

# **STRUCTURE AND PROPERTIES OF POLY(4-METHYL-1-PENTENE)**

**RADKA MOŠNOVSKÁ**



## ABSTRACT

Práce se zabývá strukturou, vlastnostmi, použitím a zpracováním poly(4-methyl-1-pentenu). Izotaktický poly(4-methyl-1-penten) vykazuje polymorfní chování. Krystalizací z roztoků lze získat pět různých krystalických forem v závislosti na typu rozpouštědla a tepelné historii. Díky mimořádným optickým vlastnostem, vysokému bodu tání, nízké hustotě, dobré chemické odolnosti a vysoké propustnosti plynů jsou možnosti použití poly(4-methyl-1-pentenu) rozsáhlé. Využívá se například k výrobě lékařských pomůcek a zařízení, přípravě tepelně odolných potravinářských fólií, průhledných trubíc či k izolaci elektrických kabelů.

This work is focused on structure, properties, applications and processing of poly(4-methyl-1-pentene). Five different crystalline forms of isotactic poly(4-methyl-1-pentene) were obtained from crystallization in semidilute solutions depending on the solvent and thermal history of the solution. Isotactic poly(4-methyl-1-pentene) has potentially a wide range of applications, owing to its optical and electrical properties, high melting point, low density, high chemical resistance, and high permeability to gases. For example, it is being used for medical equipment, heat resistant food foils, transparent pipes or for coating of electrical wires.

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I declare I worked on this Bachelor Thesis by myself and I mentioned all the used literature.

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Radka Mošnovská

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## INTRODUCTION

Polymeric materials are used in nearly all areas of daily life and their production and fabrication are major worldwide industries. Their consumption is still increasing. The birth of polymer science and technology may be tracked back to the mid-19<sup>th</sup> Century. However, the history of stereoregular polymers started at the mid-20<sup>th</sup> Century. In the 1950s, Karl Ziegler and Giulio Natta independently developed a family of stereospecific transition-metal catalysts [1]. Stereoregular polymers of 4-methyl-1-pentene (4-MP-1) were first reported in 1955 following the discovery that  $\alpha$ -olefins could be polymerized in catalyst systems of the Ziegler type [2]. Of the numerous branched polyolefins higher than polybut-1-ene developed in research laboratories since the mid fifties, only poly(4-methyl-1-pentene) (PMP), introduced in 1965 by ICI (England), has achieved commercial importance [3].

Isotactic and syndiotactic poly(4-methyl-1-pentene) are semicrystalline polyolefins with a bulky side group ( $\text{CH}_2\text{-CH}(\text{CH}_3)_2$ ) [4]. Similar to most highly stereoregular  $\alpha$ -polyolefins, isotactic PMP is polymorphic, i.e. it can crystallize in several crystal unit cells depending on crystallization conditions [5].

From commercial and application viewpoint, only isotactic poly(4-methyl-1-pentene) (i-PMP) represents interesting material, particularly due to favourable properties, such as high chemical stability, excellent electrical properties, high melting point and low density [4]. The values of fundamental mechanical properties such as tensile modulus, tensile strength at yield, tensile strength at break, and elongation at break are comparable to those of high-density polyethylene (HDPE). However, i-PMP is more brittle than HDPE [5]. In many respects, i-PMP is a unique polyolefin. Crystalline phase of i-PMP is unusually less dense at room temperature than its amorphous phase ( $d_{\text{cryst}} = 830 \text{ kg/m}^3$ ,  $d_{\text{amorph}} = 838 \text{ kg/m}^3$  at 20 °C), in contrast with ordinary crystalline polymers [6]. Isotactic PMP is transparent as highly crystalline, indicating a similarity in the refractive indices of amorphous and crystalline phases of the polymer [5].

Isotactic poly(4-methyl-1-pentene) is being produced under the trade name TPX. Mitsui Petrochemical Industries is the only producer of i-PMP. A production of i-PMP does not exceed 10 000 tons per year [7]. Several possibilities of processing the polymer exist. Isotactic PMP can be injection moulded, blow moulded, cast or blown into sheet and film, extruded for wire coating, and spun into fibers [5]. Isotactic PMP is extensively employed

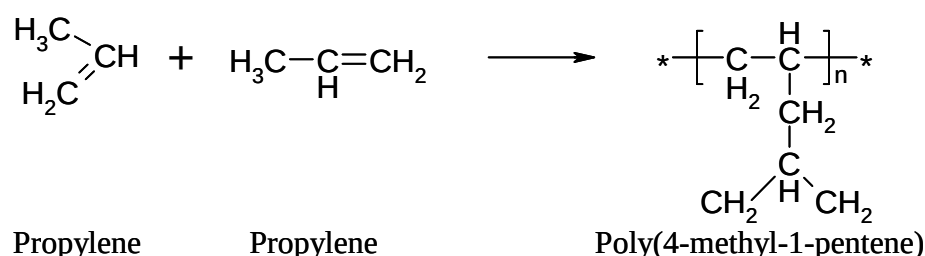
for a number of applications, such as medical and chemical equipment, microwave oven cookware or food packaging [4].

# 1 STRUCTURE OF POLY(4-METHYL-1-PENTENE)

## 1.1 Molecular structure

There are three possibilities of stereochemical arrangement of 4-methyl-1-pentene into the polymeric chains:

- Syndiotactic
- Isotactic
- Atactic



*Figure 1 Reaction of producing poly(4-methyl-1-pentene) by dimerization of propylene [3]*

The stereochemical configuration or “relative handedness” of successive monomer units in polyolefins such as poly(4-methyl-1-pentene) can strongly affect the physical and mechanical properties of the polymers [5].

The catalyst system employed and the polymerization condition are used to control polymer stereoregularity. The tacticity of PMP is strongly dependent on the catalyst system used (transition metal, solid matrix, metal alkyl cocatalyst, and donor compounds), polymerization temperature, and reaction diluent. The nature of the diluent can affect polymerization. The most active process uses the 4-MP-1 monomer as the diluent, thus maximizing the monomer concentration. The stereoregularity decreases with increasing polymerization temperature [5].

Several methods can be used to quantify the isotacticity of PMP. These methods include selective solvent extraction, infrared spectroscopy, x-ray diffraction, NMR spectroscopy.

Moreover, the atactic PMP cannot crystallize in the crystal structure so the crystallinity of the sample can reflect the tacticity of a sample [5].

### 1.1.1 Syndiotactic poly(4-methyl-1-pentene)

The discovery of homogeneous catalysts based on the group 4A metallocene/methylaluminoxane system for the polymerization of 1-alkenes has allowed the obtainment of new stereoregular hydrocarbon polymers and has induced new structural studies on polyalkenes. The syndiospecific catalytic system described by Ewen et al. [9] for the polymerization of propene is able to produce highly syndiotactic polymers of other 1-alkenes, such as crystalline poly(4-methyl-1-pentene). Also, it has been recently found that the homogeneous catalyst which promotes the syndiotactic polymerization of styrene is able to polymerize several 1,3-alkadienes. In particular, from the polymerization of 4-methyl-1,3-pentadiene, syndiotactic poly[1,2-(4-methyl-1,3-pentadiene)] is obtained. Catalytic hydrogenation of this polymer constitutes an alternative route for the obtainment of crystalline syndiotactic poly(4-methyl-1-pentene) (s-PMP) [8].

A helical conformation of the s-PMP chains with a sequence of dihedral angles of the kind (TTGG)<sub>n</sub>, has  $1.714 \pm 0.002$  structural units per helix turn, each conformational unit contains two monomeric units with the conformation TGGT. Each monomeric unit is related to the two neighbouring units two-fold axes perpendicular to the chain axis [8].

Syndiotactic PMP chains are in a  $(12_7)_2$  helical conformation packed in a tetragonal unit cell with the axis  $a = 1.803$  nm. The chain repetition occurs after 12 conformational units repeating helically (24 monomeric units) after seven turns around the chain axis. The possible packing model for s-PMP with space group P4 is presented in Figure 2 [8].

The calculated density for four chains in the cell (96 monomeric units) is  $878 \text{ kg/m}^3$ , in accordance with the experimental value ( $d = 852 \text{ kg/m}^3$  measured at  $25^\circ\text{C}$  by flotation for a sample with an X-ray crystallinity of  $\sim 45\%$ ) [8].

It is worth noting that the proposed model of packing for s-PMP is similar to that for form I of isotactic poly(4-methyl-1-pentene) in spite of the different configuration and conformations of the chains. This is pointed out by the similarity of their X-ray powder diffraction spectra. In fact, both the chains in isotactic (having  $7_2$  helical symmetry) and syndiotactic (having  $(12_7)_2$  helical symmetry) poly(4-methyl-1-pentene) have an outside

envelope similar to that of a cylinder in which hollows and bulges are periodically repeated as occurs in a screw. Such kinds of helices are generally packed in tetragonal lattices [8].

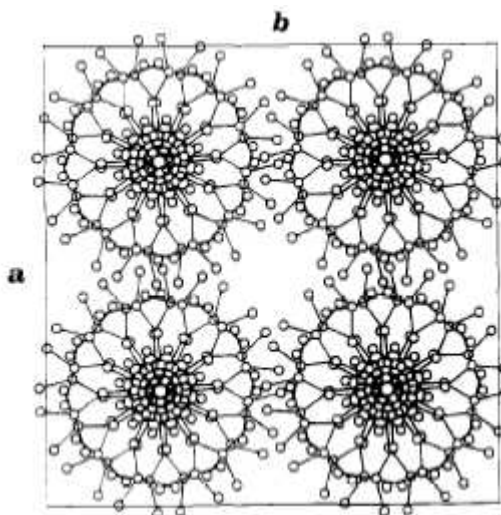


Figure 2 Possible packing model for *s*-PMP with space group *P4* [8]

### 1.1.2 Isotactic poly(4-methyl-1-pentene)

Isotactic poly(4-methyl-1-pentene) (i-PMP) presents a complex polymorphic behaviour. Five different crystalline forms have been found. The modifications of i-PMP are denoted as I, II, III, IV and V. They can be obtained from crystallization in semidilute solutions [10]. The final solid-state crystalline structure is determined by solution concentration, thermal history of the solution, cooling rate, nature of the solvent. Table 1 shows the effect of solvent on the crystalline structure of i-PMP crystallized from semidilute solutions ( $0.02 < \Phi_2 < 0.08$ ) after dissolution at temperature  $T_{max}$ . It is interesting to see that *n*-alkanes larger than  $C_9$  produce modification I, which is also obtained from the melt. Linear or branched lower alkanes ( $C_5$ - $C_9$ ), as well as cycloalkanes ( $C_6$ - $C_{10}$ ), produce modification III. Furthermore, crystallization from cyclopentane generates modification IV that can also be obtained by annealing form I above 200 °C under 450 MPa. Carbon disulfide solutions produce a mixture of modification II and III [5].

Although there seems to be a dependence of the crystalline structure on solvent-polymer interaction, it is evident that a series of systematic studies is needed to determine the

relationship between the solvent-polymer interaction and the crystalline structure obtained [5].

*Table 1 Effect of solvent on the structure of i-PMP crystallized from semidilute solution [5]*

| Solvent                | $T_{\max}$ , °C | Crystal modification |
|------------------------|-----------------|----------------------|
| <i>n</i> -Hexadecane   | 190             | I                    |
| <i>n</i> -Dodecane     | 165             | I                    |
| Xylene/amyl acetate    | 165             | I                    |
| <i>n</i> -Nonane       | 165             | I                    |
| <i>n</i> -Octane       | 165             | I+II                 |
| <i>n</i> -Heptane      | 135             | III                  |
| <i>n</i> -Pentane      | 135             | III                  |
| 2,2,4-Trimethylpentane | 165             | III                  |
| 3,4-Dimethylhexane     | 135             | III                  |
| 2,4-Dimethylpentane    | 165             | III                  |
| 2,3- Dimethylpentane   | 165             | III                  |
| 3-Ethylpentane         | 165             | III                  |
| Cyclooctane            | 135, 165        | III                  |
| Cycloheptane           | 85              | III                  |
| Cyclohexane            | 85              | III                  |
| Carbon tetrachloride   | 85              | III                  |
| Cyclopentane           | 85              | IV                   |
| Carbon disulfide       | 85,135          | II+III               |

$T_{\max}$  is the maximum temperature used for complete dissolution. The solution concentrations were  $0.02 < \Phi < 0.08$ .

The effect of thermal history of the solution on the crystalline structure obtained is shown in Table 2. Low supercooling conditions in xylene, toluene, and benzene solutions produce modification I; on the other hand, high supercooling conditions for the same solutions generate modification III. Similarly, for solutions in CCl<sub>4</sub> or cyclohexane, low supercooling conditions give rise to modification III, whereas high supercooling leads to modification V [5].

Table 2 Effect of thermal history on the structure of *i*-PMP crystallized from semidilute solution [5]

| Solvent             | Crystal modification |              |                   |               |
|---------------------|----------------------|--------------|-------------------|---------------|
|                     | Low supercooling     |              | High supercooling |               |
|                     | Low $T_{max}$        | Slow cooling | High $T_{max}$    | Rapid cooling |
| <i>n</i> -Octane    |                      | I+II         |                   | III           |
| Xylene              |                      | I            |                   | III           |
| Toluene             |                      | I            |                   | III           |
| Benzene             |                      | I            |                   | III           |
| Cyclooctane         |                      | III          |                   | II+III        |
| Cycloheptane        | III                  |              | II+III            |               |
| Carbon tetrachlorid | III                  |              | V                 |               |
| Cyclohexane         | III                  |              | V                 |               |
| Tetraethylthin      |                      | II+III       |                   | II            |
| Tetramethylthin     |                      | II+III       |                   | II            |

$T_{max}$  is the maximum temperature used for complete dissolution. The solution concentrations were  $0.02 < \Phi < 0.08$ .

## 1.2 Supermolecular structure of isotactic poly(4-methyl-1-pentene)

A complete crystal structure has been reported only for form I and form III. Only tentative unit cell parameters have been proposed for forms II and IV. The phase transitions of forms II and IV into the most stable form I under stretching or annealing prevent the obtaining of X-ray fiber diffraction patterns which are essential for the determination of the chain conformation and, hence, of the crystal structure. In the case of form IV only a partially oriented fiber, containing a mixture of forms I and IV, has been obtained by swelling a fiber of form I in saturated cyclopentane vapour at 50 °C; with the degree of orientation thus obtained, it was possible to recognize some equatorial reflections and suggest a hexagonal unit cell, but it was not sufficient for determining the chain conformation [11].

### 1.2.1 Form I

Form I is the most stable crystalline form of i-PMP. It is the only one modification that can be obtained when i-PMP is crystallized from the melt. Furthermore, form I occurs in extruded fibers; it can be also obtained from crystallization in solutions of high-boiling point solvents [10]. In this form, i-PMP has a melting temperature at ~240 °C. Due to the branched nature of i-PMP, the polymer chains are in a  $7_2$  helical conformation [5] packed in a tetragonal unit cell with the axes

$$a = 1.866 \text{ nm},$$

$$c = 1.380 \text{ nm},$$

according to the space group P4 [10]. Four chains pass through the unit cell, which contains 28 repeat units [5]. The uniform  $7_2$  helical model of i-PMP is presented in Figure 3. Slight deviations from the uniform  $7_2$  helical conformation and space group P4b2 have been suggested for form I in a refinement of the structure [10].

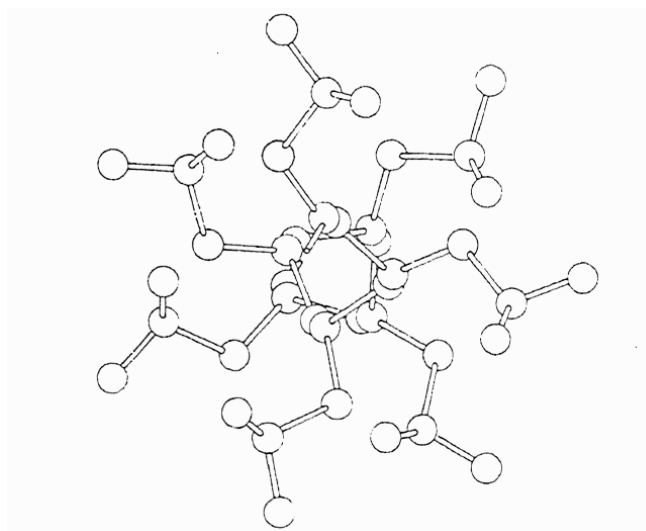
Single crystals corresponding to modification I have been extensively studied. It has been reported that:

- ❖ Isotactic PMP crystal obtained from 0.06-0.1% xylene solutions by isothermal growth presented square bases about 10 nm thick.

- ❖ The crystals had folds across the center which suggested that they grew as hollow pyramids which collapse upon removal from suspension, similar to polyethylene single crystals [5].

Charlet et al. [12] indicated that:

- ❖ Isotactic PMP single crystals grown from gradually cooled solutions in xylene are four-sectored square lamellae.
- ❖ Single crystals obtained from gradually cooled decalin solutions have a shape that resembles a square with finely serrated edges. These are due to the successive development of small sectored lateral outgrowths [5].



*Figure 3 Uniform  $7_2$  helical model of i-PMP [6]*

Electron diffraction and WAXS pattern indicated that both types of crystals had high perfection and structure corresponding to modification I.

Khoury and Barnes [13] reported very interesting results regarding the growth habits of i-PMP crystals from 1:1 xylene/amyl acetate solutions. It has been reported that:

- ❖ The crystals obtained in the temperature range between 50 and 90 °C all correspond to modification I.
- ❖ Crystals obtained at 90 °C were square mono- or multilayered with a growth habit identical to very nearly planar four sectored lamellae.

- ❖ In the multilayered crystals, the superimposed layers seemed to develop in spiral fashion through screw dislocations in the basal lamellae. These crystals had size of 20  $\mu\text{m}$  or less in length. Larger crystals (45  $\mu\text{m}$ ) were also observed; however, these were distinctly curved, having a crescentlike profile. Furthermore, the periphery of the lamellae was described as microfaceted which indicated that the constituent curved lamellae were also multifaceted [5].
- ❖ Similar curved crystals were also observed by Rybníkar and Gail [14].

Khoury and Barnes [13] also reported that:

- ❖ Lowering the crystallization temperature affected the curvature of the crystals.
- ❖ Upon crystallization at 80 °C, the curvature of the crystals increased.
- ❖ Lower crystallization temperatures produced crystals that resemble hollow fishbowls. These crystals also presented chain-folded lamellae that are multisectored [5].

Summarizing then, all crystals were multilayered with curved multilayered lamellar crystals and fourfold symmetrical shapes that are related to one another [5].

Annealing of single crystals also affects their morphology. Morrow et al. [15] utilized electron microscopy to study the effect of annealing on solution-grown single crystals of modification I. The crystals were grown from 0.02% solutions in pentyl acetate at 110 °C and 0.02% solutions toluene at  $T < 80$  °C. These authors reported that:

- ❖ The crystals had the usual square outline with screw dislocation growth terraces and irregular overgrowths and fractures running perpendicular to the edges.
- ❖ Annealing of these crystals at 170 - 200 °C caused a decrease in the number of defects and lamellar thickening.
- ❖ Annealing at higher temperatures (200 - 220 °C) developed holes, notches, and lines.
- ❖ Higher annealing temperatures (240 °C) produces sheaflike and rodlike particles having widths of 30 nm and lengths of 100 nm [5].

Although the changes were very significant, it is interesting to point out that the polymer unit cell was not affected, probably due to the fact that modification I is the most stable modification. All these changes in the morphology of the single crystals illustrate the

considerable translational mobility of the polymer chains below the melting point of the polymer. These studies demonstrated the strong dependence of crystalline morphology on temperature [5].

### 1.2.2 Form II

Form II was prepared for the first time by isothermal crystallization at 20 °C from dilute xylene solutions and, more recently, by crystallization from tetramethyltin solution, or as a minor component in a mixed structure crystallized in carbon disulfide solutions [10].

In the case of form II, neither fiber samples nor single crystals can be obtained. Samples of i-PMP in form II transform, indeed, into the most stable form, form I, by stretching. Therefore, only a few diffraction data from powder samples are available for form II. For this reason, the crystal structure of form II has not been solved yet, even though tentative values of the unit cell parameters have been proposed long ago. Despite the few diffraction data available, the crystal structure of form II has been determined by using the X-ray powder diffraction profile and packing energy calculations. Chains in  $4_1$  helical conformation are packed in a monoclinic unit cell with axes

$$a = 1.049 \text{ nm},$$

$$b = 1.889 \text{ nm},$$

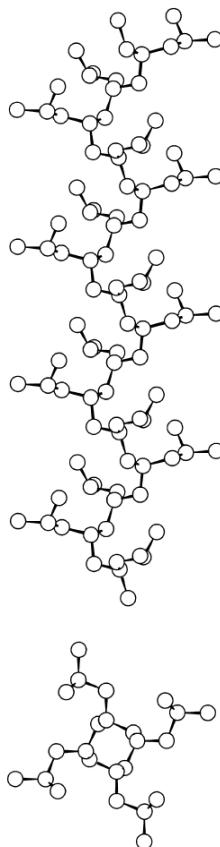
$$c = 0.713 \text{ nm},$$

$$\gamma = 113.7^\circ,$$

according to the space group  $P2_1/b$ . The  $4_1$  helical conformation assumed for the chain of i-PMP in form II is shown in Figure 4. The calculated density for this unit cell containing four chains of i-PMP in  $4_1$  helical conformation is  $862 \text{ kg/m}^3$ , in agreement with the experimental density of  $850 \text{ kg/m}^3$ , measured at 25 °C by flotation for a sample with X-ray crystallinity close to 65 % (the density of the amorphous is  $830 \text{ kg/m}^3$ ) [10].

This structure provides example of “symmetry breaking”, described for various isotactic and syndiotactic polymers. Although chains in  $4_1$  helical conformation are generally packed in tetragonal lattices, in the structure of form II of i-PMP the local  $4_1$  helical symmetry of the chains is not maintained in the lattice as crystallographic symmetry. The  $4_1$  symmetry is lost and the tetragonal symmetry is broken. The chains are, indeed, packed in a monoclinic lattice having lower symmetry. Because of the low symmetry of the lattice, the methyl carbon atoms of two successive monomeric units, related by the local  $4_1$  helical

symmetry of the chains, are not crystallographically equivalent. They present different chemical environments inside the unit cell since the contact distances with the neighbouring atoms are different, producing two distinct resonances in the NMR spectrum. Structural disorder is present in the structure, characterized by the statistical substitution of up and down chains in each site of the lattice [10].



*Figure 4 Side view and projection along the chain axis of the  $4_1$  helical conformation of the chains in form II of i-PMP [10]*

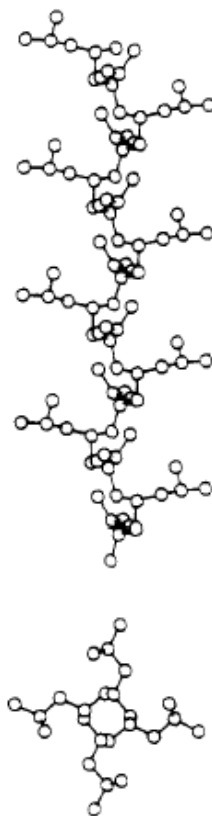
### 1.2.3 Form III

Modification III is obtained in linear (5-7 carbon atoms) and branched (6-9 carbon atoms) alkanes, as well as in carbon tetrachloride and cycloalkanes containing 6-10 carbon atoms. This form was already obtained from dilute solutions in xylene and in decalin [10]. Charlet et al. [12] have proposed, from electron diffraction of single crystals of form III, a tetragonal unit cell with axes

$$a = 1.938 \text{ nm},$$

$$c = 0.698 \text{ nm}$$

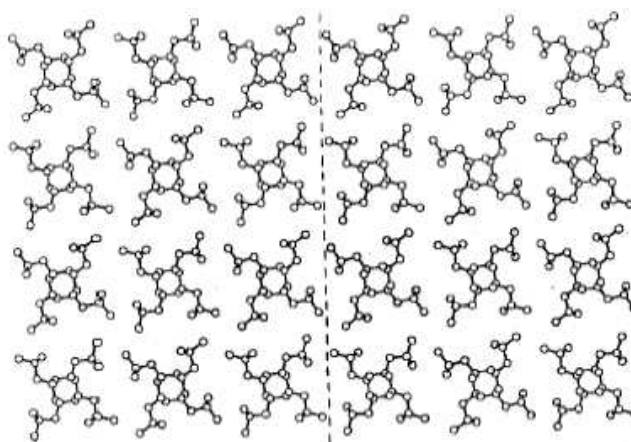
with chains in  $4_1$  helical conformation according to the space group  $I4_1$ . The projection along the chain axis and a side view of the model for the chain conformation of form III of i-PMP are reported in Figure 5 [16].



*Figure 5 Side view and projection along the chain axis of the  $4_1$  helical*

*conformation of the chains  
in form III of i-PMP [16]*

In the limit-ordered regions of the crystal every chain is surrounded by four enantiomorphous and isoclinal chains. A small amount of disorder, characterized by statistical substitution of anticlined helices, could be present at boundary regions which separate pieces of ordered crystals, composed by all up helices and all down helices, coherently juxtaposed. One of these boundaries is shown, as an example, in Figure 6 [17].



*Figure 6 Possible model of packing of form III of i-PMP showing a boundary (dashed line) that separates two pieces of ordered crystals characterized by all up helices (on the left of the dashed line) and all down helices (on the right of the dashed line) [17]*

This structure has also been considered as an example of the phenomenon of “symmetry breaking”, for which a mode of packing with low symmetry may occur even in the case of polymers which crystallize in highly symmetric single crystals. Form III of i-PMP gives, indeed, regular square single crystals, indicating a tetragonal packing, but the asymmetry of the corresponding electron diffraction pattern indicates low symmetry of the space group. The low symmetry originates from the presence of two independent chains, not related by any element of symmetry, in the tetragonal unit cell [10].

Form III transforms into form I after annealing at 100 °C and under stretching [10].

#### 1.2.4 Form IV

Form IV was obtained, in both the unoriented and uniaxially oriented state, by annealing modification I above 200 °C under pressure 450 MPa. The same crystalline modification has also been obtained from cyclopentane solutions. Stretching of an unoriented sample in form IV leads to a fiber in form I; however, a partially oriented sample in form IV was obtained by swelling a fiber of form I in saturated cyclopentane vapour at 50 °C. Charlet and Delmas [18] have proposed for form IV a hexagonal unit cell with axes

$$a = 2.217 \text{ nm},$$

$$c = 0.65 \text{ nm}$$

with chains in  $3_1$  helical conformation.

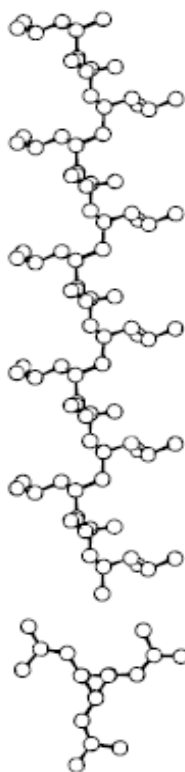


Figure 7  
Projections along  
and perpendicular  
to the chain axis

*of the model  
suggested for the  
3<sub>1</sub> helical  
conformation of  
form IV of i-PMP  
[11]*

The calculated crystalline density for this unit cell, including six chains of i-PMP in the 3<sub>1</sub> helical conformation (18 monomeric units), is 907 kg/m<sup>3</sup>, in agreement with the experimental density of 866 kg/m<sup>3</sup> (measured at 25 °C by flotation on a sample of form IV having an X-ray crystallinity index of 50 %, the density of the amorphous phase is 830 kg/m<sup>3</sup>). The projections along and perpendicular to the chain axis of the present model for the 3<sub>1</sub> helical conformation of form IV of i-PMP are reported in Figure 7. Form IV transforms into form I by annealing at 130 °C [11].

#### **1.2.5 Form V**

Form V has been obtained from concentrated cyclohexane gels and by crystallization from cyclohexane and carbon tetrachloride solutions. Form V transforms into form I by annealing at ≈ 90 °C [10].

## 2 PROPERTIES OF ISOTACTIC POLY(4-METHYL-1-PENTENE)

Isotactic poly(4-methyl-1-pentene) is linear  $\alpha$ -polyolefin with isobutyl branches and with very interesting properties [5]. It has a high melting point of 240 °C and low density, and the density of the amorphous polymer exceeds that of the crystalline material (in the case of form I) below 50 °C. Although crystalline, i-PMP unlike polyethylene (PE) and polypropylene (PP), readily produces transparent films and moulded articles [19]. From a practical point of view, i-PMP presents relatively high thermal stability and chemical resistance, in addition to excellent dielectric characteristics, microwave transparency and high optical transparency. Consequently, a wide range of applications is possible for this polymer [5].

### 2.1 Mechanical properties

Selected fundamental mechanical parameters of i-PMP and comparison of them with those of HDPE, and PP are presented in Table 3. The values of a tensile modulus, tensile strength at yield, tensile strength at break, and elongation at break are comparable to those of HDPE, although the values corresponding to i-PMP are slightly lower on average. However, in term of the “upper limit” tensile modulus, i-PMP has much lower value than HDPE. For example, the limit tensile modulus determined for drawn i-PMP has been reported to be 3.6 GPa, whereas that of HDPE has been reported higher than 200 GPa. Also, i-PMP is more brittle than HDPE [5].

*Table 3 Comparison of selected mechanical properties of i-PMP, HDPE, and PP [5]*

| Property                        | i-PMP   | HDPE    | PP      |
|---------------------------------|---------|---------|---------|
| Tensile modulus (GPa)           | 0.8-1.2 | 0.4-1.1 | 1.0-1.7 |
| Tensile strength at yield (MPa) | 23-28   | -       | -       |
| Tensile strength at break (MPa) | 17-20   | 18-33   | 29-30   |
| Elongation at break (%)         | 10-25   | 12-700  | 500-900 |
| Notched impact strength (kJ/m)  | 100-200 | 43-750  | 21-320  |

Thermoplastic generally lose strength at elevated temperatures. The extent of the loss depends upon the molecular weight, crystallinity, and crystal size. This adverse effect of

elevated temperatures on polymer properties appears to be greater for i-PMP than for PP. Strength retention versus temperature data for tensile dumbbells of i-PMP, PP and commercial polystyrene (PS) are shown in Figure 8. Similar results were obtained with fiber sample. Isotactic PMP fibers showed 40% retention of room temperature breaking strength at about 90 °C. At the same temperature, PP showed a 60% retention of room temperature strength and nylon 66 over 90% retention.

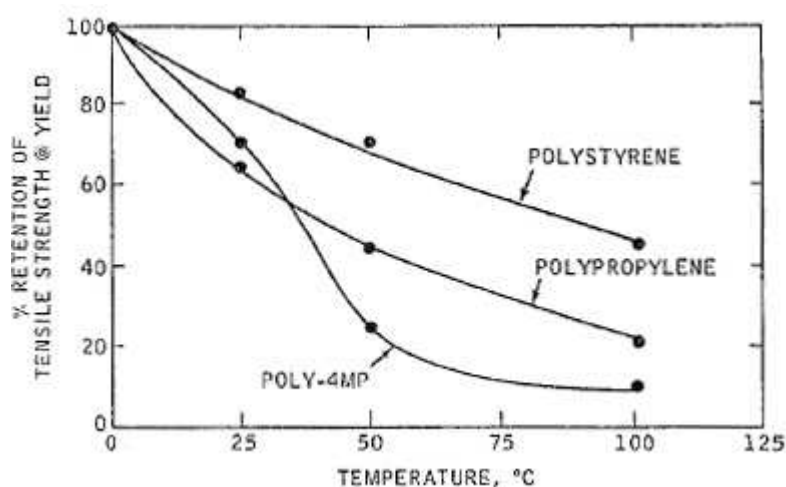


Figure 8 Adverse effect of temperature on tensile strength of i-PMP, PP, PS [19]

Table 4 Heat distortion data for various polymers [19]

| Polymer       | Heat distortion temperature, °C | Melting point, °C |
|---------------|---------------------------------|-------------------|
| i-PMP         | 58                              | 240               |
| PP            | 110                             | 170               |
| Nylon 66      | 185                             | 260               |
| Polycarbonate | 143                             | 263               |
| P3MB1         | 155                             | 310               |

The comparatively rapid loss in tensile strength with temperature is in line with the observation that i-PMP has an abnormally low heat distortion temperature. Comparative data at 450 kPa (ASTM – D648) are reported in Table 4 [19].

It is of interest that the homologue poly-3-methyl-1-butene (P3MB1) has a heat distortion temperature closer to that which we would expect from its high melting point. Treating an i-PMP pad under conditions, which can increase crystallinity and spherulite growth, raised the heat distortion temperature by as much as 35 - 40 °C. Effect of treatment on heat distortion temperature of i-PMP is presented in Table 5 . As might be expected, decreasing crystallinity results in a sharp reduction in heat distortion temperature [19].

*Table 5 Effect of treatment on heat distortion temperature of i-PMP at 450 kPa [19]*

| Treatment of test pad                                      | Heat distortion temperature, °C |
|------------------------------------------------------------|---------------------------------|
| None (control, 6 min. cooling)                             | 58                              |
| Annealing of Control Pad                                   |                                 |
| 6 hr. at 155 °C                                            | 71                              |
| 6 hr. at 195 °C                                            | 95                              |
| Extracted polymer (100% heptane-insoluble, 6 min. cooling) | 79                              |

The creep of i-PMP was studied further by obtaining deflection-time curve at 50 °C. The initial rate of creep for i-PMP is much greater than the rate for PP even at the comparatively low temperature of 50 °C. To some extent, the sensitivity to temperature of the strength and creep properties of i-PMP may be due to crystalline phase changes and spherulite growth phenomena [19].

## 2.2 Physical properties

Selected physical parameters of i-PMP are presented in Table 6.

### 2.2.1 Density behaviour

Isotactic PMP shows a very interesting density or specific volume behaviour in view of its crystallinity. There is a range of crystalline density values from 813 to 832 kg/m<sup>3</sup>. Nevertheless, most values fall between 828 and 832 kg/m<sup>3</sup>. These values have been mainly calculated from x-ray diffraction results assuming that four molecular chains of the 7<sub>2</sub> helix are present in the crystal unit cell. The dependence of the specific volume of i-PMP on temperature has been studied by Griffit and Ranby [20] and Zoller [21]. Figure 9 shows the

temperature dependence of specific volume of amorphous and semicrystalline i-PMP sample.

*Table 6 Fundamental physical properties of i-PMP [5]*

| Property                                | Value  |
|-----------------------------------------|--------|
| Density at 20°C: (kg/m <sup>3</sup> )   |        |
| Crystal                                 | 828    |
| Amorphous                               | 838    |
| Heat of fusion (kJ/mol)                 | 5.5-10 |
| Melting point (°C)                      | 240    |
| Glass transition temperature (°C)       | 40     |
| Specific heat capacity at 25 °C (J/g.K) | 1.757  |
| Refractive index at 17 °C               | 1.4600 |
| Dielectric constant at 25 °C (30-100Hz) | 2.1    |

These plots show a crossover point at about 50 °C so that at room temperature a higher crystallinity material occupies a larger volume. This is owing to the crystalline phase of i-PMP is less dense than the amorphous phase ( $d_{cryst} = 830 \text{ kg/m}^3$ ,  $d_{amorph} = 838 \text{ kg/m}^3$  at 20 °C) at room temperature. It is interesting to compare the density values of i-PMP with several isotactic helical polymers as shown in Figure 10. Kusanagi et al. [22] showed that the crystalline density of several isotactic polymers decreased almost linearly with increasing number of carbon atoms in the side groups. The only exception was i-PMP, which had a considerably lower crystalline density than the “master curve”. However, the amorphous densities of all these polymers were almost the same. The low crystalline density of i-PMP was attributed to the unusually loose packing of the crystal structure [5].

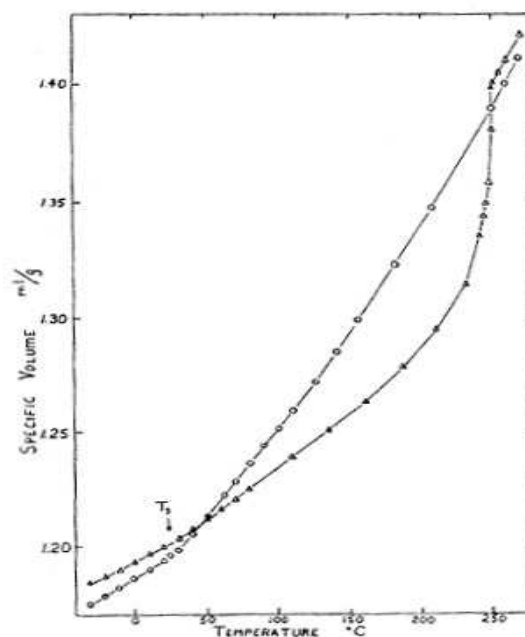


Figure 9 Specific volume-temperature curves of i-PMP: (O) amorphous, ( $\Delta$ ) 50 % crystalline [5]

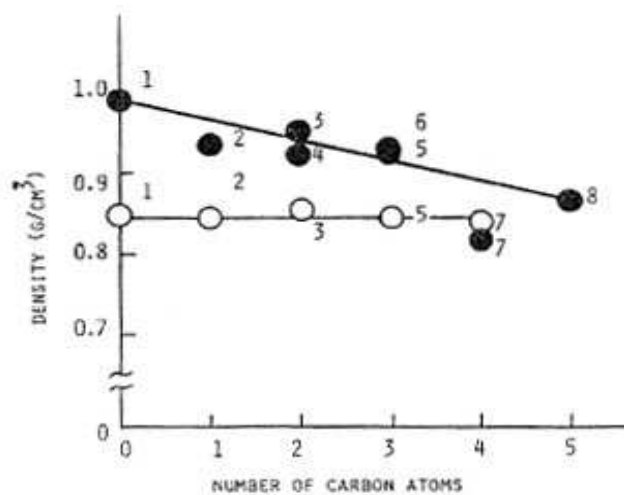


Figure 10 Density as a function of the number of carbon atoms in the sidegroups of selected isotactic polyolefins: (O) amorphous, (●) crystalline. (1) PE; (2) PP; (3) poly-1-butene (form I); (4) poly-1-butene (form II); (5) poly-1-pentene; (6) P3MB1; (7) i-PMP; (8) poly(4-methyl-1-hexene) [5]

### 2.2.2 Electrical properties

Basic electrical properties of 4-MP-1 polymers are broadly similar to those of their polyolefins. However, the dielectric constant is 2.12, which is notably low, and remains essentially constant over a wide temperature and frequency range [2].

### 2.2.3 Optical properties

Although semicrystalline, i-PMP presents high optical transparency at room temperature as its crystalline and amorphous densities are very close to each other [4]. Polymers of poly(4-methyl-1-pentene) which have previously been prepared on the laboratory scale have appeared transparent but have, in fact, shown a transparency of less than about 75 % (ASTM D 1746-62T). Transmission has been improved to a value of 90 %, which is comparable with that of PS and poly(methylmethacrylate). Furthermore, this remains essentially independent of the cooling conditions to which the material is subjected and thus of the thickness of the article made from it [2].

## 2.3 Chemical properties

### 2.3.1 Resistance to chemicals

Isotactic PMP exhibits resistance to chemical environments broadly typical of the polyolefins. 4-methyl-1-pentene polymers are highly resistant to inorganic environments; they are not attacked by aqueous solutions of inorganic salts, by most mineral acids and alkalies, even in concentrated solutions. They are appreciably affected only by highly oxidizing reagents [2]. They are resistant to alcohols, detergents, oils, fats, boiling water [3]. They also show good resistivity to many organic chemicals, although, as with other polyolefins, in certain cases absorption can occur with a resulting loss in rigidity, yield stress, and clarity [2]. Isotactic poly(4-methyl-1-pentene) is not resistant to ketones, aromatic and chlorinated hydrocarbons [3]. The effects produced by a variety of chemical reagents are summarized in Table 7 [2].

### 2.3.2 Weathering resistance

Because of tertiary carbon atoms, stabilizers must be used; even so resistance to weathering is limited. The material yellows and loses its good mechanical properties [3].

### 2.3.3 Permeability

- ❖ The permeability of isotactic poly(4-methyl-1-pentene) to gases and water vapour is considerably higher than that for other polyolefins [2].
- ❖ Mueller and Kokes [23] found that while oxygen and nitrogen permeabilities were quite high, the selectivity to one of those gases was poor.
- ❖ These authors found a large difference between the permeabilities of ethane and methane. However, when these two gases are run together, the ethane plasticizes the i-PMP, which increases the permeability of the methane and decreases the selectivity of the i-PMP for the two gases.
- ❖ Puelo, Paul, and Wong [24] found that varying the crystallinity by heat treatment (quenching or annealing) could change the crystallinity of i-PMP by 20 %. They also lowered the crystallinity by chemical crosslinking of the i-PMP. Decreasing the crystallinity increased the permeability i-PMP. The loose crystal structure of i-PMP might allow gas to permeate through the crystalline as well as the amorphous phase of the polymer.
- ❖ This would be in contrast to other semicrystalline polymers in which the crystalline fraction is considered to be an “inert filler” which has little if any interaction with the diffusing gases.
- ❖ Puelo, Paul, and Wong [24] concluded that there was a finite diffusion of gases through the crystalline phase although smaller than the permeability of the amorphous phase.
- ❖ The molecular size of the diffusing gas had a strong effect on the diffusion rate through the crystal.
- ❖ The crystalline phase has a different selectivity towards gases as compared to the amorphous phase [5].

The permeability of i-PMP to several different gases is shown in Table 8. Permeability coefficients for the amorphous and crystalline phases for different gases are shown in Table 9 [5].

Table 7 Chemical resistance of isotactic poly(4-methyl-1-pentene)<sup>a</sup> [2]

| Inorganic reagent          | Effect <sup>b</sup> | Organic reagent                  | Effect <sup>b</sup> |
|----------------------------|---------------------|----------------------------------|---------------------|
| Water                      | A                   | Acetic acid                      |                     |
| Salts, saturated solutions | A                   | glacial                          | B                   |
| Hydrochloric acid          |                     | dilute                           | A                   |
| 50%                        | A                   | Acetone                          | B                   |
| 30%                        | A                   | Amyl acetate                     | C                   |
| 20%                        | A                   | Benzene                          | C                   |
| 10%                        | A                   | Carbon tetrachloride             | C                   |
| Sulphuric acid             |                     | Chlorobenzene                    | C                   |
| 98%                        | A                   | Citric acid                      | A                   |
| 60%                        | A                   | Corn oil                         | A                   |
| 30%                        | A                   | Dioctyl phthalate                | A                   |
| 10%                        | A                   | Essential oils                   | A                   |
| Chromic acid               |                     | Ethyl acetate                    | C                   |
| dilute                     | A                   | Gasoline                         | B                   |
| coned                      | B                   | Isopropyl alcohol                | A                   |
| Nitric acid                |                     | Linseed oil                      | A                   |
| fuming                     | D                   | Motor oil                        | A                   |
| 70%                        | B                   | Olive oil                        | A                   |
| 50%                        | A                   | Petroleum ether ( bp 100-140 °C) | C                   |
| 10%                        | A                   | Petroleum spirits                | C                   |
| Sodium hydroxide           |                     | Phenol (92%)                     | A                   |
| dilute                     | A                   | Silicone oil                     | A                   |
| coned                      | A                   | Tartaric acid                    | A                   |
| Chlorine water             | D                   | Toluene                          | A                   |
| Bromine water              | D                   | Transformer oil                  | A                   |
|                            |                     | Whisky                           | A                   |

<sup>a</sup> Exposure of TPX Grade R for 6 months at 20 °C.<sup>b</sup> A, negligible effect; B, limited absorption or attack; C, extensive absorption; D, extensive attack.

Table 8 Permeability of *i*-PMP to gases [5]

| Gas                           | Permeability (Barrer) <sup>a</sup> |
|-------------------------------|------------------------------------|
| O <sub>2</sub>                | 32.3                               |
| CO <sub>2</sub>               | 92.6                               |
| He                            | 101.0                              |
| H <sub>2</sub>                | 136.0                              |
| N <sub>2</sub>                | 8.4                                |
| CH <sub>4</sub>               | 10.79                              |
| C <sub>2</sub> H <sub>6</sub> | 7.24                               |
| C <sub>2</sub> H <sub>4</sub> | 9.74                               |
| C <sub>2</sub> H <sub>2</sub> | 15.79                              |
| C <sub>3</sub> H <sub>8</sub> | 2.37                               |
| C <sub>3</sub> H <sub>6</sub> | 5.26                               |

<sup>a</sup> 1 Barrer = 10<sup>-10</sup> (cm<sup>3</sup> at STP/  
cm<sup>2</sup>.sec.cmHg )

Table 9 Permeability coefficients computed from the Maxwell equation for the amorphous and crystalline phases of isotactic poly(4-methyl-1-pentene) [5]

| Permeability (Barrer) <sup>a</sup> |                 |                   |                                               |
|------------------------------------|-----------------|-------------------|-----------------------------------------------|
| Gas                                | Amorphous phase | Crystalline phase | $\chi = P_{\text{cryst}} / P_{\text{amorph}}$ |
| He                                 | 130             | 88                | 0.68                                          |
| H <sub>2</sub>                     | 170             | 116               | 0.68                                          |
| N <sub>2</sub>                     | 19              | 2                 | 0.10                                          |
| O <sub>2</sub>                     | 55              | 17                | 0.31                                          |
| CH <sub>4</sub>                    | 42              | 4                 | 0.10                                          |
| CO <sub>2</sub>                    | 200             | 38                | 0.19                                          |

<sup>a</sup> 1 Barrer = 10<sup>-10</sup> (cm<sup>3</sup> at STP/ cm<sup>2</sup>.sec.cmHg )

### 2.3.4 Thermal degradation

Although studies of the thermal degradation behaviour of i-PMP focused on different aspects of the degradation process, the outcome indicated that i-PMP is more easily degraded thermally than PP and PE [5].

The thermal degradation of i-PMP in vacuum was studied by Reginato [25, 26] in the temperature range of 291 - 355 °C. It was reported that:

- ❖ The decomposition products comprised a volatile fraction (9 % of total weight) consisting of isobutene and propane as major components, and a heavy fraction of higher molecular weight hydrocarbons.
- ❖ A mechanism of degradation was proposed on the basis of free radical chain reaction including initiation, transfer, and termination steps.
- ❖ The initiation step would be caused by breakage of normal C-C bonds homolytically by thermal effects, producing two radicals.
- ❖ The second step would involve a transfer reaction either by inter- or intramolecular “backbiting” mechanism.
- ❖ Finally, termination would be a second-order reaction, either by recombination or disproportionation [5].

Oxidative degradation has been shown to occur not only on the i-PMP main chain but also on the isobutyl pendant units. This is due to the presence of tertiary carbon atoms on the main chain and on the side groups. Zitomer and Di-Edwardo [27], using TGA/MS, suggested that the relative susceptibility to oxidation of the tertiary carbon atom on the polymer backbone is ~ 2 times greater than that of the tertiary carbon atom on the pendant isobutyl group [5].

- ❖ The oxidation mechanism seemed to start with hydroperoxidation of the tertiary carbon atoms.
- ❖ Gabbay et al. [28] proposed that further oxidation and chain scission would produce ketones and isobutyraldehyde.
- ❖ Isobutyraldehyde could also form by a reaction involving secondary side-chain hydrogen abstraction and isomerization.

- ❖ The initiation through the secondary carbon is much less probable than through a tertiary carbon.
- ❖ Acetaldehyde could be formed by an isomerization reaction that upon further oxidation would yield acetic acid.
- ❖ Finally, acrolein would result from the decomposition and oxidation of an epoxide intermediate [5].

Gabbay et al. [28] studied the degradation products evolved from the thermal oxidative degradation of isotactic PMP and atactic PMP (a-PMP) in the presence of dry oxygen. The major volatile products of degradation were carbon dioxide, water, isovaleraldehyde, acetic acid, acetaldehyde, acetone, and acrolein. The relative abundance of these products was greater for i-PMP than for a-PMP, indicating that i-PMP is more susceptible to oxidation than a-PMP under similar conditions. The catalyst residue plays a role in the thermal degradation of polymers. It is possible that a different catalytic system might have been used to prepare isotactic or atactic PMP. Therefore, this might have been a contributing factor to obtain different susceptibility to oxidation of i-PMP and a-PMP [5].

Bilingham et al. [29] reported that crystallinity had a very important effect on oxidation. In the crystallinity range of 63 - 71 %, the oxidation rate increased ~ 45 % as crystallinity increased, indicating that oxidation is not only occurring in the crystal phase but also at a faster rate, possibly due to its less dense structure. The crystallinity of i-PMP decreased dramatically with increasing oxidation time [5].

#### ***Comparison of i-PMP thermal stability with those of polypropylene and polyethylene***

Studies on the oxidative degradation of PE and PP have indicated that the degradation behaviour is dependent on the crystallinity of the polymer. There is evidence suggesting that oxidative degradation is confined to amorphous regions of the polymer. In contrast, i-PMP showed increased sensitivity to oxidation as crystallinity was increased, implying that the crystalline regions of i-PMP are more sensitive to oxidation. This is an important point when stabilization is considered. In PE, PP, and i-PMP, the stabilizing additives (UV, antioxidants, etc.) are rejected from the crystalline structure. For PE and PP this is an advantage; however, in i-PMP the crystalline regions would be unprotected by the antioxidant; therefore, the sensitivity to oxidation may not be changed significantly [5].

The different sensitivity to oxidation is reflected in the induction periods,  $t_i$ , of PP and i-PMP:

- ❖ For oxidation at 150 °C, unstabilized PP presented  $t_i = 0.12$  h and unstabilized i-PMP had  $t_i = 0.57$  h, indicating that i-PMP is more stable.
- ❖ Upon stabilization, PP had  $t_i > 200$  h and i-PMP showed  $t_i = 14.8$  h [5].

Consequently, i-PMP did not improve nearly as much by addition of antioxidants. This suggested that the rejection of stabilizers during crystallization reduced the stabilizer efficiency [5].

### 2.3.5 Radiation stability

Radiation can be used for sterilization of polymeric materials. In this type of application, one should be concerned with the effect of radiation on the structure, properties, and integrity of the material. In other words, it must be known whether radiation-induced degradation occurs in the form of crosslinking reactions or chain scission. In this sense, it is known that in an inert atmosphere, polymers containing quaternary carbon atoms undergo radiation-induced chain scission, whereas those with secondary carbon atoms principally undergo crosslinking, and those with tertiary carbon atoms, such as PP, suffer chain scission. Isotactic PMP would be expected to have behaviour similar to PP [5].

The i-PMP unit contains two tertiary carbon atoms; one on the main chain and the other on the side chain. Consequently, radiation damage might be different in i-PMP:

- ❖ If the attack occurred preferentially on the side chain, then there would not be effective chain scission.
- ❖ If the attack occurred on the main chain, chain scission would be eminent [5].

In this context, Goodhead [30] reported that under most condition of irradiation (electrons, x-ray, UV), the predominant species formed in i-PMP is due to the loss of hydrogen from a main chain tertiary carbon atom. The stability of this alkyl radical in vacuum at room temperature is of the order of days, similar to those found in PP and PE [5].

### 2.3.6 Flammability

Isotactic PMP burns slowly with a luminous flame giving rise to burning droplets and a chocking paraffin-like odour [3].

### **2.3.7 Toxicological assessment**

For i-PMP contact with food is permitted. Isotactic PMP can be sterilized and is physiologically inert [3].

### **2.3.8 Resistance to stress cracking**

Isotactic PMP is susceptible to stress cracking [3].

### 3 APPLICATIONS OF ISOTACTIC POLY(4-METHYL-1-PENTENE)

The unique combinations of properties make i-PMP the plastic of the choice for many applications. It possess especial properties:

- ❖ A high melting point
- ❖ A high clarity
- ❖ A low density
- ❖ An excellent electrical properties
- ❖ A good chemical resistance

Isotactic poly(4-methyl-1-pentene) is of interest for coating of electrical wires because the thermal properties are sufficient to use in the wiring of commercial buildings without the danger associated with toxic fumes from PVC during a fire. Okada et al. [31] have found additives which reduce the brittleness of i-PMP wire coatings, and which make them flame retardant and nonreactive with copper [5].

#### 3.1 Fibers and films

Isotactic poly(4-methyl-1-pentene) is one of the most permeable plastics to gases [5]. It is still being evaluated for fiber and film applications [2]. Numerous patents have been issued which describe cast films and hollow fiber membranes, and processes for producing such membranes [5]. Films and coatings designed to allow water vapour, but not water itself, to pass may be useful [2].

#### 3.2 Lighting

Isotactic poly(4-methyl-1-pentene) is not suitable for continuous outdoor exposure. However, there are many lighting applications where no ultraviolet radiation is present and where form stability at high temperatures combined with transparency can make it possible for more intense light sources to be used. Blow-moulded isotactic poly(4-methyl-1-pentene) lampshades and vacuum-metallized automobile taillight reflectors have been made of isotactic poly(4-methyl-1-pentene) [2].

### 3.3 Applications utilizing chemical resistance

There are a variety of applications in which isotactic poly(4-methyl-1-pentene) is especially advantageous with its transparency and form stability at high temperatures, combined with its excellent chemical resistance. These properties provide uses in chemical laboratory equipment such as cells for spectroscopic and optical analysis [5], beakers, flasks, graduated cylinders, and connectors. The connector pieces for general chemical purpose have been moulded from i-PMP. The connectors can operate intermittently up to 200 °C and above, and their clarity allows visual inspection of the material being conveyed. Packing rings for distillation and gas-scrubbing towers made of isotactic poly(4-methyl-1-pentene) are lightweight and resistant to hot corrosive fluids. Isotactic poly(4-methyl-1-pentene) is used for injection-moulded bobbins for the dyeing of polyester fibers, where aqueous disperse dyeing systems are employed at temperatures up to 140 °C. The bobbins have good form stability at these temperatures, and do not readily pick up dye [2].

### 3.4 Electrical applications

The applications for isotactic poly(4-methyl-1-pentene) in the electrical industry arise not only from its good electrical properties, but also from its form stability at elevated temperatures, its low moisture absorption, its transparency where visual inspection through the item is necessary, and its oil resistance. Thus it can be used both for direct dielectric applications and for items of ancillary equipment. Its high melting point is particularly important in enabling it to withstand soldering and encapsulation processes, as well as operation at elevated temperature. Isotactic poly(4-methyl-1-pentene) is particularly useful for high-frequency applications, such as coaxial connectors where low electrical losses and the ability to withstand soldering and encapsulation temperatures are important. Here, isotactic poly(4-methyl-1-pentene) may fill the gap which has long existed between the lower-melting polyolefins and materials such as polytetrafluorethylene. At microwave frequencies spacing discs and bushes of isotactic poly(4-methyl-1-pentene) combine low electrical losses with a better resistance to creep than competitive materials. Ancillary equipment items include slot closures for electric motors. The extrusion process for making these closures is simple, and they can be expected to have adequate long-term stability for continuous operation up to 125 °C [2].

### 3.5 Medical applications

Applications of i-PMP in the medical fields are mainly based on its toxicological inertness [2] and high optical transparency. This allows use hypodermic syringes, blood collection, transfusion equipment [5], laboratory ware, and respiration equipment made of isotactic poly(4-methyl-1-pentene) in medical applications. Isotactic poly(4-methyl-1-pentene) have the clarity of glass, better impact resistance, and withstand repeated sterilization by steam, ethylene oxide, dry heat, or radiation [2].

### 3.6 Packaging

The high permeability of film made from i-PMP to gases and water vapour, while ruling it out for general-purpose packaging applications, may lead to specialized uses, such as the packaging of meat and vegetable products where the permeability to oxygen is advantageous. For prepacked food which require being reheated or cooked at temperature up to 220 °C containers may be either injection-moulded, blow-moulded, or shaped from extruded isotactic poly(4-methyl-1-pentene) films. Isotactic poly(4-methyl-1-pentene) may be a possible replacement for aluminum foil in such application; it permits the heating by hot-air or microwave ovens [2].

## 4 PROCESSING OF ISOTACTIC POLY(4-METHYL-1-PENTENE)

Polymer of 4-methyl-1-pentene can be made either as freeflowing powder blends or as compounded granules for use in all normal thermoplastics fabrication processes [2].

The melt-flow properties of the grades which have been made available are designed principally for:

- ❖ An injection moulding
- ❖ A blow moulding
- ❖ An extrusion processes

Processing is characterized by:

- ❖ A high melting temperature of the polymer
- ❖ A narrow melting range
- ❖ A low melt viscosity
- ❖ A significant thixotropy in the melt

It has been demonstrated that i-PMP can be processed with ease on conventional thermoplastics fabrication equipment. Stability at processing temperature is adequate to prevent degradation of the polymer in such processes, provides the polymer is not deliberately maintained at elevated temperatures for excessively long periods; in such a case discoloration and brittleness of the final product can result [2].

### 4.1 Injection moulding

Isotactic PMP can be moulded satisfactorily on injection machines equipped with adequate heating capacity and good temperature control. The low density and relatively higher heat content of isotactic poly(4-methyl-1-pentene) must be taken into account in calculations of plasticizing and of “shot” capacity [2]. The high enthalpy results in the plasticizing capacity of machinery being only 65% of that for PS [3]. Basic principles established for other polyolefins may be employed to establish the optimum conditions and avoid difficulties such as sink marks, voids, and “shorts” [2]. The optimum conditions of the injection moulding of i-PMP are presented in Table 10. Mould shrinkage is normally between 1.5 and 3.0 %, although values in excess of this have been recorded in some cases

of thin – walled mouldings or mouldings where restricted gates are used; with very small mouldings, shrinkage of less than 1.5 % have been obtained [3].

*Table 10 Optimum conditions in the course of injection moulding of isotactic poly(4-methyl-1-pentene) [3]*

|                         |               |
|-------------------------|---------------|
| Processing temperatures | 280 to 310 °C |
| Mould temperature       | 70 °C         |
| Shrinkage               | 1.5 to 3.0 %  |

## 4.2 Extrusion

Isotactic PMP can be extruded for wire coating [5]. The best results are obtained with high-compression screws having a sharp transition into the metering zone and a length: diameter ratio of 20:1 or greater. It is advisable to use a breaker plate and gauzes in order to increase backpressure. Extruders with a decompression zone are not recommended. Twin-screw extruders have been used with success [2].

## 4.3 Finishing

The chemical inertness of isotactic poly(4-methyl-1-pentene) necessitates the use of special processes to prepare the surface of fabricated articles before finishing by printing, painting, and metallizing. As with PP, satisfactory results can be obtained by treating the surface with chromic acid, acidified potassium permanganate, or specially formulated dipping primers [2].

## CONCLUSION

The aim of this Bachelor Thesis was to compile an overview of structure, properties and applications of poly(4-methyl-1-pentene). It is a stereospecific polymer with the interesting properties and many possibilities of applications. The stereochemical arrangements of 4-methyl-1-pentene into the polymeric chains are syndiotactic, isotactic and atactic.

In the crystalline regions, syndiotactic PMP chains are in a  $(12_7)_2$  helical conformation packed in a tetragonal unit cell. Nevertheless, the commercial products are mostly isotactic produced by Ziegler-Natta polymerization of 4-methylpentene-1. Isotactic PMP presents polymorphic behaviour; therefore five different crystalline forms of i-PMP are described. The following conformations has been proposed for each of them:

- ❖ Form I of i-PMP has a tetragonal unit cell with chains in a  $7_2$  helical conformation.
- ❖ Form II of i-PMP has a monoclinic unit cell with chains in a  $4_1$  helical conformation.
- ❖ Form III of i-PMP has a tetragonal unit cell with chains in a  $4_1$  helical conformation.
- ❖ Form IV of i-PMP has a hexagonal unit cell with chains in  $3_1$  helical conformation.
- ❖ The conformation of form V has not been solved yet.

Isotactic PMP excels mainly owing to its physical properties such as low density, high melting point, high optical transparency and high permeability to the gases. These properties allow, in combination with good chemical resistance, to use i-PMP in medical field, chemical laboratory ware, microwave oven cookware, and insulation material for wire and cable coating.

Mechanical behaviour is similar to that of PP with tensile modulus of 0.8 - 1.2 GPa, tensile strength of 23 - 28 MPa, although some values corresponding to i-PMP are lower such as that for elongation at break (10 - 25 %). Isotactic PMP is rather brittle under the glass transition temperature (40 °C) and it is more easily degraded thermally than PP and PE.

The research concerning PMP has not been finished yet because some information available in the literature are not complete. The study of poly(4-methyl-1-pentene) is useful because i-PMP offers special properties which can be employed in a number of branches.

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**REVIEW OF SYMBOLS**

|              |                                                        |
|--------------|--------------------------------------------------------|
| 4-MP-1       | 4-methyl-1-pentene                                     |
| PMP          | Poly(4-methyl-1-pentene)                               |
| i-PMP        | Isotactic poly(4-methyl-1-pentene)                     |
| s-PMP        | Syndiotactic poly(4-methyl-1-pentene)                  |
| a-PMP        | Atactic poly(4-methyl-1-pentene)                       |
| PE           | Polyethylene                                           |
| HDPE         | High – density polyethylene                            |
| PP           | Polypropylene                                          |
| PS           | Polystyrene                                            |
| P3MB1        | Poly-3-methyl-1-butene                                 |
| $d_{cryst}$  | Density of crystalline phase [kg/m <sup>3</sup> ]      |
| $d_{amorph}$ | Density of amorphous phase [kg/m <sup>3</sup> ]        |
| $T$          | Temperature [°C]                                       |
| $T_{max}$    | Maximum temperature used for complete dissolution [°C] |
| $\Phi$       | Voluminous fraction [-]                                |
| $a$          | Crystal lattice parameter [nm]                         |
| $b$          | Crystal lattice parameter [nm]                         |
| $c$          | Crystal lattice parameter [nm]                         |
| $P_{cryst}$  | Permeability of crystalline phase [Barrer]             |
| $P_{amorph}$ | Permeability of amorphous phase [Barrer]               |
| $t_i$        | Induction period [h]                                   |
| °C           | Degree Celsius                                         |
| kPa          | Kilopascal                                             |
| MPa          | Megapascal                                             |

|               |                     |
|---------------|---------------------|
| GPa           | Gigapascal          |
| $\mu\text{m}$ | Micrometer          |
| nm            | Nanometer           |
| kJ/m          | Kilojoule/meter     |
| kJ/mol        | Kilojoule/mol       |
| J/g.K         | Joule/gramme.Kelvin |
| Hz            | Hertz               |

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