Molecular weight and tacticity effect on morphological and mechanical properties of Ziegler–Natta catalyzed isotactic polypropylenes

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Abstract

The morphological and mechanical properties of Ziegler–Natta catalyzed isotactic polypropylenes as influenced by the molecular weight and tacticity was investigated. Polypropylene samples were injection moulded into standard disks with a HAAKE MiniJet II injection moulder at 190 °C and 200 bar for morphological and mechanical tests. The morphological and mechanical properties of specimens were investigated by means of optical microscope (OM), scanning electron microscopy (SEM), microhardness (MH) and dynamic mechanical analysis (DMA). The samples exhibited a typical α-modification spherulite structure of isotactic polypropylenes crystallized from the melt. It was found that the most important factor affecting the structure and properties of these polymers is the isotacticity content. A clear molecular weight effect was also found for samples with low molecular weights. The microhardness and storage modulus values increased as crystallinity did. Accordingly, isotacticity degree is considered as the main parameter affecting the crystallinity of samples.

Keywords: *mechanical property, molecular weight, morphological property, polypropylene, tacticity.*

1. Introduction

Polypropylene is one of the most common polymers in use today. Its good mechanical properties and relatively low price result in the continuous growth of its production and the expansion of its market. Its continuously increasing application accelerates research in all related fields, including the preparation of isotactic polypropylene based composites and blends[1]. The mechanical and physical properties of polypropylene are influenced by a number of factors. The mechanical properties of the majority of polypropylene homopolymers are, apart from processing conditions, influenced by their rheological and crystallization behaviour. The degree of crystallinity is considered to be the most influential property affecting the physical and mechanical properties of a polypropylene sample[2-4]. An increase in crystallinity is often related to an increase in properties such as the stiffness or storage modulus of a sample, while other factors such as the impact strength generally decrease with increasing crystallinity. The storage modulus can be defined as the ratio of stress to strain under vibratory conditions which can be calculated from data obtained from either free or forced vibration tests, in shear, compression, or elongation. The Stiffness can be defined as the rigidity of the material to which it resists deformation in response to an applied force. An increase in crystallinity can lead to an increase in the lamellar thickness which leads to higher storage modulus and stiffness values[2-4]. The effects of molecular weight[5-8], molecular weight distribution[9] and tacticity[10-13] on the crystallization have been investigated by several authors. Cheng et al.[6] showed that the linear growth rate of crystals decreases with the increase of molecular weight,

but the overall crystallization rate might increase because an increasing number of intramolecular folded-chain nuclei could result in a higher nucleation density[7]. For samples with similar molecular weights and different tacticities the linear crystal growth rate might increase by three orders of magnitude when the isotacticity (*mmmm* %) of isotactic polypropylene increases from 78.7 to 98.8%[11,14]. The degree of crystallinity of isotactic polypropylene is commonly in the range of 40 to 70%[1]. Atactic polypropylene, on the other hand, is considered uncrystallizable, since the chain structure lacks regularity. Isotactic polypropylene can crystallize in three different crystal forms as was described by Bruckner et al.[15], depending on the polymer structure and the crystallization conditions: the α-form with a monoclinic, the γ-form with an orthorhombic and the β-form with a hexagonal unit cell[15].

The molecular weight has also been shown to influence the glass transition temperature (T_g) of polymers, with higher molecular weight samples having a higher T_g[16]. This in turn influences the mobility of chains at room temperature, and since polypropylene has a T_g range in the region of 0 °C, variations in the T_g temperature range can have an effect on the ability of the material to displace energy at low temperatures.

The aim of the current study is to explore narrowly the structure–property relationships of polypropylene. The morphological and mechanical properties of different samples were investigated by means of optical microscope (OM), scanning electron microscopy (SEM), microhardness

(MH) and dynamic mechanical analysis (DMA) to demonstrate the effect of isotacticity and molecular weight on the properties of polypropylene samples. To the best of our knowledge the investigation of how the molecular weight affect the thermal, morphological and mechanical properties of isotactic polypropylene has not been done yet to polymer studies which has previously been overlooked.

2. Experimental Section

2.1 Materials

Polypropylene polymers and fractions used in this study were selected from our previous study as shown in Amer and van Reenen[17] and Table 1. These polymers were prepared using a commercial Ziegler-Natta catalyst with 2.78 wt% Ti content purchased from Star Chemicals & Catalysts Co. (China) and labeled as P3−P17. P4[120], P5[120], P8[120] and P9[110] refer to polypropylene TREF fractions eluted at 120 and 110 °C, respectively.

2.2 Polymerization procedure

All polymerization reactions were carried out under an inert gas atmosphere. The polymerization reactions were carried out in a 350-mL stainless steel Parr autoclave with a gas inlet and pressure gauge. Typically the reactor was charged with the catalyst (43 mg, Ti content 2.78 wt%) and triethylaluminium (2 mmol, Al/Ti mole ratio 80) in toluene (25 mL). The catalyst solution was stirred for 5 min and then the propylene was added. The reactor was pressurized with hydrogen and the contents stirred for 1 h at room temperature. The reaction was then quenched by the addition of 100 ml 10% HCl/MeOH. The resulting polymer was filtered off, washed several times with methanol, and subsequently dried under vacuum at 80 °C for 15 h, to yield about 3-5 g of polypropylene as a white powder.

2.3 Sample preparation for mechanical tests

Test specimens were injection moulded into standard disks for morphological and mechanical tests with a HAAKE MiniJet II injection moulder. The injection moulding temperature was 190 °C and the injection pressure was 200 bar. The dimensions of the standard disks are 20.0 mm in diameter and 1.5 mm in thickness.

2.4 Preparation of etching reagent

Permanganic etching of polyolefins was used to prepare samples for the study of the morphology. This technique has been used in several studies involving polyolefins[18-21]. Potassium permanganate (1 g) (obtained from Sigma-Aldrich) was dissolved in 100 mL of a concentrated solution of 33 vol % phosphoric acid and 67 vol % sulphuric acid (Sigma-Aldrich). The solution was prepared by adding potassium permanganate very slowly to the beaker containing both acids, with rapid agitation. After adding all the potassium permanganate, the beaker was closed and the content stirred until all the potassium permanganate was dissolved (a dark green purple solution formed). All polypropylene samples were etched at room temperature.

2.5 Etching procedure

Specimens from each polymer, with approximate dimensions of length 10 mm, width 5 mm and thickness 1.5 mm, were cut from the disks prepared by injection moulding. Each sample was immersed in about 10 mL of the etching reagent in a beaker for a period of 60 minutes. This permanganic acid solution preferentially etches the amorphous part of the polymer in the spherulites in such a way that the lamellae then appear clearly. Subsequently, the specimens were carefully washed with hydrogen peroxide, distilled water and acetone, in order to avoid any artefacts caused by pollution effects. Samples were finally dried in a vacuum oven at 45 °C for 5 hr.

2.6 Polymer characterization

A Zeiss Axiolab OM, (magnification × 50-100 μm) with a high resolution camera CCD-IRIS (Sony) was used to examine the etched piece, to investigate the crystal structure.

SEM analysis of etched piece was performed using a Leo® 1430VP scanning electron microscope operated at 15 kV of acceleration voltage at room temperature. All the surfaces to be studied were coated with gold under vacuum in order to eliminate any undesirable charge effects during the SEM observations.

Samples for compressive DMA were analyzed using a Perkin Elmer DMA 7e calibrated according to standard procedures. The samples were first melted at 180 °C for 8 minutes and then melt pressed at 5 MPa and same temperature. The samples were analyzed using a 5 °C/min

Table 1. Characterization data of the polypropylenes and fractions.

Samples	M_w^a (g/mol)	M_w/M_n	$mmmm^b$ (%)	T_m^c (°C)	T_c^c (°C)	ΔH_m^c (J/g)	X_c (%)
P3	184 759	6.1	93.0	161.2	124.2	104.5	50.0
P4	252 956	5.4	94.0	160.6	116.5	103.9	50.0
P5	312 580	4.1	96.0	161.9	118.4	108.9	52.0
P8	228 960	6.4	94.0	162.0	124.4	103.9	50.0
P14	215 397	5.9	86.0	157.5	119.8	90.5	43.0
P17	65 498	8.2	93.0	156.5	120.8	100.5	48.0
P4[120]	195 693	4.3	98.0	160.0	116.0	119.7	57.0
P5[120]	207 823	2.9	96.0	161.0	118.0	103.2	49.0
P8[120]	178 423	3.5	96.0	158.6	116.3	106.9	51.2
P9[110]	110 387	3.4	98.0	158.7	118.4	110.7	53.0

[a]determined by GPC. [b]determined by NMR. [c]measured by DSC.

heating ramp with an applied force oscillating at a frequency of 1 Hz. The static force was kept constant at 110% of the dynamic force. The temperature range analyzed was between –40 °C and 230 °C.

MH measurements were conducted on a UHL microhardness tester equipped with a Vickers indenter. Measurements were obtained using an indentation speed of 25 μm/s and a dwell time of 15 s. Samples were analyzed at indentation loads of 10 gf. Ten measurements were recorded for each sample analyzed.

3. Results and Discussions

3.1 Morphological properties

Table 1 summarizes the polypropylene polymers and fractions used in this study.

3.1.1 Optical Microscopy analysis

First, the effect that the molecular weight has on the crystal structure of different polypropylene samples was studied. Figure 1a-c shows OM micrographs of polypropylene fractions $P5^{(120)}$, $P4^{(120)}$ and $P9^{(110)}$ respectively, which differ in molecular weight (see Table 1). They exhibit a typical α-modification spherulite structure of isotactic polypropylenes crystallized from the melt. These micrographs show that all the isotactic polypropylene fractions have well-defined and large α-spherulitic morphology. The spherulites grew,

impinged on each other, and formed particular polygonal spherulites with clear boundaries. Indications are that, since all the observed spherulites grew at the same rate and their observed size can be considered uniform, the nuclei are formed immediately after cooling to the crystallization temperature and their number remains constant thereafter.

The only effect of the molecular weight that can be noticed in Figure 1 is the slight morphological differences in the sign of birefringence, magnitude of the birefringence and spherulite texture. Second, the effect of tacticity on the crystal structure of different isotactic polypropylenes was studied. Figure 2a-c show OM micrographs of polypropylenes P5, P4 and P14, which differ in their tacticities (Table 1). The graphs show that, under similar crystallization conditions, the dimensions of the crystal structures of these different isotactic polypropylene samples decrease in size with tacticity. This effect can be explained by the restriction of movement of polymer chains caused by chain defects in low tacticity polymers during the crystallization process, resulting in slower crystallization and hence the formation of smaller spherulites. Similar results were obtained in other studies[22-24].

3.1.2 Scanning Electron Microscopy analysis

Figure 3a-c shows SEM micrographs of the typical crystallization morphologies of the isotactic polypropylene fractions $P5^{(120)}$, $P4^{(120)}$ and $P9^{(110)}$ respectively, which differ in molecular weight. All these isotactic polypropylenes

Figure 1. Optical micrographs of isotactic polypropylene fractions: (a) $P5^{(120)}$ (M_w = 207823 g/mol), (b) $P4^{(120)}$ (M_w = 195693 g/mol) and (c) $P9^{(110)}$ (M_w =110387 g/mol) (500x magnification).
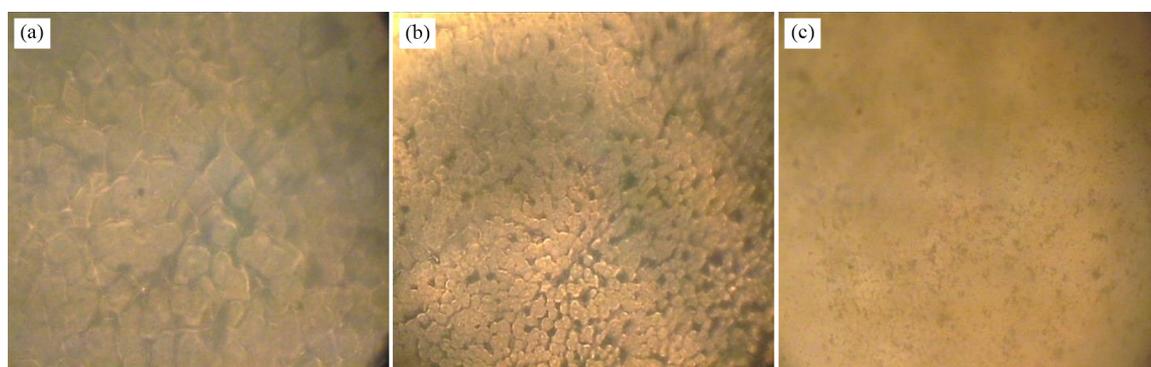

Figure 2. Optical micrographs of isotactic polypropylene polymers: (a) P5 (*mmmm* = 96%), (b) P4 (*mmmm* = 94%) and (c) P14 (*mmmm* = 86%) (500x magnification).

revealed well-defined and large spherulitic morphology, comprising a mixture of α1 (disordered) and α2 (ordered) crystal form structures. The spherulites grew, impinged on each other, and formed particular polygonal spherulites with clear boundaries. Moreover, one can clearly see the individual lamellae and lamellar branching structure in the SEM micrographs in Figure 3. The samples consist of crosshatch-type lamellar branching structures, which is the typical characteristic of the α crystal form of isotactic polypropylenes[25,26]. In contrast to OM results, clear differences can be distinguished between the three different isotactic polypropylene samples shown in Figure 3. These differences exist in the variety of spherulite sizes and spherulite types classified by their appearance, including the sign and nature of birefringence and crystal lattice. The average diameter of P5[(120)] spherulites is about 5-15 μm (Figure 3a). Smaller dominant α spherulites (about 5-10 μm) are observed for P4[(120)] and P9[(110)] (Figure 3b, c respectively).

Figure 4a-c illustrates SEM micrographs of polypropylenes (P5, P4 and P14) that differ in their tacticities (Table 1). Similar to those results obtained from OM above, SEM also shows in Figure 4, that the sizes of the spherulites were decreased drastically with decreasing tacticity. In addition, with decreasing tacticity, the spherulites showed less perfection and the sharp spherulite boundaries became more diffuse (Figure 4c).

The sample P5 with 96.0% tacticity has the biggest spherulite sizes (15-25 μm) while samples P4 and P14 with 94.0% and 86.0% tacticities have spherulite sizes about 5-15 and 1-3 μm respectively. SEM micrographs (Figure 4a, b) also show small dimples on the etched surface

of samples P5 and P4 may grow to craters and holes. This is due to the extractions of the rubbery materials by the etchant solution[19,20,27,28].

3.2 Mechanical properties

In order to correlate the structure of the polypropylene polymers with the mechanical properties, the samples were analyzed using microhardness and DMA.

3.2.1 Microhardness

According to literature[29-33], all the parameters that lead to an increase of crystallinity and crystallite sizes (lamellar thickness) will also lead to higher MH values. Hence, the higher the isotacticity, the greater the MH values obtained. The effect of the molecular weight and molecular weight distribution on the crystallinity of the polypropylene samples P3, P4, P5, P8, P17, P4[(120)] and P8[(120)] was investigated and results are illustrated in Figure 5. The samples of low molecular weight generally have a broader molecular weight distribution, and vice versa. The molecular weight distribution has an effect on the crystallinity: the samples with a higher degree of crystallinity have a lower molecular weight distribution, and samples with lower degree of crystallinity have a higher molecular weight distribution. On the other hand, there is a slight increase in the crystallinity of the samples with an increase in the molecular weight.

Figure 6 shows the combined effect of the molecular weight and isotacticity on the degree of crystallinity of the polypropylene samples P3, P4, P5, P8, P17, P4[(120)], P8[(120)] and P9[(110)]. There is a remarkable increase in crystallinity as the isotacticity is increased, from about 93% to 98%.
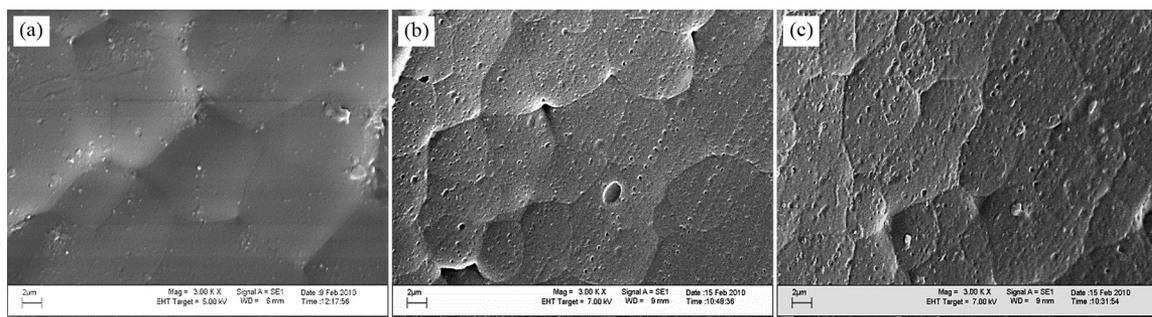

Figure 3. SEM micrographs of isotactic polypropylene fractions: (a) P5[(120)] (M_w = 207823 g/mol), (b) P4[(120)] (M_w = 195693 g/mol) and (c) P9[(110)] (M_w =110387 g/mol) (3000x magnification).

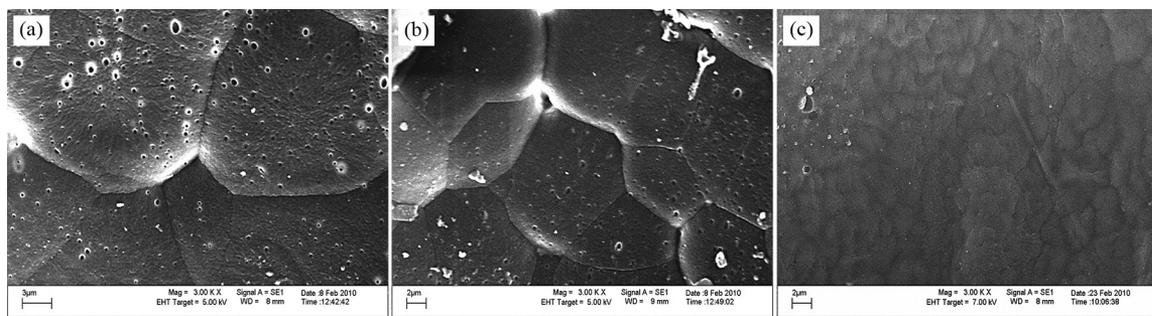**Figure 4.** SEM micrographs of isotactic polypropylene polymers: (a) P5 (*mmmm* = 96%), (b) P4 (*mmmm* = 94%) and (c) P14 (*mmmm* = 86%) (3000× magnification).

In general, the samples with high molecular weight have high isotacticity, as expected, since the more stereospecific sites have a higher propagation constant rate (K_p). This is in agreement with the results obtained by Sakurai et al.[34] with regards to the relationship between isotacticity and molecular weight. Moreover, Figures 5 and 6 show that the crystallinity of the samples was largely affected by the isotacticity, which clearly dominates over other effects such as molecular weight and molecular weight distributions. Nevertheless, when the isotacticity values from the polymer samples are similar, the molecular weight and molecular weight distributions exert significant influence on crystallinity.

Looking at the combined effect of the molecular weight and crystallinity on the microhardness of the samples P3, P4, P5, P8, P17, P4(120), P8(120) and P9(110), as shown in Figure 7, generally one can see that there is a major increase in the MH with increasing molecular weight and crystallinity of the samples. Since that the most important factor affecting

the crystallinity of these polypropylene polymers is the isotacticity content, the combined effect of the molecular weight and isotacticity on the MH of the samples P3, P4, P5, P8, P17, P4(120), P8(120) and P9(110) is illustrated in Figure 8. It appears that there is a significant increase in the MH with increasing isotacticities of the samples. Hence, it can be said that the higher the isotacticity the greater the MH. This means that the most important factors affecting the MH of these polypropylene polymers are those that lead to an increase in crystallinity. In addition, the main parameter which affects the crystallinity can be considered to be the degree of isotacticity of the samples.

It is reasonable that the higher isotacticity content allows easier recrystallization upon the application of an external force to the sample, thus improving the hardness of the sample upon indentation. The magnitude of the effect of the tacticity of the polypropylenes on the properties of the polymer has also been discussed by De Rosa et al.[35].
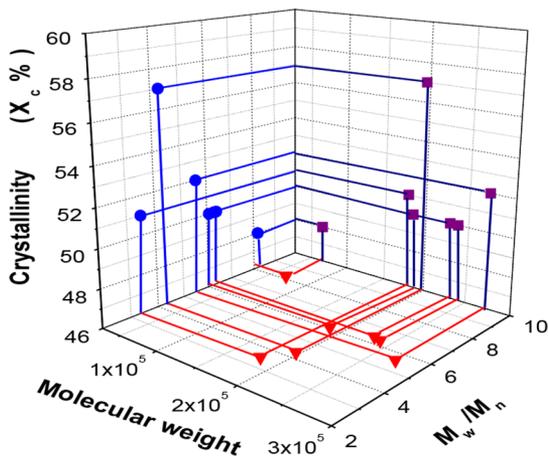

Figure 5. The effect of molecular weight and molecular weight distribution on the crystallinity of the isotactic polypropylene polymers P3, P4, P5, P8, P17, P4(120) and P8(120).

Figure 7. The combined effect of molecular weight and crystallinity on the microhardness of the isotactic polypropylene polymers P3, P4, P5, P8, P17, P4(120), P8(120) and P9(110).
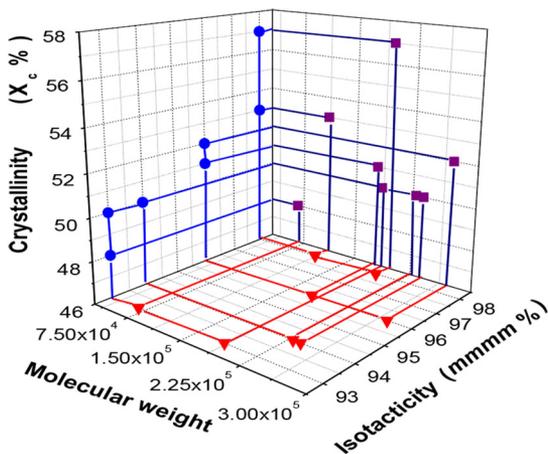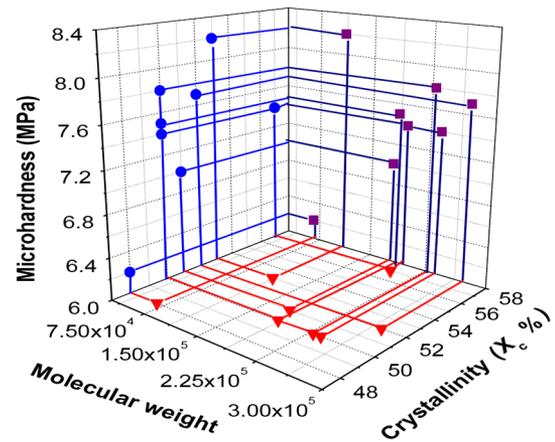

Figure 6. The combined effect of molecular weight and isotacticity on the crystallinity of the isotactic polypropylene polymers P3, P4, P5, P8, P17, P4(120), P8(120) and P9(110).
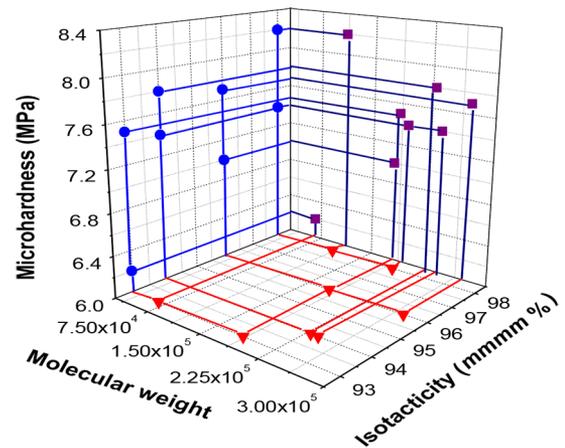

Figure 8. The combined effect of molecular weight and isotacticity on the microhardness of the isotactic polypropylene polymers P3, P4, P5, P8, P17, P4(120), P8(120) and P9(110).

3.2.2 Dynamic Mechanical analysis

3.2.2.1 Effect of molecular weight

Figure 9 shows the storage modulus of different isotactic polypropylene samples with different molecular weights, as a function in temperature. The storage modulus values increase with increasing molecular weight in the temperature range measured for the different samples. This is in agreement with the results obtained above from the microhardness test. Similar behaviour has been observed by other researchers[8]. The reason for the increase in the storage modulus values with increasing molecular weight is due to the higher degree of crystallinity and the presence of a larger number of molecular weight entanglements per chain for the higher molecular weight polymers. Furthermore, an increase in the lamellar thickness as the molecular weight increases also leads to higher storage modulus values[8].

The detailed plot of loss tangent (tan δ) of these isotactic polypropylene samples, as a function of the temperature, ranging from –40 to 80 °C is presented in Figure 10. The tan δ curves represent the ratio of the ability of the material to store and lose energy, which is sometimes referred to as the clamping ability of a material. It can also be taken as a measurement of the impact properties of the material. It is apparent from Figure 10 that β-transition, corresponding to the T_g of isotactic polypropylenes, which occurs over the temperature range 10-20 °C, is slightly shifted to a higher
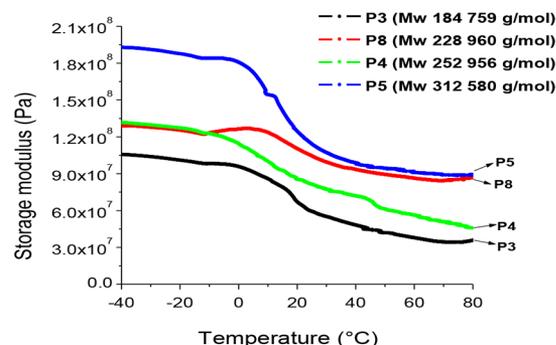
temperature as the molecular weight increases (from 16 °C for P3 sample with M_w 184 759 g/mol to 20 °C for P5 sample with M_w 312 580 g/mol). The samples with lower molecular weights are less crystalline and therefore contain more amorphous material. The explanation is that the chains have far greater mobility in the amorphous phase in the lower molecular weight samples compared to the samples with higher molecular weights. We do, however, also have to take into consideration the change in the molecular packing in the amorphous phase. Denser packing of the molecular chains leads to a reduction in the molecular motion. The areas of the β-transitions of the samples, after subtraction of a linear baseline, are given in Figure 11.

Figure 11 shows that the magnitude of the β-transition increases with increasing molecular weight. Similar results were obtained by Stern et al.[8], who found that the higher molecular weight polymers are generally characterized by larger β-transition. In fact, a decrease in the mechanical transition of the β process is associated with a reduction in the mobility of the polymer chains in the amorphous phase[8,36,37].

3.2.2.2 Effect of isotacticity

Figure 12 shows the difference in the storage modulus curves, as a function of temperature, for isotactic polypropylene samples with various isotacticities. Compared to the results obtained from varying the molecular weight, isotactity of isotactic polypropylene samples has further effect on the overall viscoelastic response as shown in Figure 12. The storage modulus is greater in the higher isotactic polypropylene samples than in those with lower tacticity, over the whole temperature range studied (1.51×10^8 Pa for P4(120) with 98 *mmmm* % vs 0.84 × 10^8 Pa for P14 with 86 *mmmm* %) as shown in Figure 12. Moreover, this effect is also observed in the location and intensity of the β-transition temperature, as shown in Figure 13.

As the isotactic content increases, the location of the β-transition temperature is considerably shifted to higher temperatures, but its intensity decreases significantly in the higher isotactic polypropylene fractions P5(120) and P4(120), as can be seen in Figure 14, which shows the areas of the β-transitions of the different samples. All of these features

Figure 9. Storage modulus curves as a function of temperature for isotactic polypropylene samples with various molecular weights.

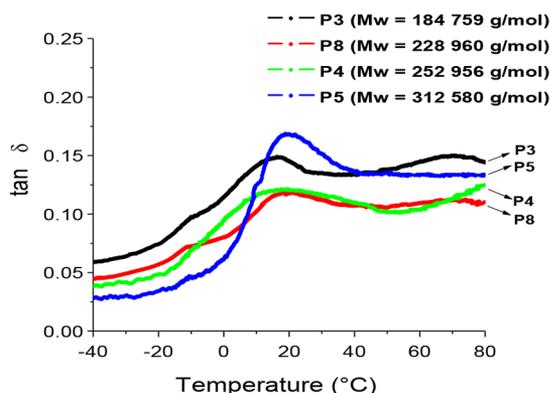**Figure 10.** Tan δ curves as a function of temperature for isotactic polypropylene samples with various molecular weights.
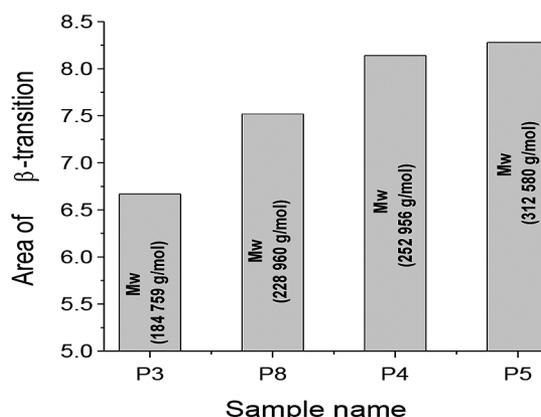

Figure 11. The magnitude of the area of the β-transition for isotactic polypropylene samples with various molecular weights.

can be associated with the higher degree of crystallinity that more regular chains can be reached, i.e. as isotacticity is increased in the isotactic polypropylene macromolecules. Therefore, the lowest content of amorphous regions is in the P4$^{(120)}$ sample, because its higher crystallinity (X_c = 57%, Table 1) leads to its higher storage modulus, a decrease in magnitude of the β-transition and the displacement of its location to higher temperatures due to the higher hindrance of motions within the crystalline phase.
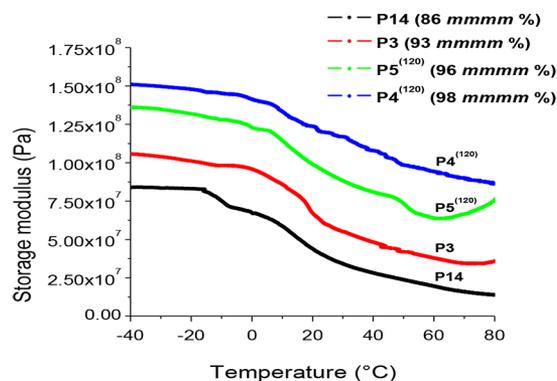

Figure 12. Storage modulus curves as a function of temperature for isotactic polypropylene samples with various isotacticities.
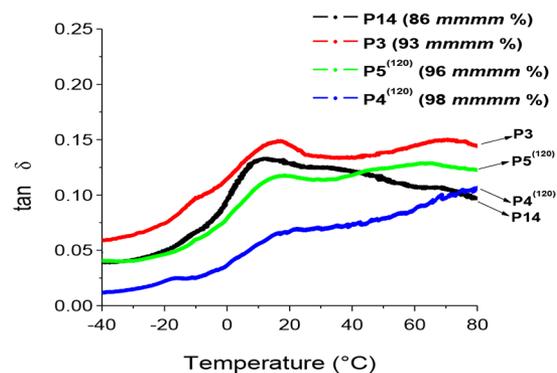

Figure 13. Tan δ curves as a function of temperature of isotactic polypropylene samples with various isotacticities.
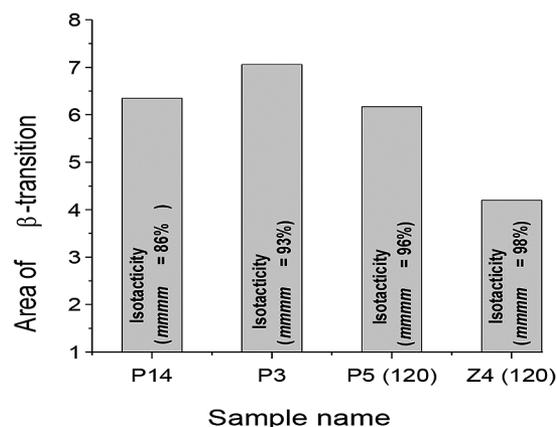

Figure 14. The magnitude of the area of the β-transition of isotactic polypropylene samples with various isotacticities.

4. Conclusions

The relationship between structure and properties was established for different polypropylene samples through their morphological and mechanical characterizations. The effect of isotacticity and molecular weight on the properties of polypropylene samples was investigated. The most important factors affecting the structure and properties of these polypropylene samples are those that lead to an increase of crystallinity. Consequently, the main parameter is the degree of isotacticity, followed by molecular weight. OM and SEM results showed that all isotactic polypropylene samples had well-defined α-spherulitic morphology. OM and SEM also showed that tacticity had a greater effect on the morphological structure of the isotactic polypropylenes than molecular weight. A decrease in isotacticity leads to a clear decrease in the dimensions of the crystal structures for the different isotactic polypropylene samples. Results of the MH and DMA showed that all the parameters that lead to an increase in crystallinity and crystallite sizes (lamellar thickness) will provide higher MH, storage modulus and β-transition temperature values. The crystallinity of the samples was shown to be affected by the molecular weight and molecular weight distribution, as well as by the isotacticity of the samples.

5. Acknowledgements

6. References

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