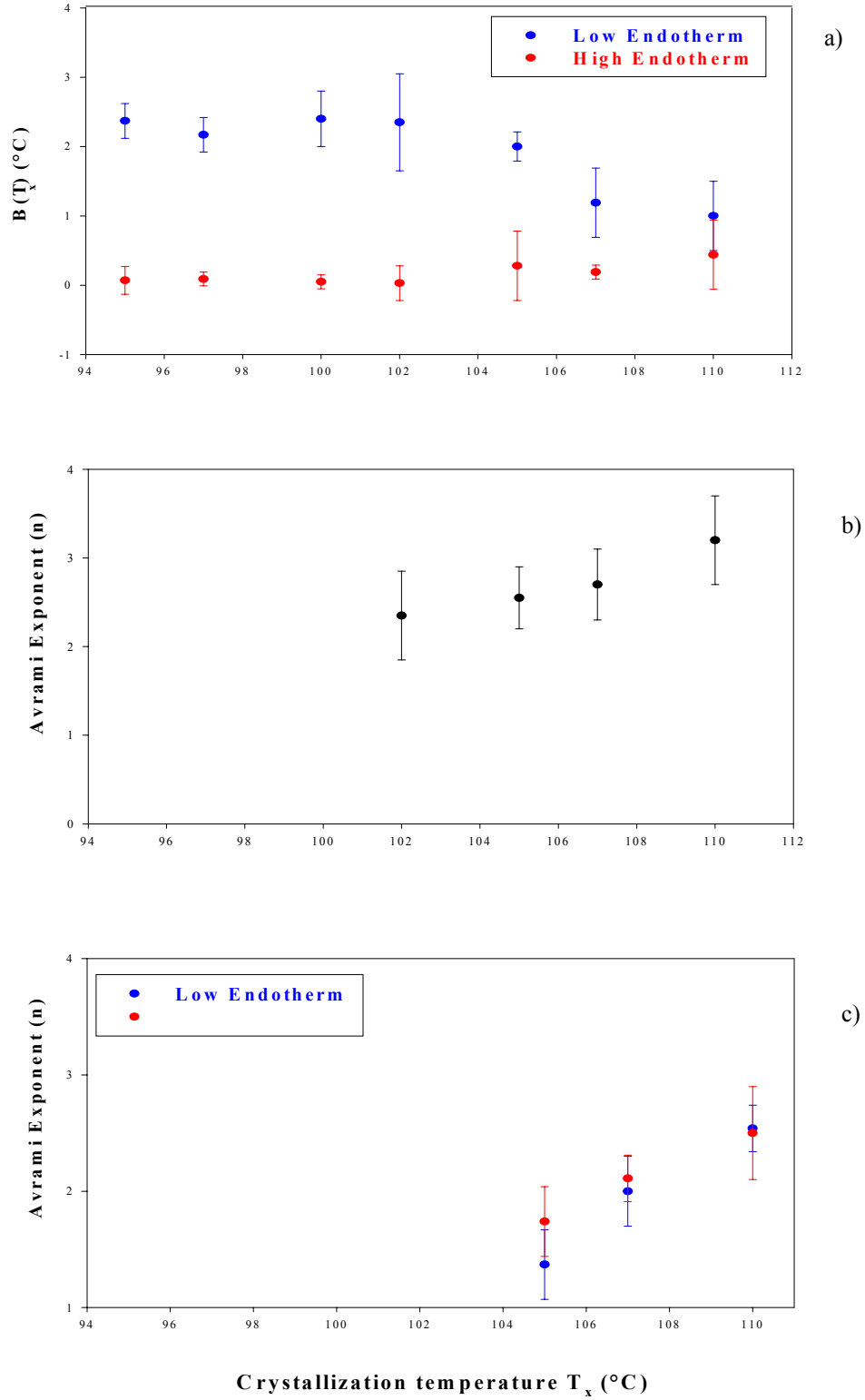


Fig 4.29 PH-3.05%, isothermal crystallization at different temperatures for different times a) $B(T_x)$, b) $n(T_x)$, c) $n_{low}(T_x)$, $n_{high}(T_x)$

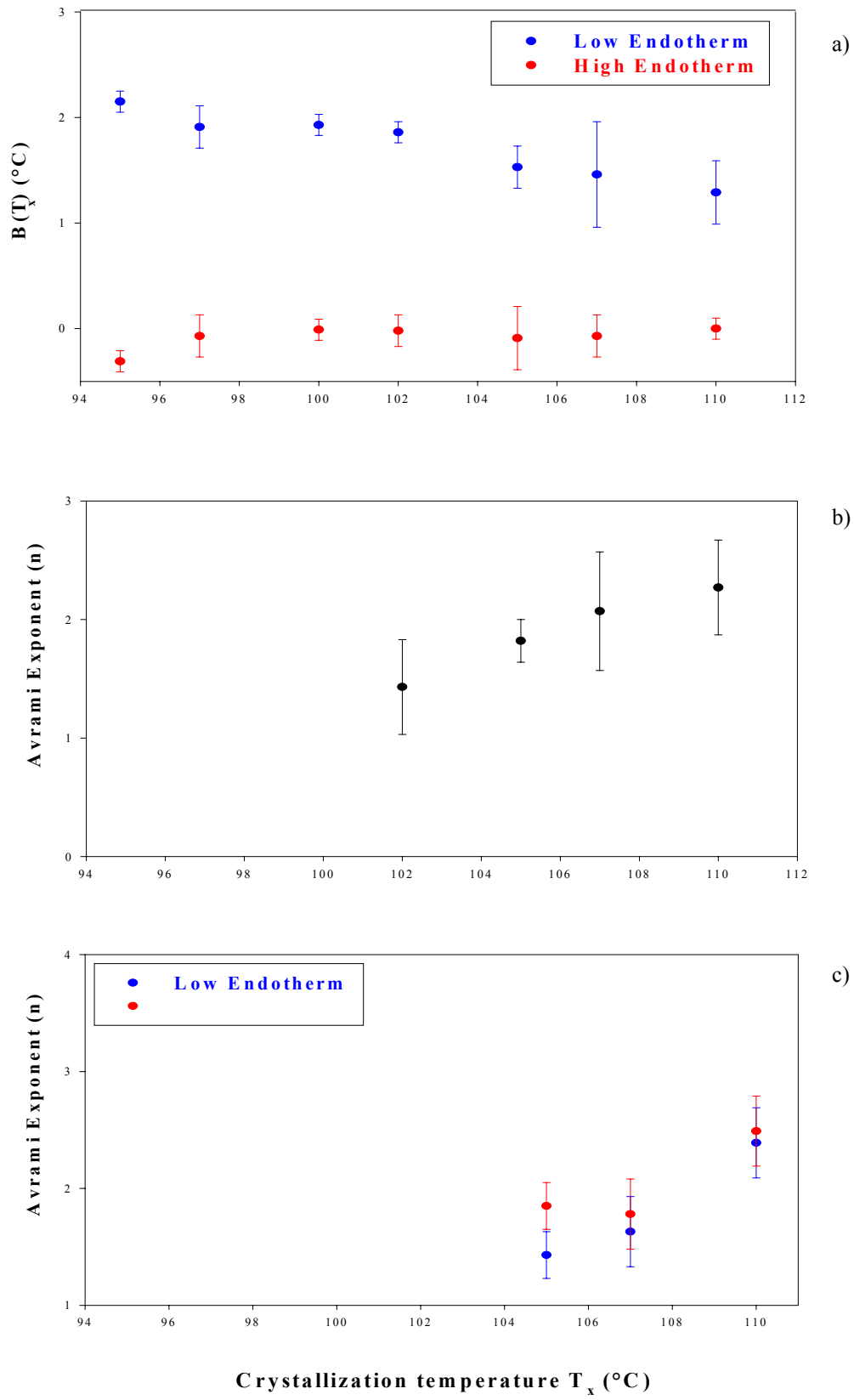


Fig 4.30 PO-3.43%, isothermal crystallization at different temperatures for different times a) $B(T_x)$, b) $n(T_x)$, c) $n_{low}(T_x)$, $n_{high}(T_x)$

opolymers that n increases as the crystallization temperature increases. The same holds true when the Avrami exponent is calculated for the individual endotherms.

4.1.1.3 Heating rate studies

We now focus on studies of the heating rate dependence of the melting behavior for samples crystallized either at high or low temperature. The crystallization temperatures were chosen based on the cooling rate studies. The lower temperature lies in the region where the crystallization process quickly yields the samples that have reached their maximum crystallinity. The higher temperature is chosen such that the crystallization process takes place very slowly but over manageable time scales.

Results from the previous section showed that crystallization at low temperatures leads to a multiple melting behavior where the higher endotherm is more prominent, while crystallization at higher temperatures leads to a multiple melting behavior where the lower endotherm is more prominent. Studying the effect of heating rate on the location and the relative strength of endothermic transitions in a material exhibiting multiple transitions can help decide whether the individual endotherms correspond to the melting of individual or separate crystal populations or is associated with the melting-recrystallization and remelting of a unique crystal population during the heating scan. These studies will therefore help in the interpretation of results reported in the previous two sections.

Samples were first kept in the melt state at 200°C for 2 minutes to erase the previous thermal history. They were then quenched to the specific crystallization temperature and allowed to reside at that temperature for a long enough duration so that appreciable crystallinity could develop. The sample was then cooled to 20°C at a rate of 40°C/min, allowed to reside at that temperature for 2 min to reach thermal equilibrium after which it was heated at a specific rate (1, 2.5, 5, 10 and 20°C/min). The heat flow rate was recorded during heating.

The heating scans are presented after corrections in Fig 4.31-Fig 4.35 for all four copolymers (~3 mol% comonomer). Analysis of these DSC traces allowed to follow the heating rate dependence of the overall enthalpy of fusion, of the individual enthalpies of fusion associated with the low and high endotherms and of the peak melting temperatures for each endotherm. This data is presented in Fig 4.36, 4.37 for PE copolymers, Fig 4.38,

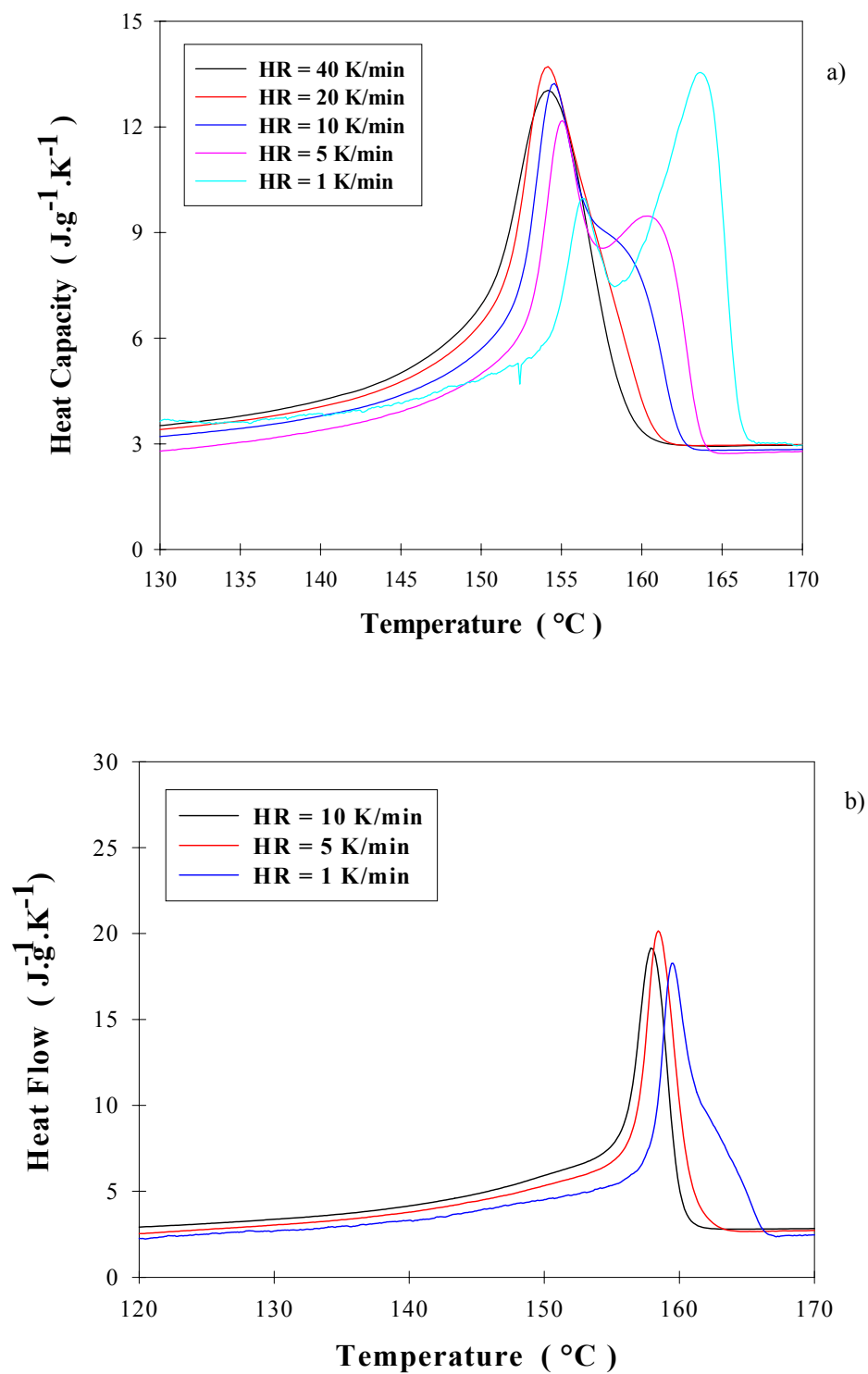


Fig 4.31 Subsequent heating at different rates for pure it-PP after a) quenching from the melt b) cooling from the melt at $5^{\circ}\text{C}/\text{min}$ (Dr. Xu's data)

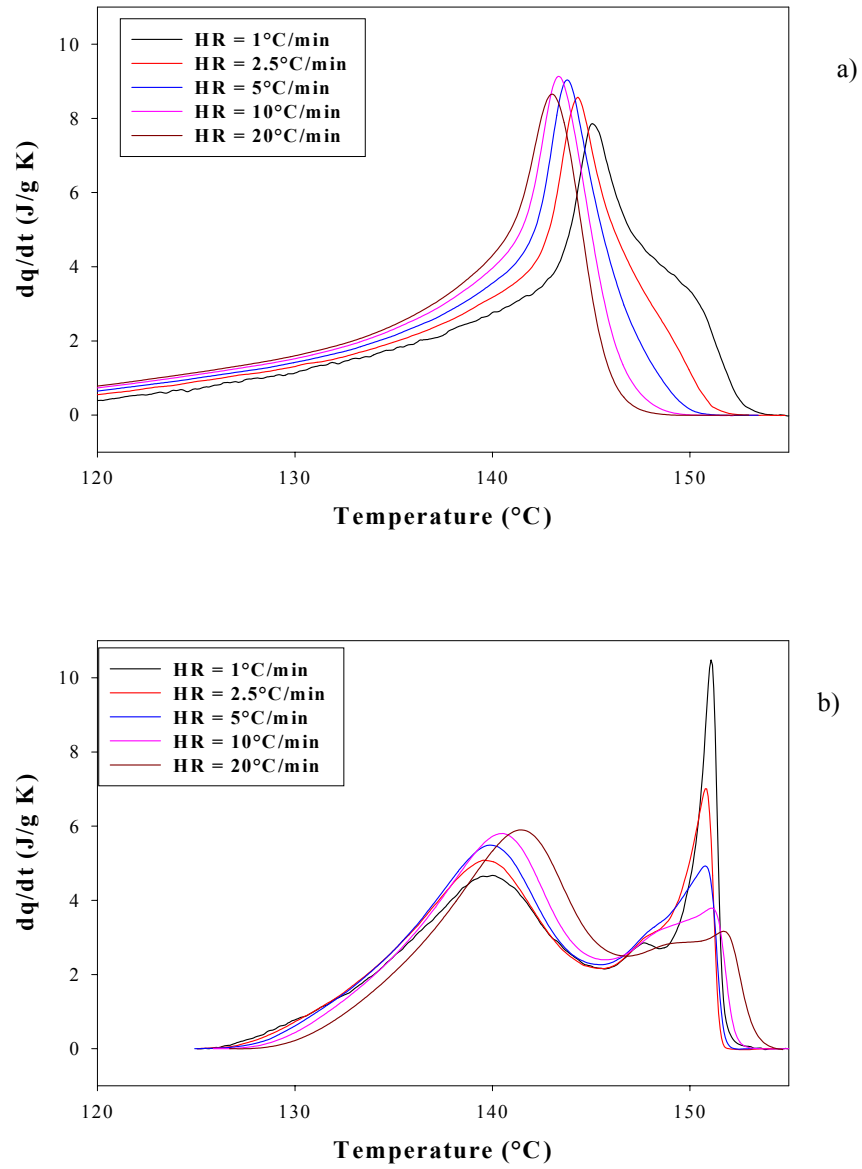


Fig 4.32 PE-2.63%, crystallized at a) 70°C for 15 min and at b) 125°C for 60 min, quenched and subsequently heated till melting

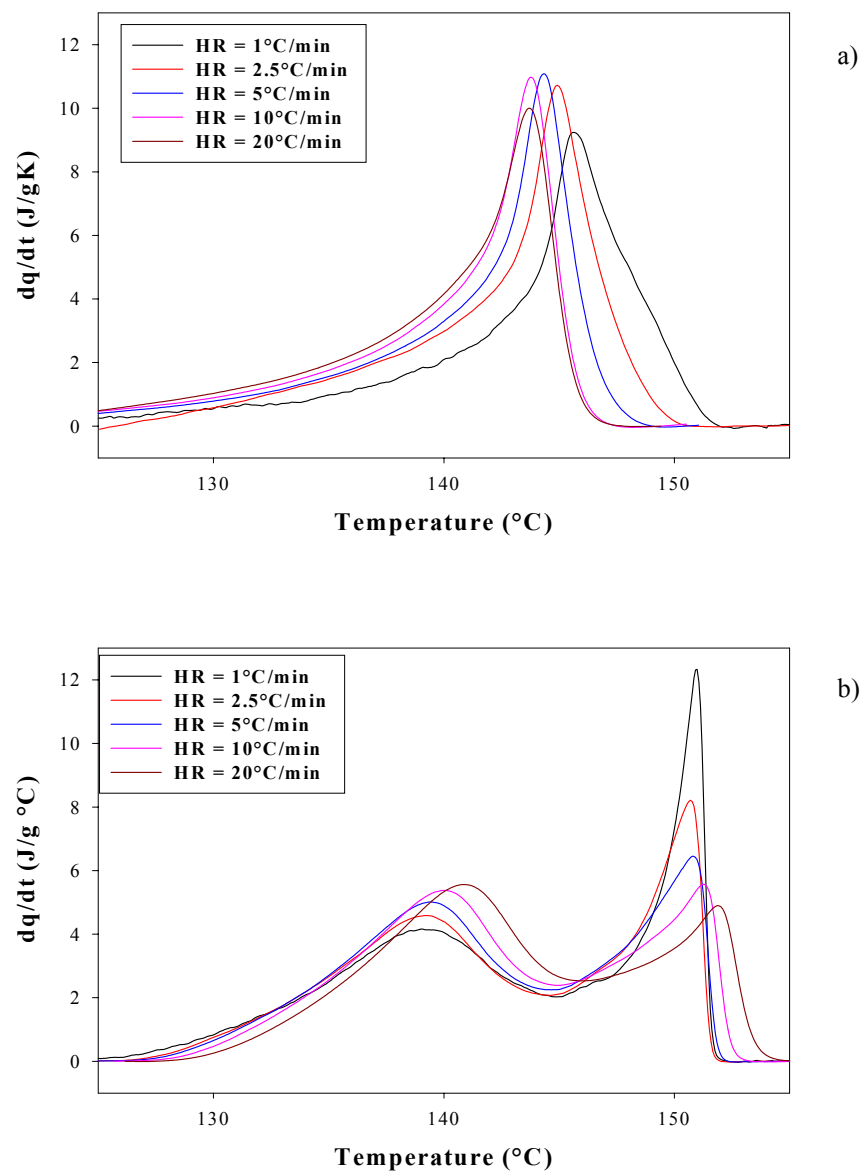


Fig 4.33 PB-3.28%, crystallized at a) 80°C for 15 min and at b) 125°C for 60 min, quenched and subsequently heated till melting

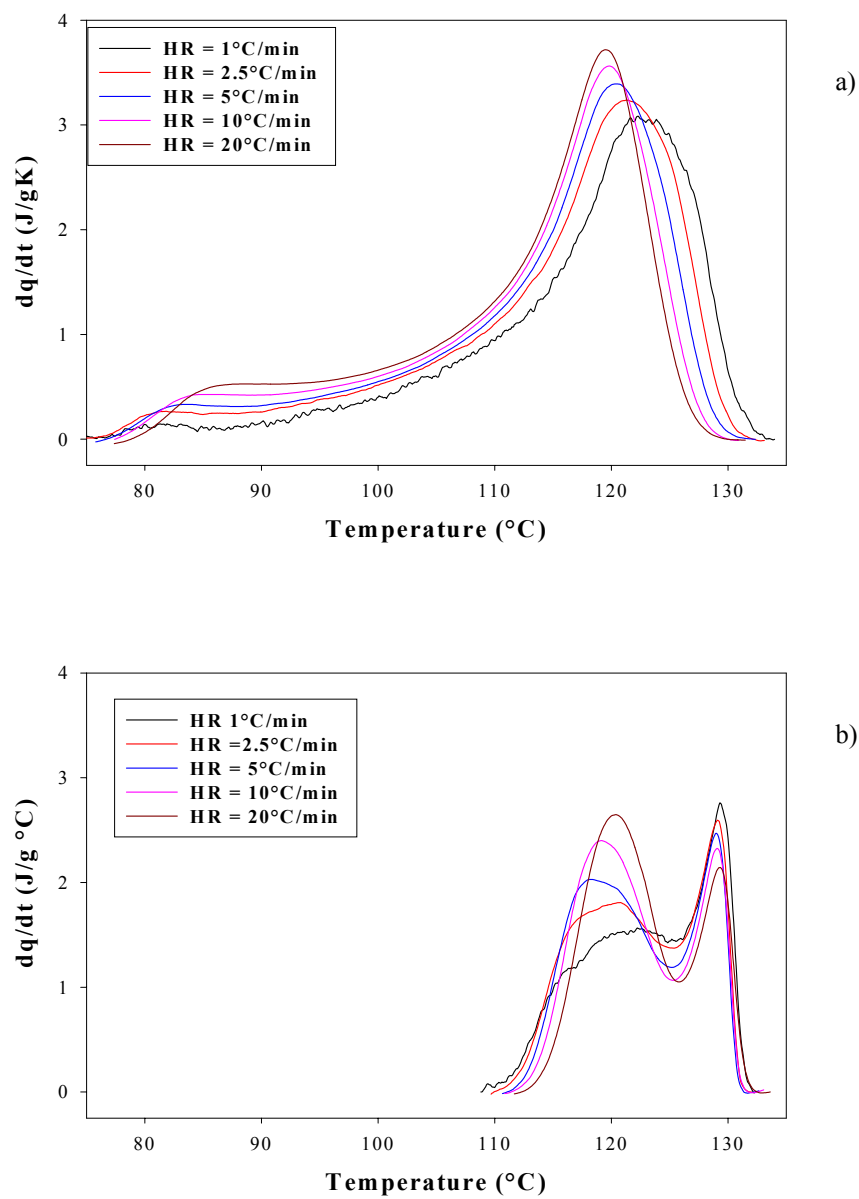


Fig 4.34 PH-3.05%, crystallized at a) 75°C for 15 min and at b) 110°C for 60 min, quenched and subsequently heated till melting

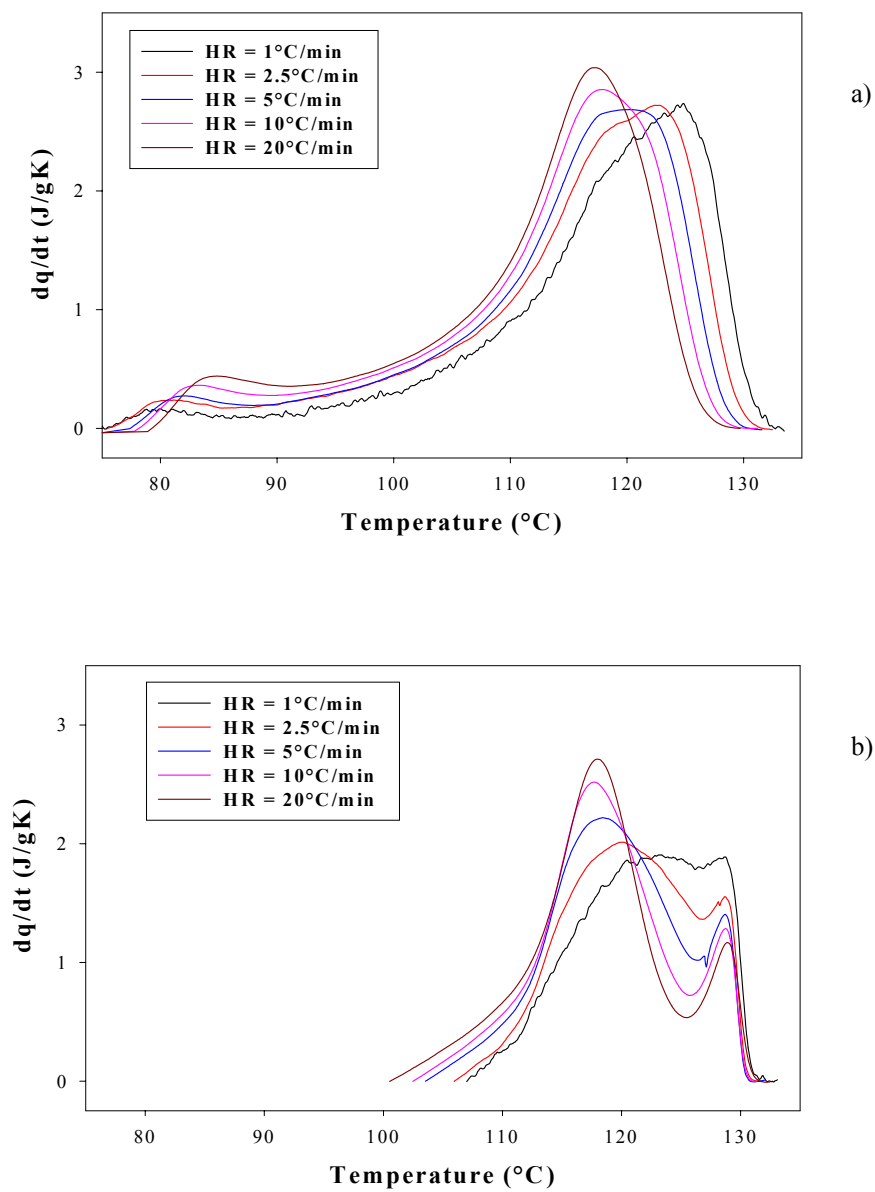


Fig 4.35 PO-3.43%, crystallized at a) 75 $^{\circ}\text{C}$ for 15 min and at b) 110 $^{\circ}\text{C}$ for 60 min, quenched and subsequently heated till melting

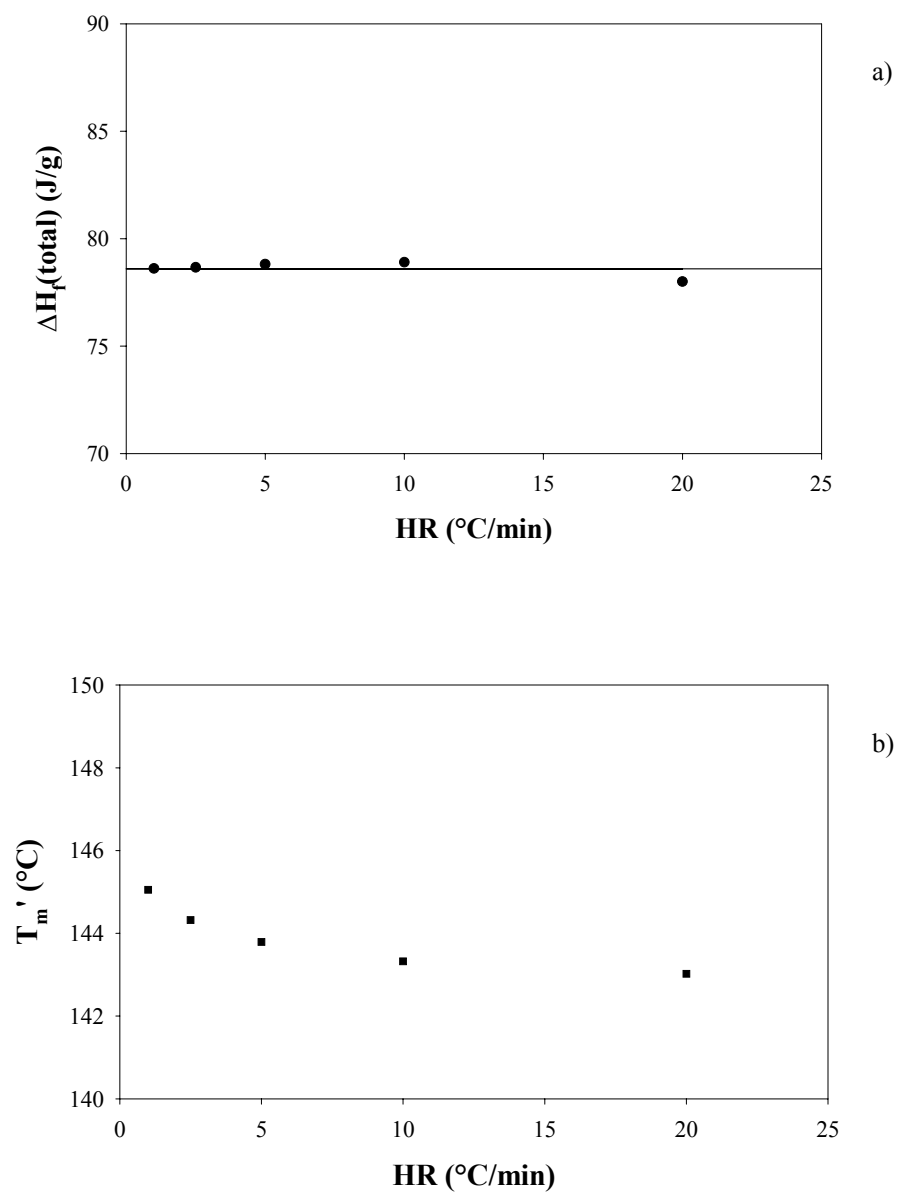


Fig 4.36 PE-2. 63% crystallized at 70 $^{\circ}\text{C}$ for 15 min, quenched and heated till melting a) ΔH_f (total) and b) T_m' at different heating rates

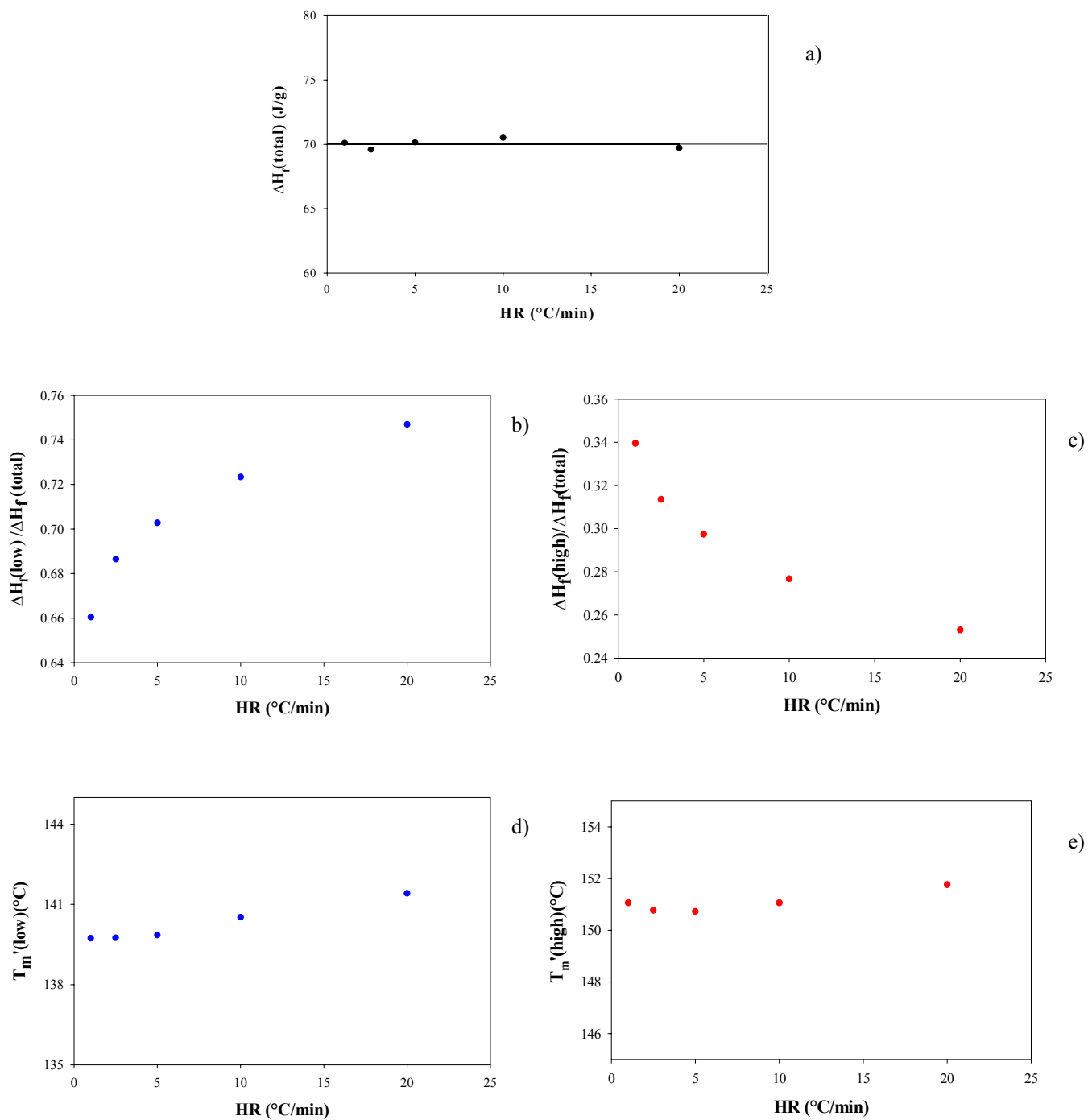


Fig 4.37 PE-2.63% crystallized at 125°C for 60 min, quenched and heated till melting a) $\Delta H_f(\text{total})$ b) $\Delta H_f(\text{low})$ c) $\Delta H_f(\text{high})$ d) $T_m'(\text{low})$ e) $T_m'(\text{high})$ for different heating rates

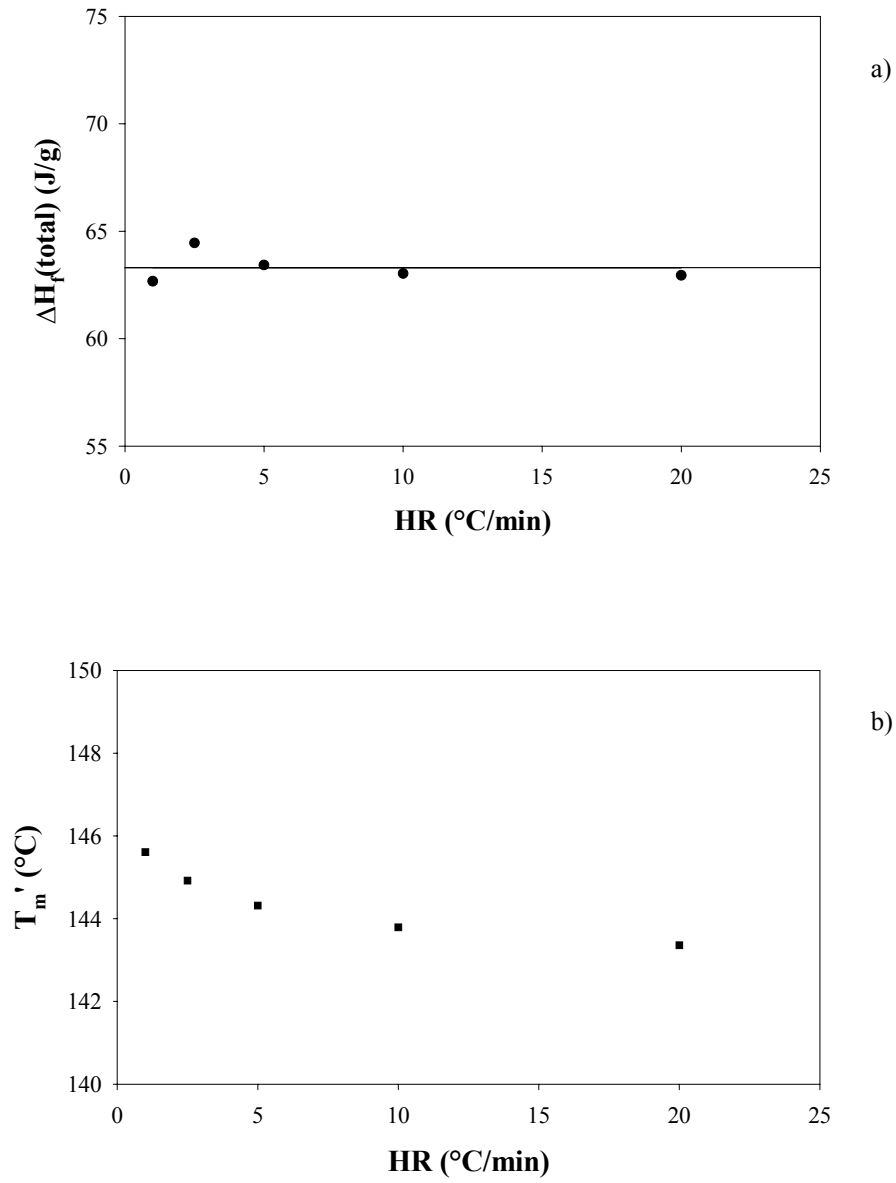


Fig 4.38 PB-3.28% crystallized at 80°C for 15 min, quenched and heated till melting a) ΔH_f (total) and b) T_m' at different heating rates

4.39 for PB copolymers, Fig 4.40, 4.41 for PH and Fig 4.42, 4.43 for PO copolymers. These figures show again that PB behaves very similarly to PE, while PH behaves very similarly to PO.

The following observations can be made within the uncertainty of measurements:

1. The overall heat of fusion is independent of the heating rate, as should be expected.
2. For all copolymers crystallized at low temperatures, the peak melting temperature of the high endotherm decreases with increasing heating rate and levels off for heating rates slightly in excess of 20°C/min.
3. For all copolymers crystallized at high temperatures, the melting temperature associated with the high endotherm is approximately independent of heating rate.
4. For PE and PB crystallized at low temperatures, the low endotherm is absent at all heating rates, while for PH and PO copolymers crystallized at low temperatures, the low endotherm is clearly present and shifts to higher temperature with increasing heating rate.
5. For PH and PO crystallized at high temperature, the low endotherm shifts to higher temperature when the heating rate becomes very low and its location is approximately independent of heating rate for high heating rates.
6. For PE and PB crystallized at high temperatures, the low endotherm shifts to higher temperature with increasing heating rate.
7. For PE and PB crystallized at high temperature, the high endothermic enthalpy of fusion decreases notably with increasing heating rate, while this effect is much less pronounced for PH and PO.
8. For PE and PB crystallized at low temperature, an endothermic shoulder is observed on the high temperature side and grows when the heating rate is reduced. Such behavior is not observed for PH and PO copolymers.

4.1.2 Wide Angle X-ray Diffraction

Wide Angle X-ray Diffraction experiments were carried out in order to determine the nature of crystal phases present in these samples. Some of these experiments were carried out by a co-worker in the lab (Jiannong Xu). The data for those runs have been included to give a more complete picture.

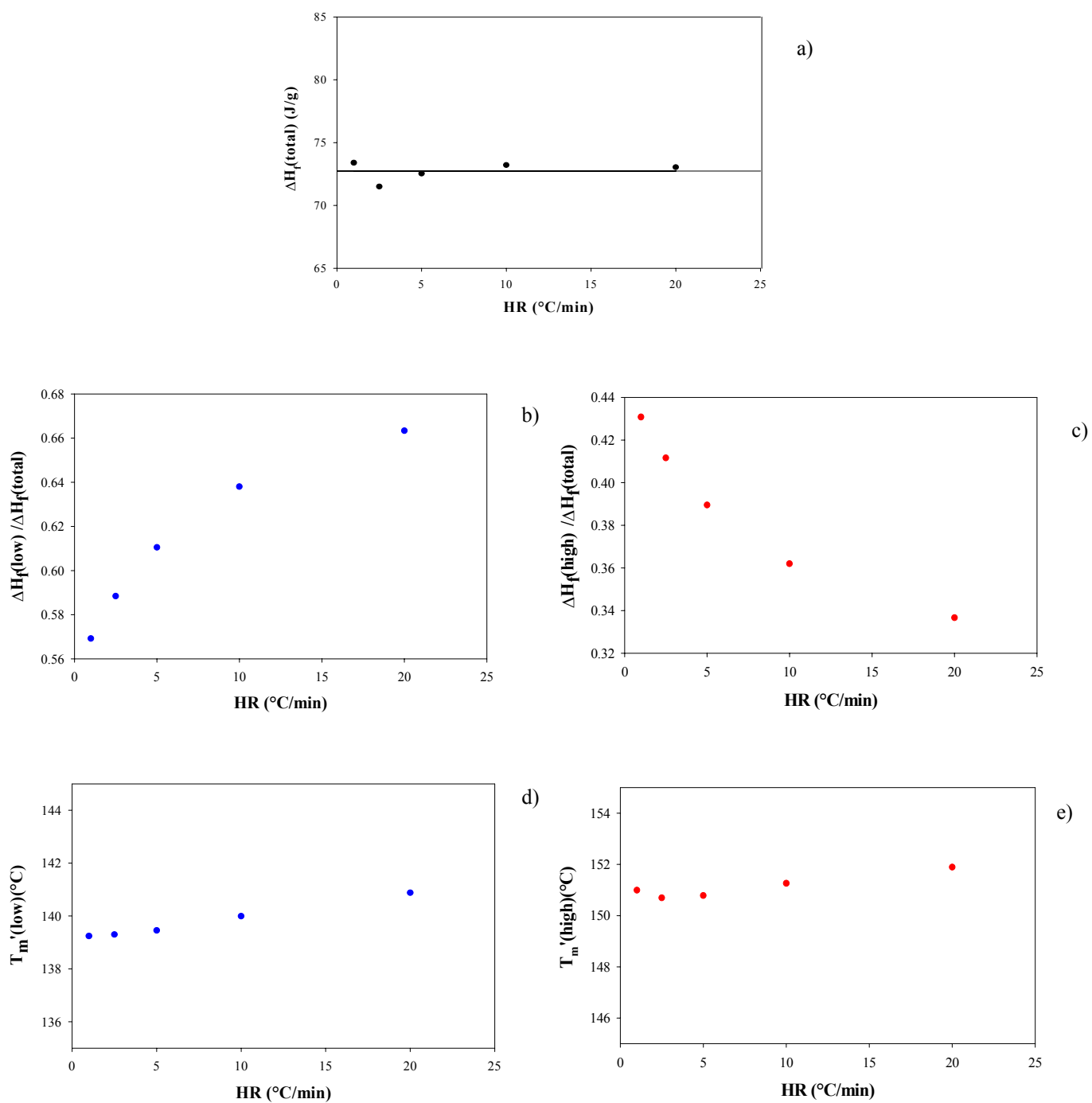


Fig 4.39 PB-3.28% crystallized at 125°C for 60 min, quenched and heated till melting a) $\Delta H_f(\text{total})$ b) $\Delta H_f(\text{low})$ c) $\Delta H_f(\text{high})$ d) $T_m'(\text{low})$ e) $T_m'(\text{high})$ for different heating rates

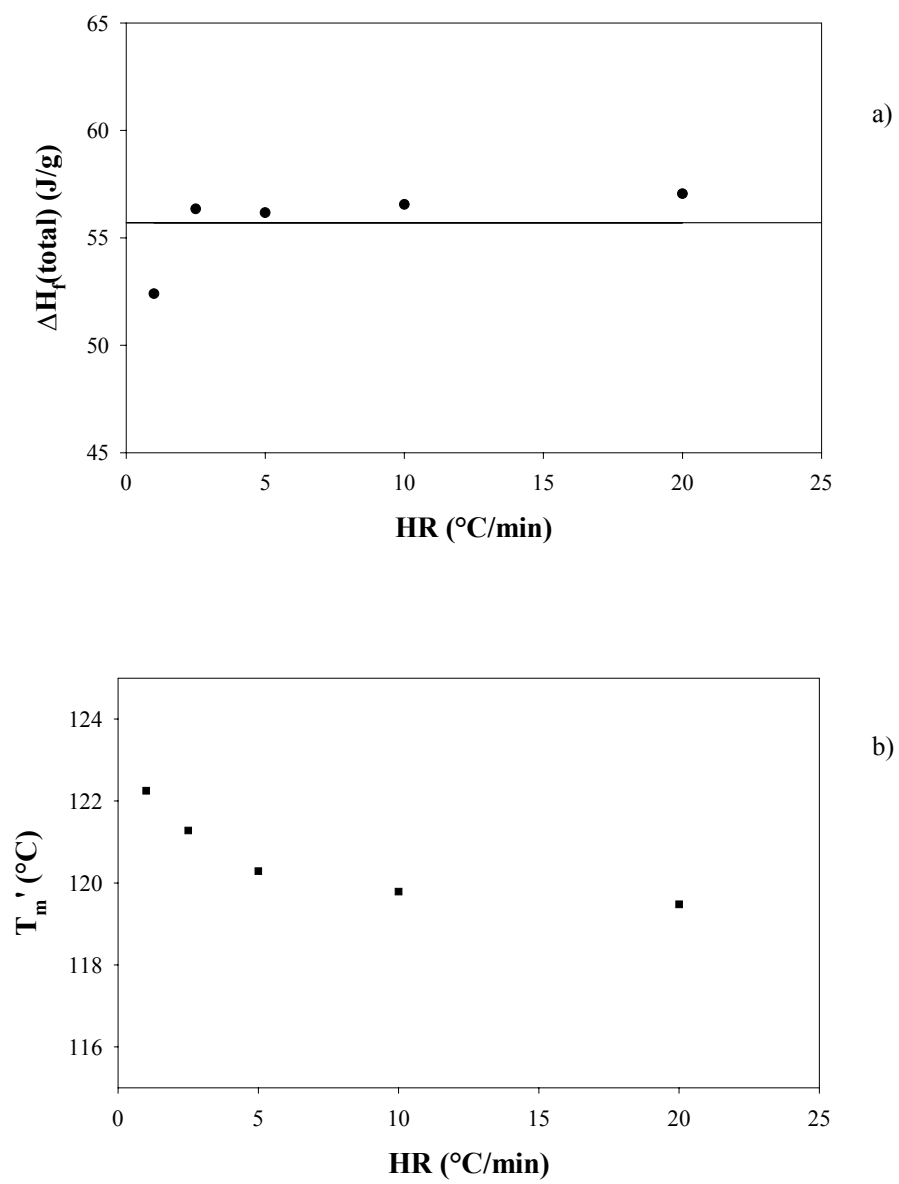


Fig 4.40 PH-3.05% crystallized at 75 $^{\circ}\text{C}$ for 15 min, quenched and heated till melting a) ΔH_f (total) and b) T_m' at different heating rates

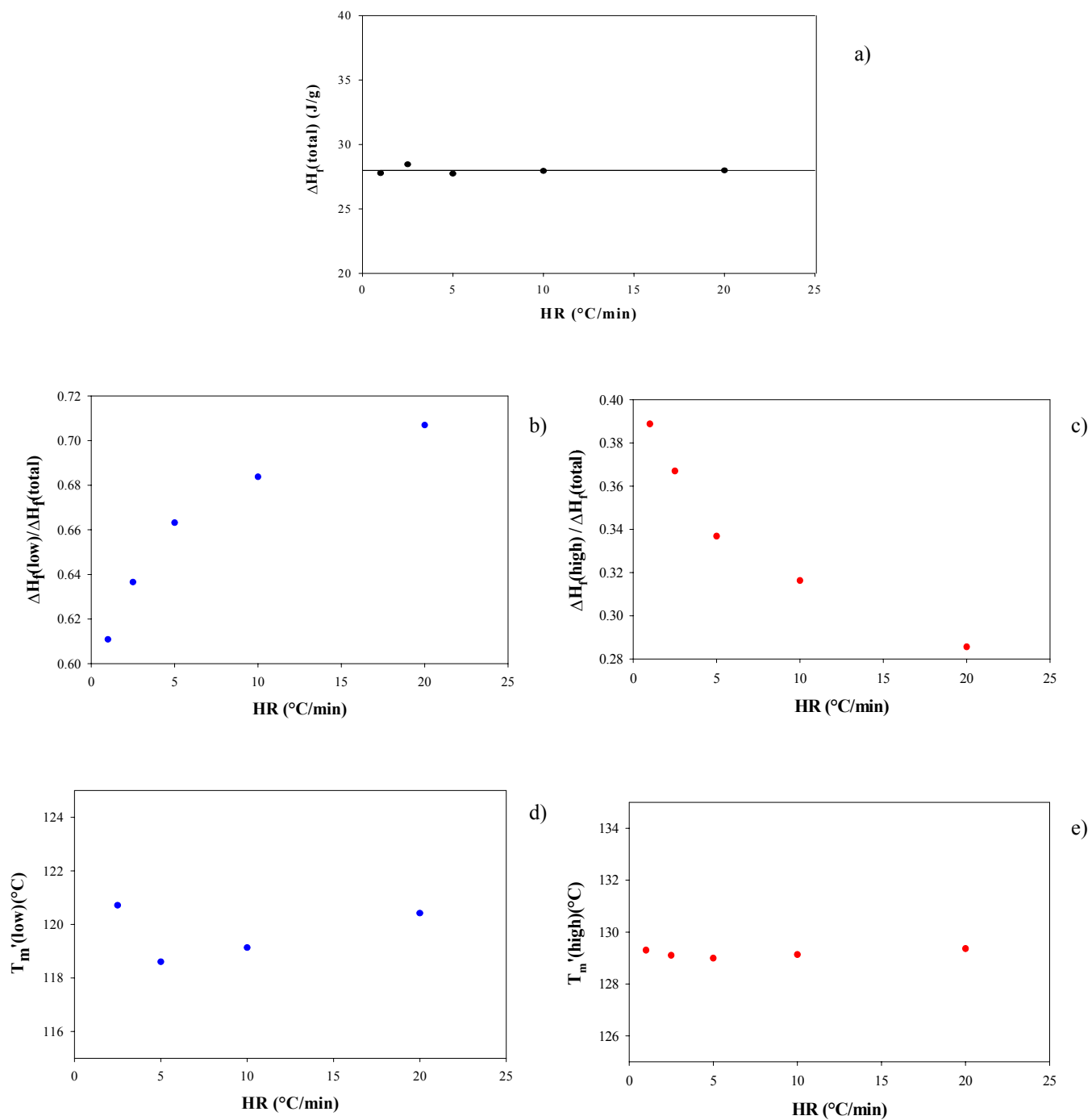


Fig 4.41 PH-3.05% crystallized at 110 $^{\circ}\text{C}$ for 60 min, quenched and heated till melting a) $\Delta H_f(\text{total})$ b) $\Delta H_f(\text{low})$ c) $\Delta H_f(\text{high})$ d) $T_m'(\text{low})$ e) $T_m'(\text{high})$ for different heating rates

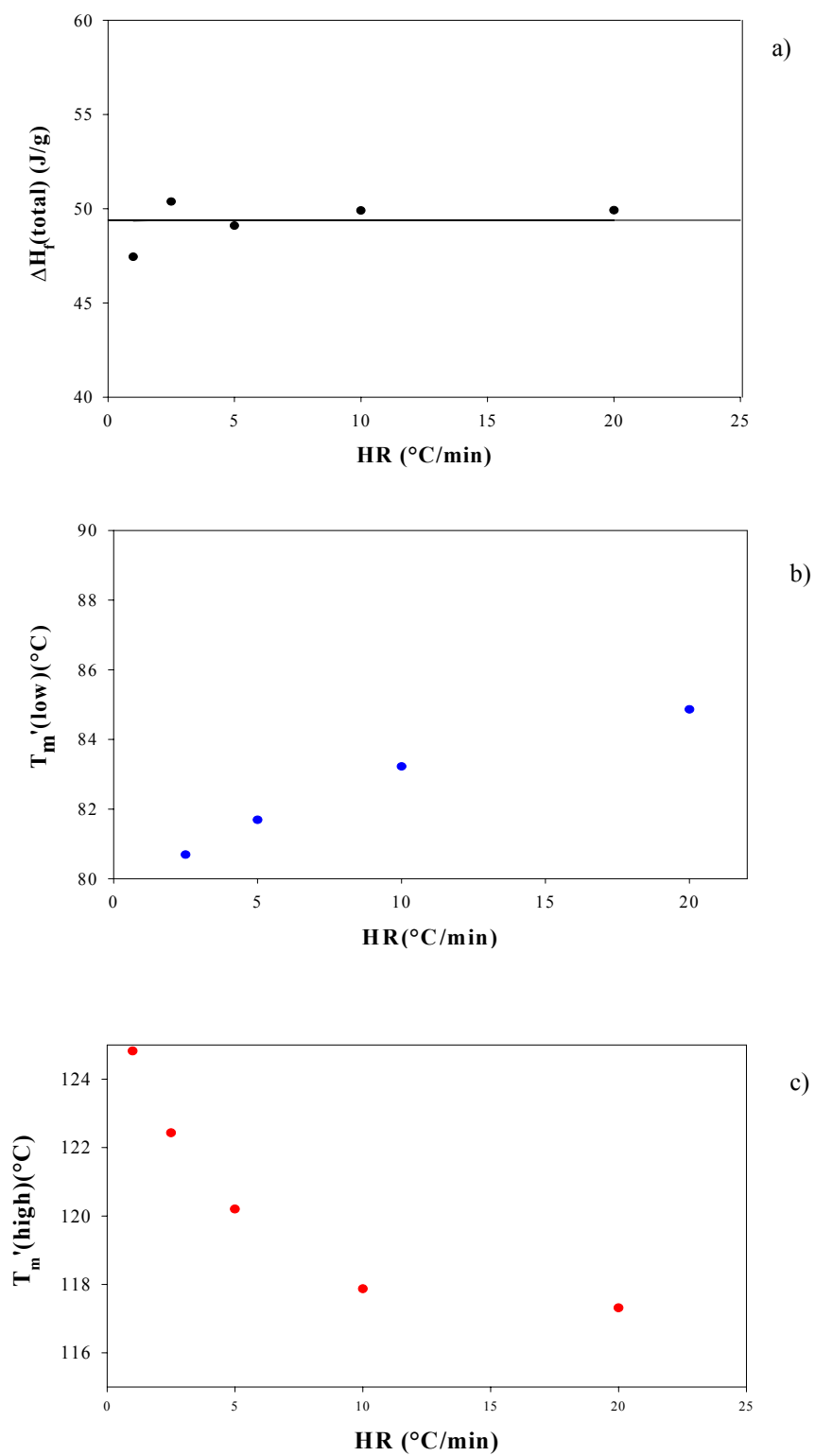


Fig 4.42 PO-3.43% crystallized at 80°C for 15 min, quenched and heated till melting a) ΔH_f (total), b) $T_m'(\text{high})$ and c) $T_m'(\text{low})$ at different heating rates

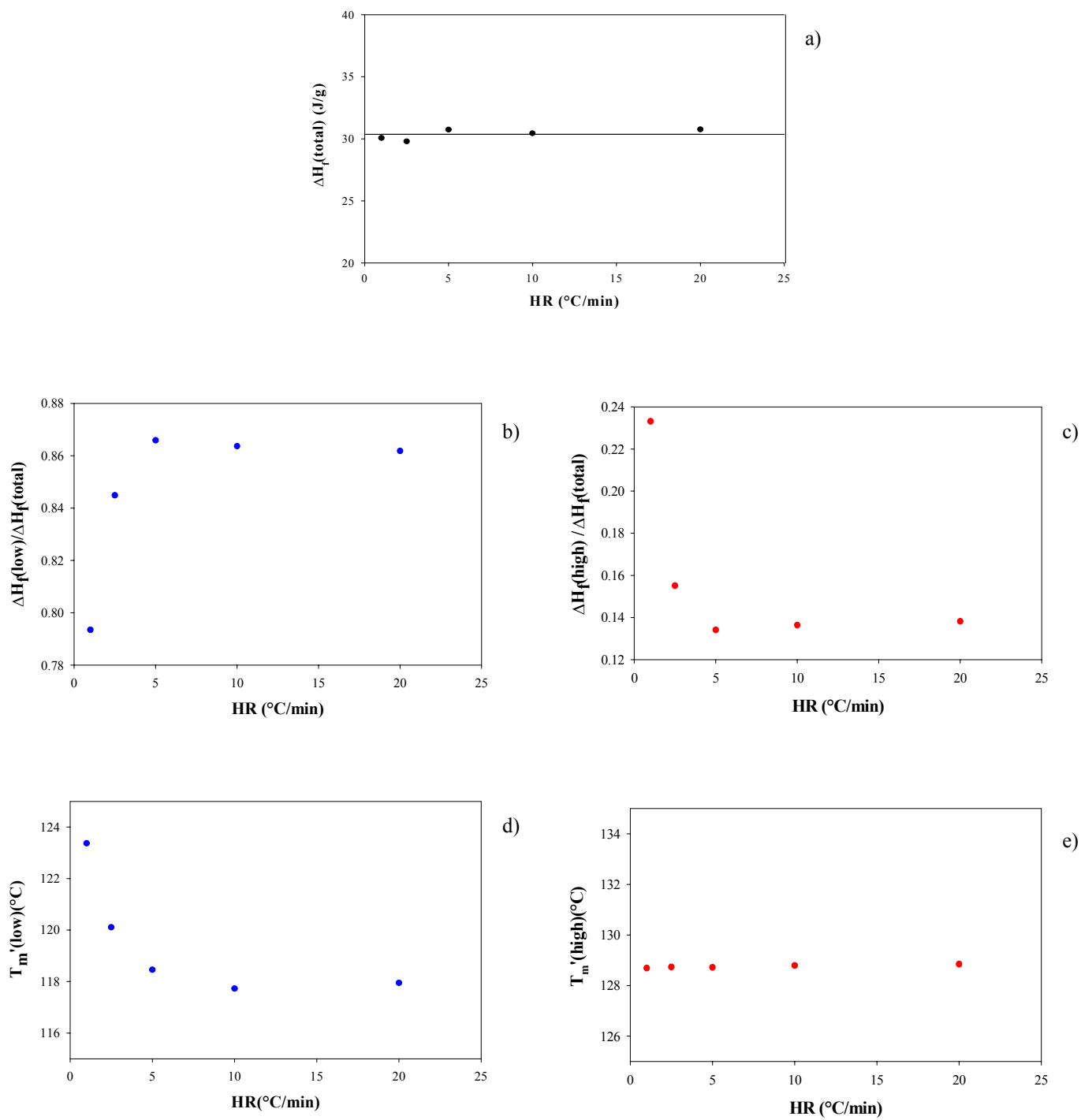


Fig 4.43 PO-3.43% crystallized at 110°C for 60 min, quenched and heated till melting a) $\Delta H_f(\text{total})$ b) $\Delta H_f(\text{low})$ c) $\Delta H_f(\text{high})$ d) $T_m'(\text{low})$ e) $T_m'(\text{high})$ for different heating rates

Dr. Xu's samples were crystallized by natural cooling in the nitrogen atmosphere subsequent to melt pressing at ca. 200°C and ca. 170 psi, under the nitrogen atmosphere. The other samples (PO-3.43%) were made by slow cooling (4°C/hour). For PO-3.43, another sample was made which was quenched from melt. All the samples are 1.5 mm thick, and disk shaped.

The experiments were carried out using the following parameters:

scan rate: 1 deg/min (For Jiannong Xu's data)

: 0.1 deg/min (For Amit's data)

scan range: 5 - 35 deg

The presence of a Bragg reflection at $2\theta = 19-20^\circ$ in these diffractograms (Fig 4.44-4.47) clearly indicates that γ – phase crystals are present in copolymers slowly cooled from the melt. The X-ray data recorded for PB and PH further suggest that the relative γ – phase content increases with the comonomer concentration (Fig 4.45 and 4.46). From Fig 4.47 we conclude that the relative gamma phase content increases when the PO copolymer is cooled at a slower rate from the melt (i.e. when the copolymer crystallizes at higher temperature). We also note that the half width at half height of Bragg reflection for PH and PO copolymers is much larger than that for PE and PB copolymers at approximately identical comonomer content (Fig 4.44). This observation suggests that PH and PO crystals are significantly smaller and/or more defective than PE, PB crystals.

4.1.3 Atomic Force Microscopy

Study of the morphological features of propylene copolymers was carried out using an Atomic Force Microscope. The micrographs obtained for these copolymers are shown in Fig 4.48- Fig 4.52. While PE and PB clearly exhibit some cross-hatching (i.e. crystallographic lamellar branching), PH and PO do not. The lamellar details for these pairs look starkly different from each other. The samples were prepared at the highest temperature possible where crystallization reaches completion over still practical time scales. Thus, the PE and PB copolymers were melted and quenched to 130°C and allowed to crystallize at that temperature for 24 hours before being slowly cooled to room temperature. For PH and PO, the crystallization was carried out at 110°C. The

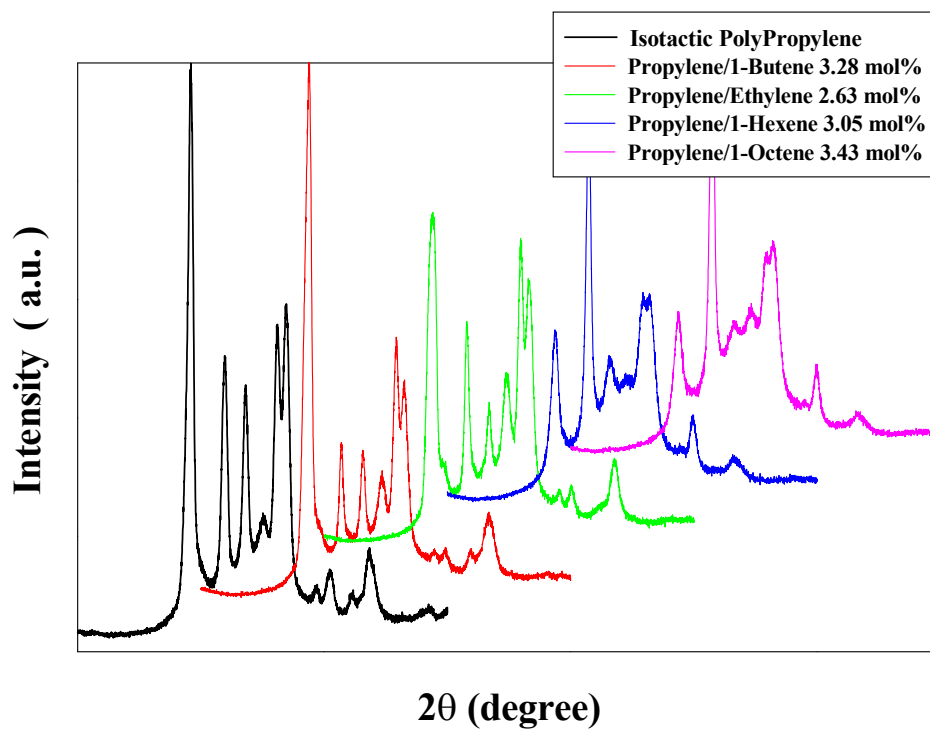


Fig 4.44 Wide angle X-ray diffractogram of propylene copolymers (data obtained by Dr. Xu)

γ fraction % = 0.47, PB-3.28

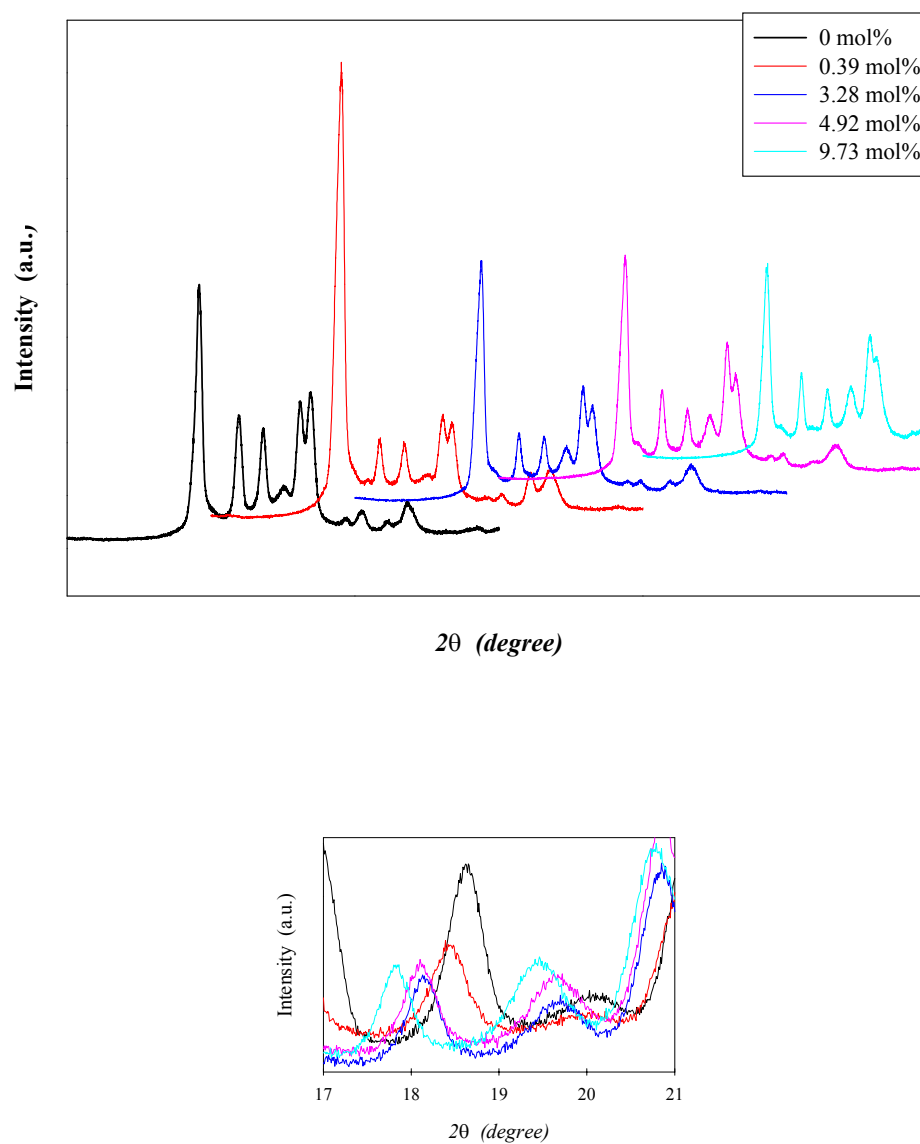


Fig 4.45 Wide angle X-ray diffractogram of propylene/1-butene Copolymers (data obtained by Dr. Xu)

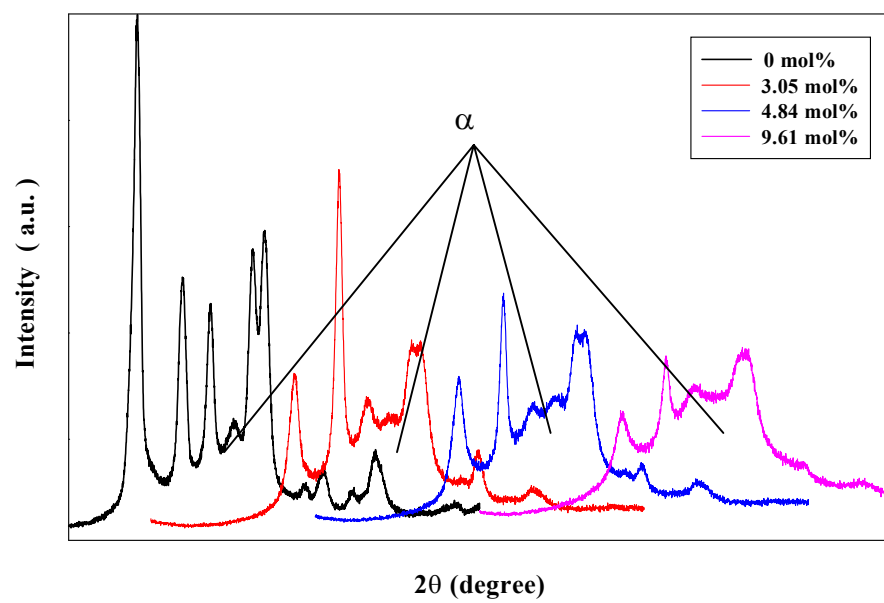


Fig 4.46 Wide angle X-ray diffractogram of propylene/1-hexene copolymers (data obtained by Dr. Xu)

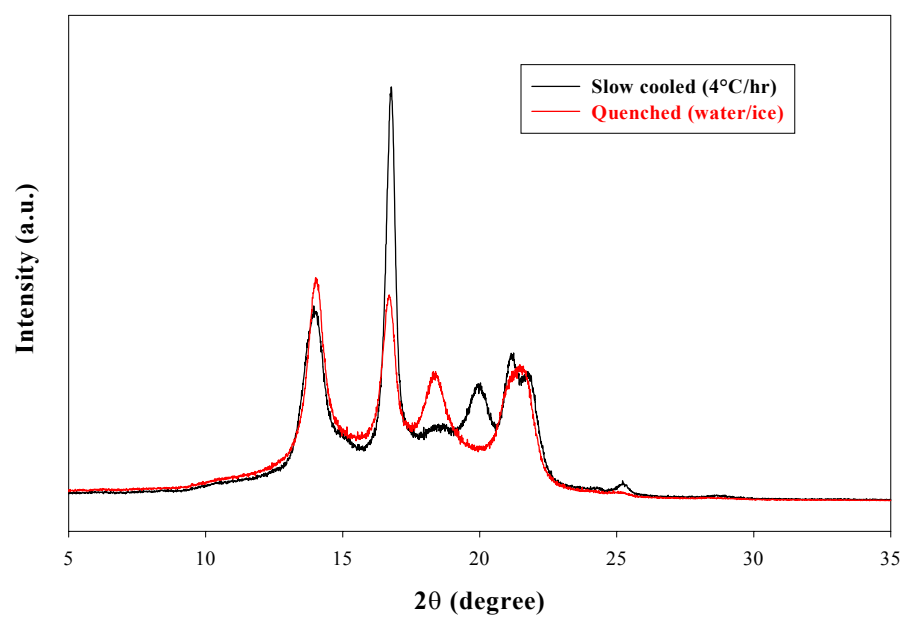
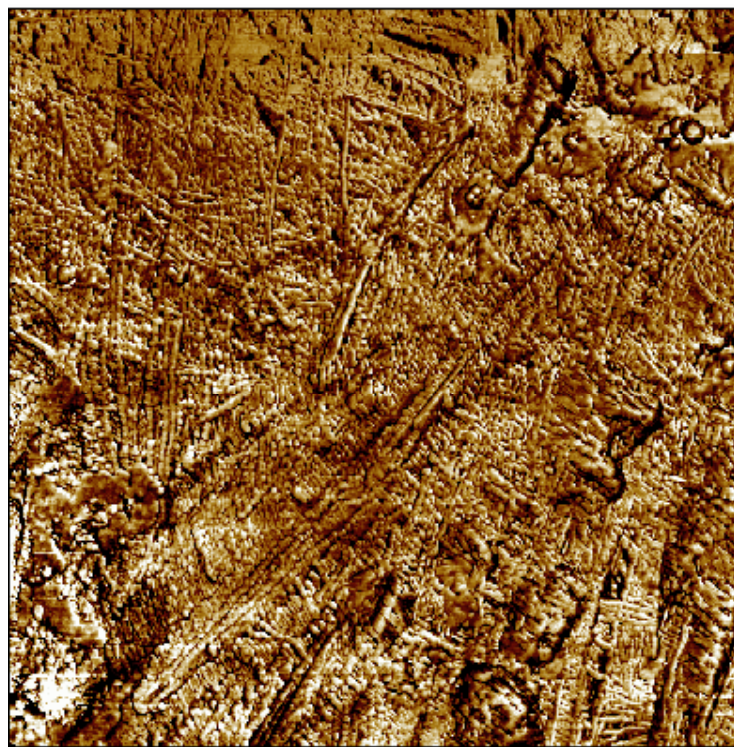
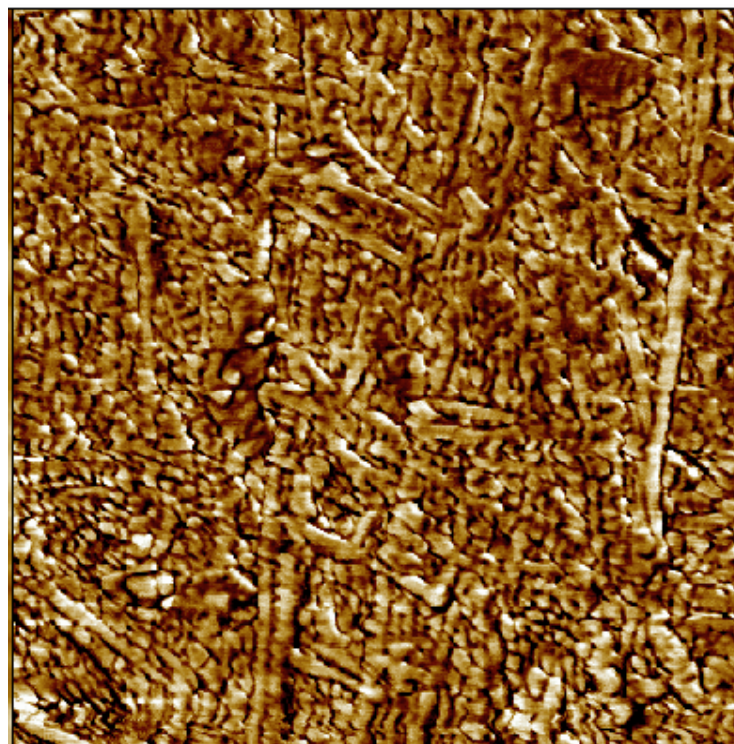


Fig 4.47 Wide angle X-ray diffractogram of Propylene/1-octene 3.43mol% copolymer

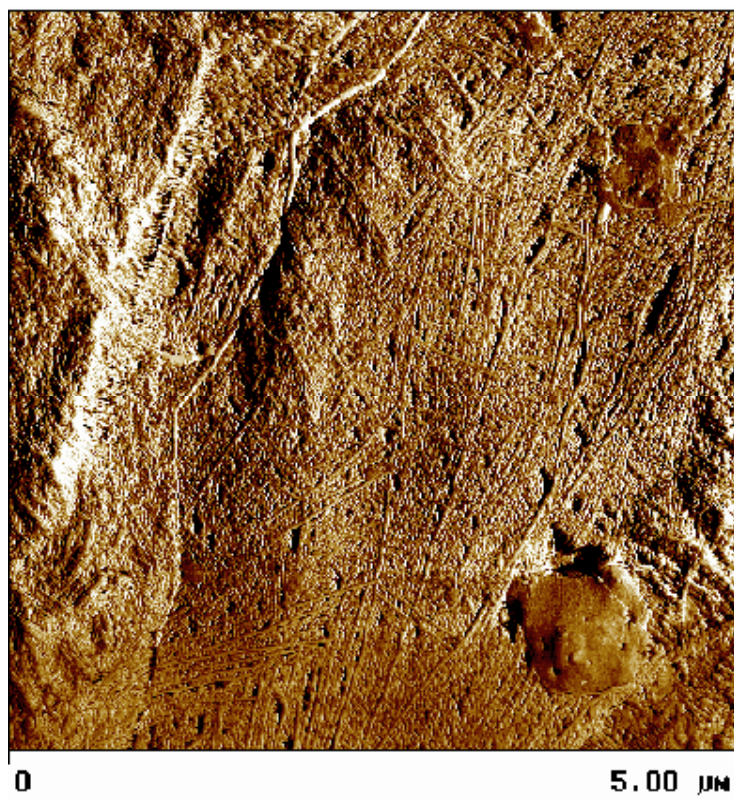


a)

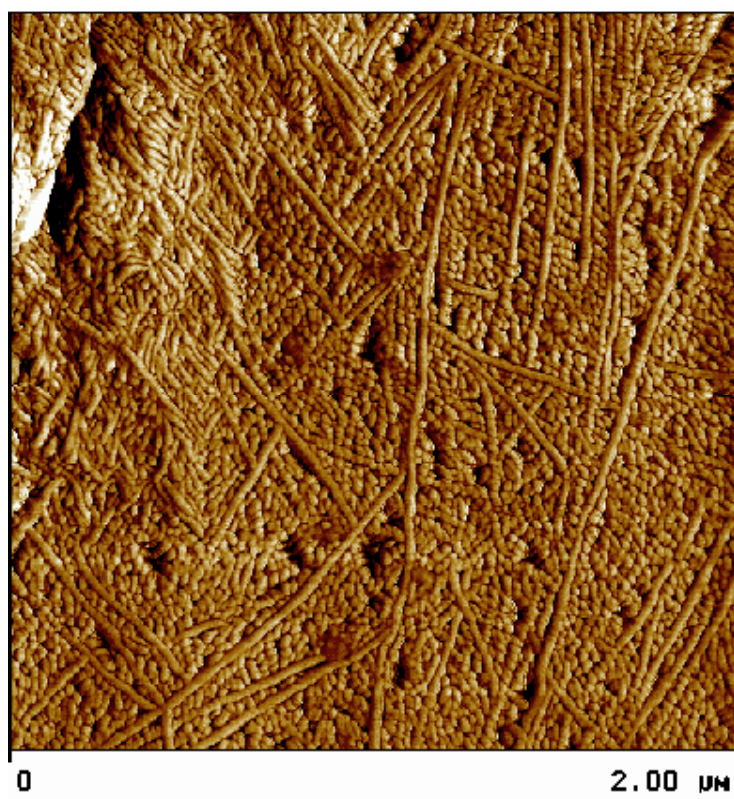


b)

Fig 4.48 AFM pictures (phase-images) for PB-3.28%, isothermally crystallized at 130°C and then slowly cooled (0.3°C/min) to room temperature a) 0-5μm b) 0-2μm



a)



b)

Fig 4.49 AFM pictures (phase-images) for PE-2.63%, isothermally crystallized at 130°C and then slowly cooled (0.3°C/min) to room temperature a) 0-5μm b) 0-2μm

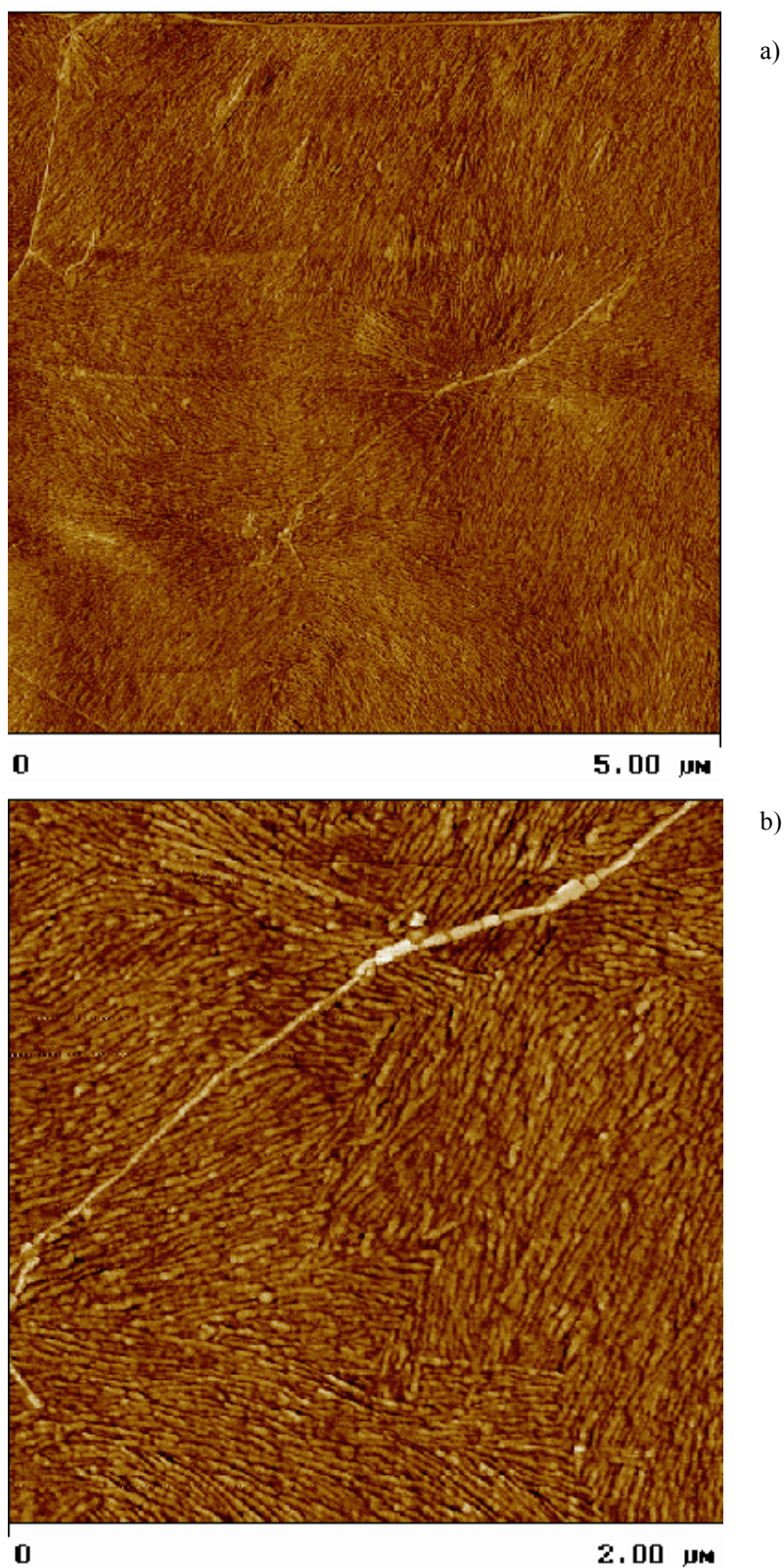


Fig 4.50 AFM pictures (phase-images) for PH-3.05%, isothermally crystallized at 115°C and then slowly cooled (0.3°C/min) to room temperature a) 0-5μm b) 0-2μm

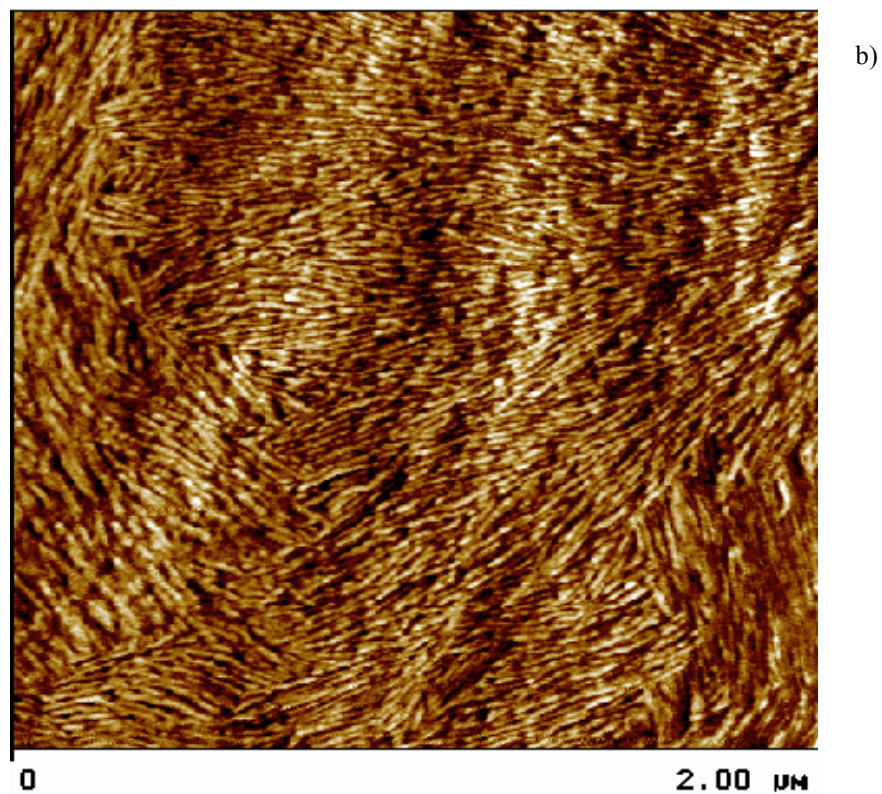
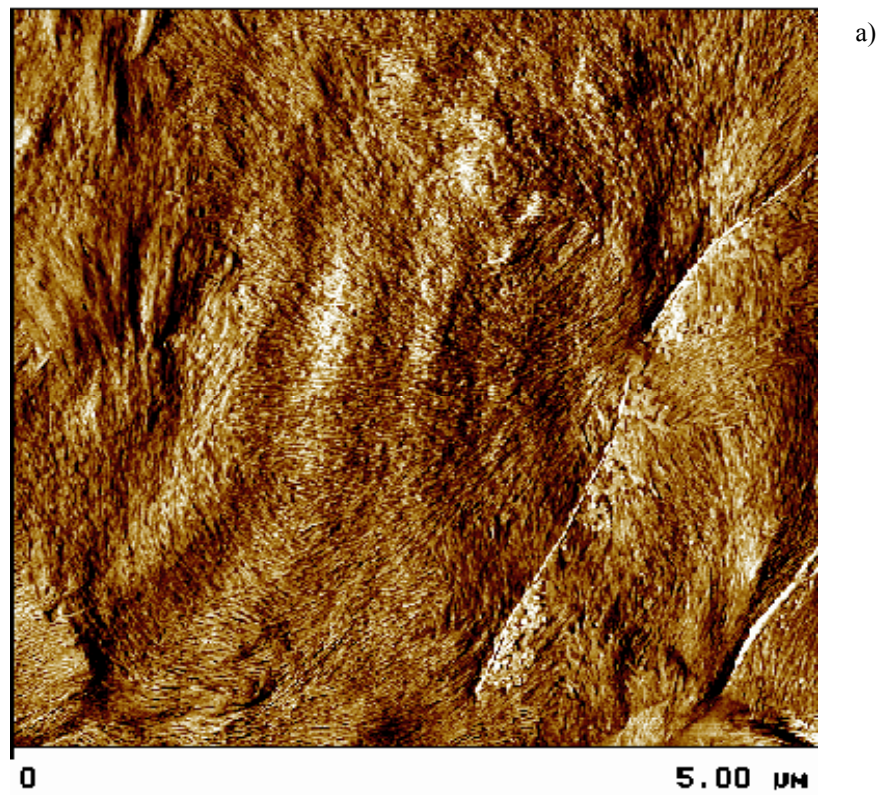


Fig 4.51 AFM pictures (phase images) for PO- 3.43%, isothermally crystallized at 115°C and then slowly cooled (0.3°C/min) to room temperature a) 0-5μm b) 0-2μm

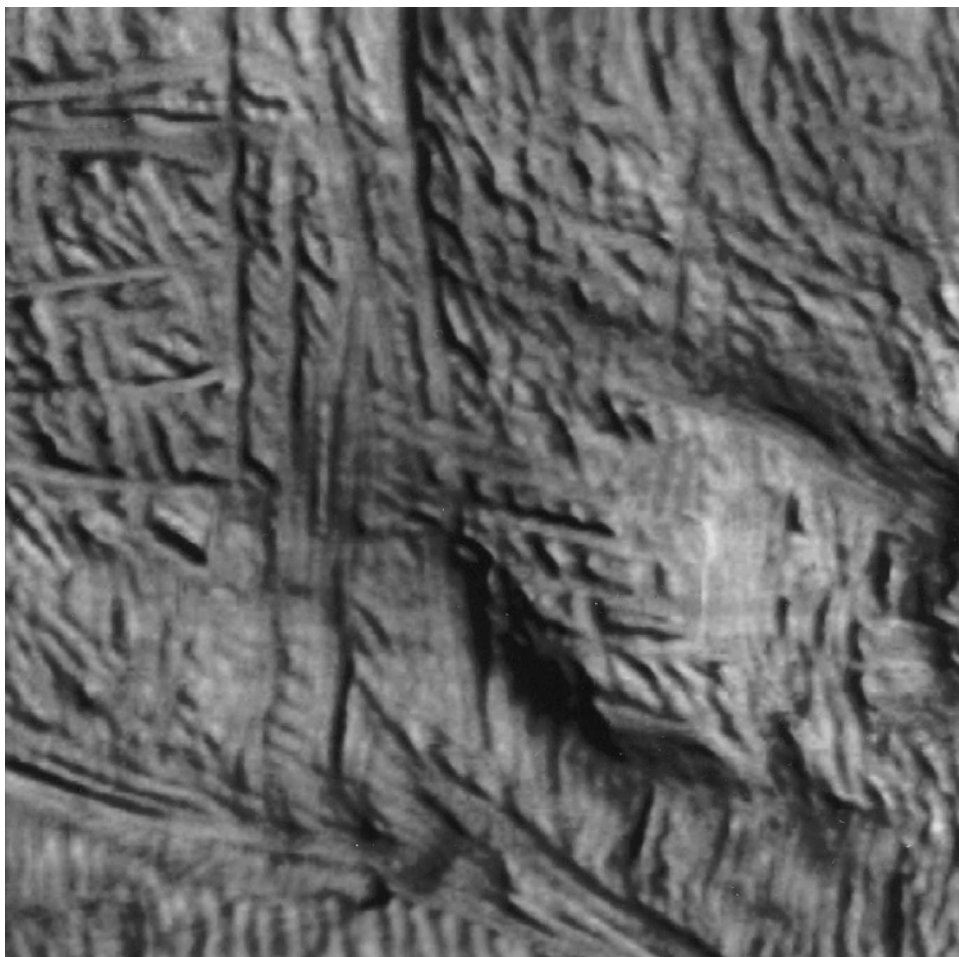


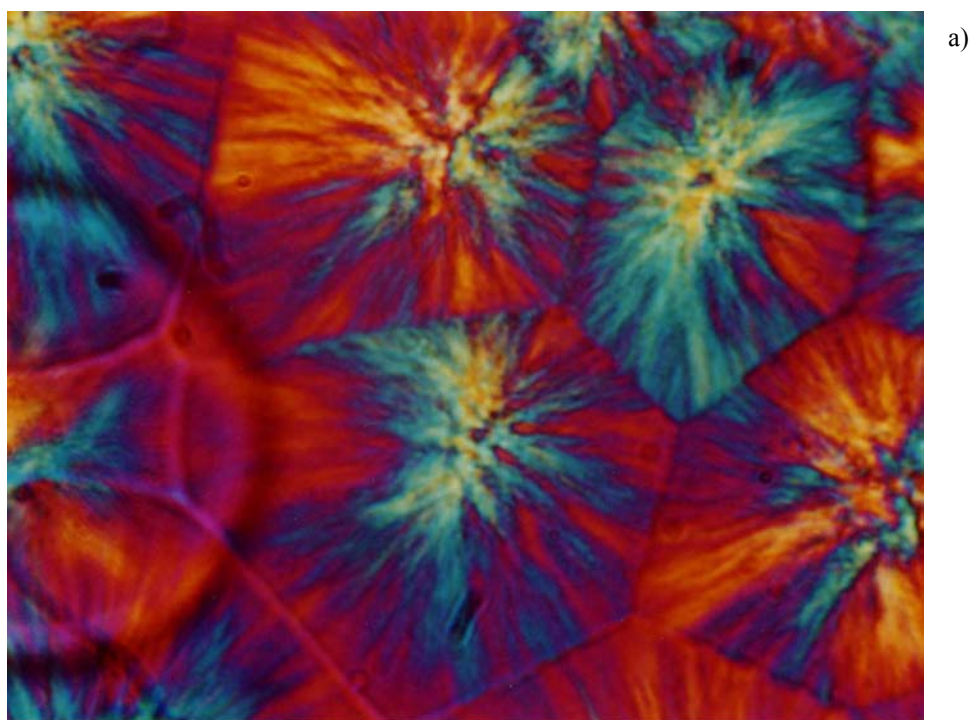
Fig 4.52 AFM picture (phase-image) for PB-3.28%, isothermally crystallized at 125°C (scale used is 0-1 μm on both axes)

temperature thus chosen enabled us to get larger and thicker lamellae so that they could be observed much more easily. The images shown here are all phase images obtained from the AFM in tapping mode. While some of the branching in PE, PB copolymers is observed with branching angles of 80° (characteristic of α - α branching), some of the branching with branching angle of 40° is also observed. This latter mode of branching is characteristic of the epitaxial nucleation of γ -phase crystals on α -phase crystals. The latter branching mode, although suggested from micrographs in Fig 4.48b and Fig 4.49b, is better evidenced on a micrograph obtained by Dr. Xu (Fig 4.52).

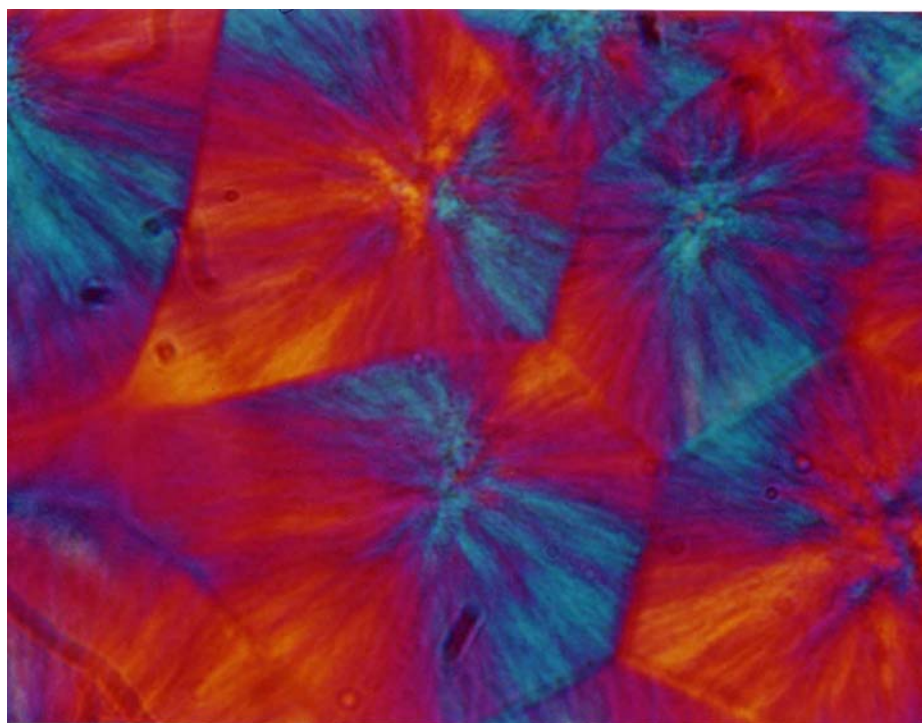
4.1.4 Optical Microscopy

Fig 4.53 shows the optical micrographs for PB-3.28. The micrograph on Fig 4.53a was recorded at the crystallization temperature of 125°C , while Fig 4.53b was recorded after subsequent heating to 148°C . The change in spherulite birefringence from the first to the second micrograph is clearly visible.

From the fact that yellow and blue are clearly visible in all quadrants of the spherulite (Fig4.53a), we can conclude that the spherulites are mixed birefringence at the crystallization temperature. The presence of yellow and blue in opposite quarters (Fig 4.53b) is representative of a negative birefringence. This suggests that the transformation on heating is from a cross-hatched morphology to radial lamellae, because radial lamellae exhibit negative birefringence while tangential exhibit positive birefringence.



a)



b)

Fig 4.53 Optical micrographs, for PB-3.28 isothermally crystallized at 125°C, recorded at a) 125°C and after subsequent heating to b) 148°C

4.2 Discussions

4.2.1 Introduction and Scope

As seen, from the literature review (Chapter 2), investigation of the crystallization and melting behavior of propylene/ α -olefin copolymers have been mostly restricted to propylene/ethylene copolymers. All these studies work together to bring out the following salient features regarding the crystal structure and properties of copolymer systems with randomly distributed comonomer units:

1. the presence of γ -phase along with the more common α -phase.
2. γ -phase formation is favored by slow cooling or by crystallization at higher temperature.
3. Increase in the comonomer content favors the formation of γ -phase crystal.

We know from previous studies and from this work that *it*-PP and propylene-based copolymers exhibit multiple melting behavior. This behavior can be attributed to any of the following:

1. Melting of alpha and gamma type crystals at the high and low endotherms, respectively.
2. Melting of thinner (daughter) and thicker (parent) lamellae at the low and high endotherms, respectively.
3. Melting of less stable crystals at the lower endotherm region, their recrystallization at higher temperatures during the heating process and their remelting in the higher endothermic region.

The aim of the present study is to understand the melting behavior of propylene copolymers keeping in mind the above issues. In order to do so, we need first to identify the presence of crystals of a particular phase. This can be done on the basis of WAXD results because we know that the crystals of each phase show characteristic Bragg peaks on a $\theta/2\theta$ scan (Section 2.3.2). Further confirmation for the presence of such crystals is obtained by examination of cross-hatching morphology using AFM which shows details on the lamella.

Analysis of the heating rate dependence of the melting behavior enables us to address the issue of recrystallization-remelting.

Putting all the above together, we provide in the following sections a tentative explanation for the multiple melting behavior for the propylene copolymers with ethylene, 1-butene, 1-hexene and 1-octene.

Studies reported in Section 4.1 clearly indicate that the crystallization and melting behavior of PE and PB copolymers are qualitatively similar to each other, but very different from those exhibited by PH and PO. In turn PH and PO copolymers are found to be almost identical, qualitatively and quantitatively. We will therefore discuss the experimental results for these two sets of copolymers separately.

4.2.2 PE and PB copolymers

4.2.2.1 Cooling Rate Studies

We established through cooling rate studies the temperature range in which crystallization takes place for PE and PB copolymers. Once this range was established, further experiments were carried out to understand the isothermal crystallization and melting behavior and morphologies of these substances.

The crystallization exotherms (Fig 4.2, Fig 4.3) show a marked shift towards lower temperature as the comonomer content was increased, which is an indication that the presence of ethylene and 1-butene comonomers hinders the crystallization process. The shift of these exotherms towards lower temperature with increasing cooling rate is a strong indication of the kinetic effects in the crystallization process of homo and copolymers.

4.2.2.2 Multiple Melting Behavior

4.2.2.2.1 Differential Scanning Calorimetry

The melting endotherms (Fig 4.6, Fig 4.7) recorded during heating subsequent to cooling, show two peaks for the slowest cooling rate samples. The presence of multiple peaks can be explained either as a result of a melting-recrystallization-remelting phenomenon or as a result of the presence of two different crystal populations in the as-crystallized sample.

To differentiate between these two possibilities, we studied the heating rate dependence of the melting behavior of PE and PB copolymers (Fig. 4.32 and 4.33, respectively). We analyzed the evolution of peak melting temperatures and heat of fusion associated with each endotherm with changes in heating rate for samples crystallized at

low and high temperatures (Fig. 4.36-Fig 4.39). For samples crystallized at high temperature, the interval between the high and low endotherm melting peaks decreases with increasing heating rate, while the ratio of low to high endotherm heats of fusion increases. These observations can be taken as evidence for melting-recrystallization-remelting effects during heating. Indeed, as the heating rate increases, less time is allowed for recrystallization above the initial melting endotherm, thus a smaller fraction of the material has time to recrystallize and a lower heat of fusion is observed for the upper endotherm. The fact that both the ratio of the heats of fusion associated with the high and overall endotherms and the interval between low and high endotherms appear to level off at high heating rates, suggests, however, that melting-recrystallization-remelting effects, while noticeable are not sufficient to explain the existence of two melting transitions. Furthermore, one does not expect recrystallization processes to take place to a significant extent for high molar mass polymers at heating rates in excess of 20°C/min. These conclusions are substantiated by examination of the heating rate dependence of the melting behavior for samples crystallized at low temperatures. In this case, a new endotherm appears at high temperature at the slowest heating rate. This endotherm is clearly associated with the melting of crystals formed during the heating scan. Comparison of the melting behavior of samples crystallized at low and high temperatures indicates that less melting-recrystallization-remelting effects are observed for samples crystallized at high temperatures than for samples crystallized at low temperatures. This is indeed expected as crystallization at higher temperature leads to crystals that are more stable and less susceptible to melting-recrystallization effects. Finally one should note that the multiple melting behavior is more pronounced for samples crystallized at high temperatures than for samples crystallized at low temperatures. Taking all these observations together we conclude that while some melting-recrystallization does occur for heating at the slowest rates in samples crystallized at the lowest temperatures, sole consideration of this mechanism is not sufficient to explain the multiple melting behavior. Therefore, the observation of multiple melting peaks must be associated with the existence of separate populations of crystals. At this point, one cannot conclude whether the multiple melting behavior is associated with the presence of lamellar crystals of the same phase but of different thicknesses or lamellar crystals of different

modifications. Distinction between these remaining two possibilities will be addressed in the next section, using results of the morphological studies. The same observations are made for PE copolymers, thus the same conclusions are reached in this case.

4.2.2.2.2 Morphological Studies

Using Atomic Force Microscopy, the cross-hatching morphology was established for PE and PB copolymers. Branching angles of 80° degrees and of 40° were observed in Fig. 4.49 and 4.50 and are characteristic of lamellar branching of the α - α and α - γ types, respectively. Previous studies by Bassett and White (128) have shown that daughter lamellae of the α -crystal phase, which form by homoepitaxial branching on a parent α -phase lamella, are thinner than the parent lamella, especially when crystallization is carried out at the highest possible temperatures. Daughter lamellae are therefore expected to melt at lower temperature than parent lamellae. These observations therefore suggest a possible origin for the multiple melting behavior. The low endotherm would be associated with the melting of daughter lamellae of the α -crystal phase and the high endotherm with the melting of parent lamellae α -crystal phase (primary radial lamellar structures).

A different explanation for the observed multiple melting behavior can also be proposed. As noted above, the observation of a 40° branching angle is indicative of the nucleation and growth of γ -phase daughter lamellar crystals onto parent α -phase lamellae (again through homoepitaxy). It is well known that γ -phase crystals are less stable than α -phase crystals. One could therefore also conclude that the lower endotherm is associated with the melting of γ -phase daughter lamellae, while the upper endotherm is associated with the melting of α -phase parent lamellae.

These two possible explanations are indeed consistent with the observations made by polarized optical microscopy (Fig. 4.53a and Fig. 4.53b). The polarized optical micrographs shown in these figures indicate that the birefringence characteristic of spherulites crystallized at 125°C changes from near zero (mixed birefringence) to negative as the PB spherulites were heated from 125°C to 148°C. A decrease in birefringence from a positive or near zero value to a negative value indicates a morphological change from spherulites having both radial and tangential lamellae to spherulites having only radial lamellae. Examination of the melting trace of a PB sample

crystallized at 125°C (Fig. 4.20) indicates that the lower endotherm ends at a temperature in the vicinity of 148°C. It can therefore be concluded that the low endotherm is associated with the melting of daughter (mostly tangential) lamellae and the high endotherm with the melting of radial parent lamellae.

Wide angle X-ray diffraction studies of PB-3.28 samples slowly cooled from the melt (crystallization taking place in the vicinity of 125°C) suggest that approximately half of the crystalline fraction is of the γ -modification (Fig. 4.47). Heating trace of a PB sample crystallized isothermally at 125°C suggests that approximately half of the overall heat of fusion is associated with the low endotherm. One can therefore conclude that most of the crystals melting at the low endotherm are γ -phase daughter lamellae. With the information available at this time, one cannot conclude in a definitive manner whether the difference in thickness between α -phase daughter and parent lamellae is sufficient to account for their melting at significantly different temperatures (low and high endotherms). The approximate match between the γ/α ratio of the content in the two crystal phases suggested by the WAXD analysis and the ratio of the heat of fusion associated with the low and high endotherm heats of fusion suggested by the DSC experiment, leads us to speculate that this may not be the case and that most of the α -phase crystals (daughter and parent lamellae) melt in the high endothermic region. This speculation could also explain the observation of two melting peaks in the high endothermic region and some of the melting-recrystallization effects observed within the high endotherm.

Focusing, now, on propylene/ethylene copolymers, one can conclude that the multiple melting behavior exhibited by PE-2.63 (Fig. 4.32) is very similar to that just discussed for PB-3.28. Wide angle X-ray diffraction studies reported in the literature (34) for PE copolymers indicate the coexistence of γ and α -phase crystals for samples crystallized slowly from the melt or isothermally at high temperatures. The heating rate dependence of the multiple melting behavior of PE copolymers (Fig. 4.32) is very similar that described above for PB copolymers. Polarized optical microscopy studies (note reported here) of PE-2.63 after crystallization and during heating show very similar changes in optical birefringence as witnessed in the case of PB-3.28. AFM micrographs shown in Fig. 4.49 also indicate clearly the existence of cross-hatching with branching

angles of 40° and 80°, consistent with the occurrence of α - α and α - γ crystallographic lamellar branching. We therefore conclude that the multiple melting behavior of PE copolymers is explained in exactly the same manner as for PB copolymers, in terms of a melting process for γ -phase daughter lamellae at the low endotherm and a melting process for the α -phase parent lamellae at the high endotherm. We also speculate that the α -phase daughter lamellae contribute to the higher endotherm.

4.2.2.3 Isothermal Crystallization Kinetics

Now, we examine the kinetics of isothermal crystallization for PE-2.63 and PB-3.28 copolymers. The kinetics of isothermal crystallization was followed by recording heating traces of samples crystallized for increasingly longer times. Typical data is shown in Fig. 4.18d for PE-2.63 for crystallization at $T_x = 125^\circ$. From the graph, we see that as the crystallization time increases, both melting endotherms rise or increase in magnitude at the same rate, at least initially. For longer crystallization times ($t_x > 40$ minutes), a slightly different behavior is observed. While the lower endotherm still continues to grow, the higher endotherm seems to level off. The crystallization behavior was studied for temperature ranging between 118°C to 130°C. The above mentioned trend can be observed at all temperatures. From the suggestion that the lower endotherm corresponds to γ -phase crystals, this data seems to indicate that the amount of γ -phase crystals continues to increase at long times, even after the α -phase crystal content has reached a maximum. Examination of heating traces for short crystallization times, suggest that the two endotherms develop simultaneously, thus the crystallization rates for the α and γ -phases would be identical. This is further confirmed in Fig 4.28c, where we show the Avrami exponents as calculated from each endotherms. We see that within the limits of experimental error, these two match perfectly. Thus we can safely conclude that the crystallization rates for the two different crystal populations are same at short crystallization times. Exactly the same argument holds true for PB-3.28 considering the analysis of Fig 4.19 and Fig 4.27c. Identical rates of crystallization for the alpha and gamma crystal phases at short times is consistent with the fact that the rate of crystallization of γ -crystal (daughter lamellae) is controlled by that of the parent (α -crystal) lamellae. The growth of alpha-phase crystals proceed until impingement of the spherulites, after which α -phase crystallization stops. In-filling of γ -phase crystals

between α -phase primary lamellae however continues as long as non-crystallized melt is available.

The higher the crystallization temperature, the lower the concentration of primary α -phase lamellar crystals (the smaller the high endotherm), the longer the content in γ -phase daughter lamellae (the larger the low endotherm).

4.2.3 Propylene/1-Hexene and Propylene/1-Octene Copolymers

4.2.3.1 Cooling Rate Studies

The crystallization curves, given in Fig. 4.12a and 4.12b, show that the degree of crystallinity of PH and PO copolymers increases rapidly at high temperature and more slowly but steadily at lower temperatures. This observation can be easily explained in terms of the exclusion model. The initial increase in crystallinity at high temperature is accounted by the crystallization of the longest propylene sequences. As the temperature is lowered further, shorter and shorter sequences crystallize. As the comonomer content increases, the sequence length distribution shifts toward smaller sequence length values, leading to a decrease in the fraction of long sequences and an increase in the fraction of shorter sequences. Finally, we note that the crystallization behavior of these copolymers under cooling at a constant rate is very reminiscent of that for ethylene/styrene (24) and ethylene/1-octene (104) random copolymers, which were studied in our laboratory. These similarities are indeed expected as the styrene and 1-octene units in the latter copolymers are excluded from the crystal lattice of polyethylene (see section 4.3.3).

4.2.3.2 Multiple Melting Behavior

PO and PH copolymers exhibit multiple melting behavior subsequent to isothermal crystallization. Melting studies reported in the previous chapter (Fig. 4.41, 4.42 and 4.43) show that the multiple melting behavior is more prominent for crystallization carried out at high temperatures, when the heating rate is larger (see for instance Fig. 4.35). While some reorganization is indeed apparent during heating at the slowest rates for materials crystallized at the highest undercoolings, it is clear that as was discussed in the case of PE and PB copolymers, the multiple melting behavior of PH and PO copolymers cannot be explained solely by melting-recrystallization effects. One might consider that the heating rate dependence of the heats of fusion associated with the low and high endotherm for PO and PH copolymers (Figures 4.41b, 4.41c, 4.43b, 4.43c)

suggest significant melting recrystallization effects. However, careful examination of the original melting endotherms (Figures 4.33b and 4.34b) suggests that these trends are very likely artifacts of the crude “deconvolution” process used in this work (see figure 4.24).

A better clue for the understanding of this multiple melting behavior is obtained through considerations of results from the isothermal crystallization studies. It should be noted, first, that the evolution of the melting behavior of PH or PO copolymers as a function of crystallization time and temperature appears to be identical to that reported recently by our laboratory for ethylene/styrene and ethylene/1-octene copolymers. The high endotherm melting temperature is independent of crystallization time, while the low endotherm shifts to higher temperatures with longer crystallization times (Figures 4.21 and 4.22) at a rate that decreases with crystallization temperature (Figures 4.29 and 4.30). This behavior is in sharp contrast with that exhibited by PE and PB copolymers (Fig 4.27 and 4.28) where both melting endotherms shift to higher temperature with longer crystallization time and where the rate of shift of each melting temperature with crystallization time increases with increasing crystallization temperature. It is therefore easy to conclude that the mechanisms responsible for the multiple melting behavior in PE or PB copolymers must differ from that responsible for the multiple melting behavior in PH or PO copolymers.

To support the last statement, it is worthwhile examining again the morphologies exhibited by these different copolymers. AFM micrographs shown in Figures 4.48-4.52 show that while cross-hatching is clearly observed for PE and PB copolymers, it is not observed for PH and PO copolymers. We also recall the conclusion from a previous section that the multiple melting behavior of PE and PB copolymers is explained by invoking the cross-hatching morphology (i.e. the lamellar branching process). We therefore conclude that multiple melting behavior observed for PH and PO copolymers is not explained by the presence of parent and daughter lamellae. We interpret the multiple melting behavior of PH and PO copolymer in light of the results obtained for ethylene/1-octene and ethylene/styrene copolymers, and assign the high melting endotherm to the melting of lamellae formed during primary crystallization and the low melting endotherm to the melting of small crystals formed during secondary crystallization. Secondary crystallization would involve sections of copolymer chains, characterized by propylene

sequences which did not participate in the primary crystallization process because they were too short to lead to the formation of stable chain folded lamellae. Previous studies of ethylene copolymers showed that these secondary crystals are either fringed-micellar or mosaic-block in nature, depending on the crystallization temperature and are principally located near the interfaces of primary lamellar crystals.

Wide angle X-ray diffraction studies (Figures 4.44, 4.46 and 4.47) show that both α and γ -phase crystals are present in these copolymers. Fig. 4.47 specifically shows that the γ -phase content becomes very significant when crystallization is carried out by slow cooling. With the information available at this stage and in the absence of visible cross-hatching, we can only speculate that the γ -phase crystals are responsible for the low endotherm. Such speculation is based on the observation that both the γ -phase content and the relative importance of the low endotherm, increase with crystallization temperature. Using wide angle X-ray diffraction during heating of these copolymers would certainly resolve this issue.

Another important issue, which this study has not resolved, is concerned with the relationship between the α and the γ -phase crystals in these copolymers. All studies of PE and PB copolymers, including the present work, suggest that the γ -phase nucleates by homoepitaxy on the surface of α -phase crystals as in the case of pure *it*-PP. What happens in the case of PH or PO copolymers is not known. One can easily speculate that the absence of cross-hatching (i.e. the absence of homoepitaxy) is associated with the presence of butyl or hexyl branches on the *a*-*c* lateral surface of the α -phase lamellar crystals which are formed during primary crystallization. The butyl and hexyl branches, originating from the 1-hexene and 1-octene comonomers, would prevent the adsorption of new crystallizable sequences in the crystallographic registration required for epitaxial nucleation of a daughter lamella.

4.2.4 Inclusion/Exclusion of Comonomers

Recent NMR studies of propylene/ethylene copolymers by Alamo et al. (120) suggest that ethylene comonomers are included in the *it*-PP crystal structure. Further studies by the same authors (126) indicate that while ethylene and 1-butene comonomers are indeed included in the crystalline phase of these propylene-based copolymers, 1-hexene and 1-octene are not included because of their larger size (steric effects). These

authors also indicate that both the crystallinity and the melting points of PE copolymers are much higher than these of the PH and PO copolymers. This latter observation also holds true for our studies. PE (Fig. 4.10a) and PB (Fig. 4.11a) show degrees of crystallinity in the vicinity of 40%, while PH and PO copolymers exhibit degrees of crystallinity of ca. 30% for similar comonomer content (ca. 3 mol%). Alamo et al. (126) further suggest from indirect SAXS measurements that the inclusion of ethylene comonomers would result in an increase in the number and length of crystallizable sequences, which, in turn, would lead to thicker and well-defined lamellae. Our AFM studies (Fig. 4.48- Fig 52) indeed confirm that PE-2.63 and PB-3.28 have thicker and better-defined lamellae than PH-3.05 and PO-3.43. These latter observations are consistent with the suggestion that while ethylene and 1-butene are included in the propylene lattice, 1-hexene and 1-octene are not.

These conclusions are fully consistent with the results of cooling rate studies discussed in the previous sections (4.2.2.1 and 4.2.3.1).

Further support for the exclusion of 1-hexene and 1-octene units and for the inclusion (at least partial) of ethylene and 1-butene units is provided by examination of the evolution of both the melting temperature and the enthalpy of fusion of copolymers as a function of comonomer content. According to Flory's Copolymer theory, the melting temperature and the degree of crystallinity of a random copolymer should be independent of the nature of the comonomer if the comonomer is excluded. Figures 4.13-4.16 indeed show that for a given comonomer content, the melting temperature and the enthalpy of fusion of PB is higher than that of PE, and that these melting temperatures are significantly higher than these of PH and PO. In turn, the melting temperatures and enthalpies of fusion for PO copolymers are, within the uncertainty of the measurements, identical to those of PH copolymers.

One can therefore conclude this section by stating that on the basis of NMR results by Alamo et al. (120, 126) and on the basis of our calorimetric and morphological work, it is now well established that ethylene and 1-butene comonomers are included in the propylene lattice, while 1-hexene and 1-octene comonomers are not.

Chapter 5

Conclusions and Scope for Future Work:

The primary goal of this thesis was to understand the crystallization and melting behavior of polypropylene copolymers with ethylene, 1-butene, 1-hexene and 1-octene and to correlate this melting behavior with the morphology and presence of different crystal phases. The inclusion and exclusion of comonomers in the crystal lattice was another issue that was addressed. The following section enumerates the conclusions that can be drawn from this study.

5.1 Conclusions

The data clearly suggests that copolymers of propylene/ethylene and propylene/1-butene show similar behavior while propylene/1-hexene and propylene/1-octene act similar. In addition these two pairs behave in a manner, rather different from each other. This may be attributed to the inclusion of ethylene and 1-butene comonomers in the crystal lattice and the exclusion of 1-hexene and 1-octene from it. While, we cannot draw any quantitative conclusions regarding the level of inclusion or of exclusion of these comonomers in the it-PP lattice, the depression in melting temperature, crystallinity and crystallization rate suggests the following trend in the extent of inclusion in PP lattice Hexene = Octene=0 << Ethylene < Butene.

This study has confirmed that the formation of γ phase crystals is favored by crystallization at high temperatures or during extremely slow cooling for all four copolymers. Conversely, crystallization at low temperatures or fast cooling favors the formation of α -phase crystals.

PB and PE show the presence of both tangential and radial lamellae. The typical cross-hatching behavior is clearly seen from the AFM micrographs and inferred from the optical microscopy studies. PH and PO do not have any tangential lamellae, showing the presence of predominantly γ -phase obtained on slow cooling.

PB and PE copolymers exhibit the following characteristics:

1. Their crystallization is very similar to PP-homopolymer.

2. The formation of γ -phase and α -phase daughter lamellae is controlled by the growth of α phase primary lamellae.
3. The gamma-phase daughter lamellae melt at the lower endotherm, while the parent alpha lamellae melt at the high endotherm.
4. Melting-Recrystallization-Remelting processes, while present principally for copolymers crystallized at low temperatures, do not explain the multiple melting behavior.

PH and PO exhibit the following characteristics:

1. Their crystallization behavior is very similar to that of ethylene/octene and ethylene/styrene copolymers.
2. Their melting temperature, degree of crystallinity and crystallization rate decrease with increasing hexene and octene content.
3. The crystals show very little reorganization on heating.
4. High and low endotherms correspond to the melting of crystals formed during primary and secondary crystallization, respectively.

This study has provided a significant first step towards a better understanding of the crystallization and melting behavior of propylene copolymers and of the correlation between morphology and crystal structure. Further work needs to be done, to understand more thoroughly the crystallization mechanism, especially in the case of propylene/1-hexene and propylene/1-octene copolymers.

5.2 Suggested Future Work:

For the four copolymer systems, DSC analyses should be complemented with more extensive WAXD data. This will give a better understanding of the correlation between α/γ phase content and crystallization. The change in crystal phase content with temperature should also be studied.

Further AFM studies should be carried to investigate the location and nature of secondary crystals in the case of PH and PO copolymers.

In order to understand the industrial applications of such copolymer systems, it is very important to understand the structure-property relationships. Also worthwhile would be looking at the effect of various processing conditions on the structure and hence property of such substances.

In this study, we've shown the effect of various crystallization conditions on the formation of α and γ -phases. Also the formation of the lamellae (thick and thin) was shown to be a function of the crystallization temperature as well as the rate of cooling. We've also shown that certain comonomers (ethylene, 1-butene) are included in the crystal lattice while others (1-hexene, 1-octene) are not. On the basis of these observations, we need to further probe the effect of these structures on the properties of copolymers of propylene. Once we are able to establish the relationship between the aforementioned behavior and the mechanical and thermal properties, we would be in a much better position to judge the industrial applications of these polymer systems. As shown in Chapter 1, propylene/1-ethylene copolymers are the only ones that are widely used commercially. Further use of the copolymers mentioned in this study can be promoted once the processing-structure-property relationships are better understood for them.

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