

**INVESTIGATION OF THE CRYSTALLINITY AND  
ORIENTATION OF POLYPROPYLENE WITH RESPECT TO  
TEMPERATURE CHANGES  
USING FT-IR, XRD, AND RAMAN TECHNIQUES**

**A THESIS SUBMITTED TO THE DEPARTMENT OF  
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FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF MASTER OF SCIENCE**

**BY**

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**AUGUST 2004**

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## **ABSTRACT**

### **INVESTIGATION OF THE CRYSTALLINITY AND ORIENTATION OF POLYPROPYLENE WITH RESPECT TO TEMPERATURE CHANGES USING FT-IR, XRD, AND RAMAN TECHNIQUES**

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**M.S. in Chemistry**

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**August 2004**

Having good mechanical and barrier properties, polypropylene films are widely used in food-packing industry. The relation of crystallinity and orientation of polypropylene with these properties are well known. Temperature increase has an important effect on the crystallinity and orientation of polypropylene. The purpose of this study is to understand better crystallinity and orientation changes of the cast and bi-axially oriented polypropylene films with respect to temperature effect. These changes were investigated using especially in-situ FT-IR and dichroism as well as XRD and Raman spectroscopy.

For this purpose, an in-situ variable temperature set-up is developed and adapted for FT-IR studies. Accordingly, the changes in the peaks related to the amorphous and crystalline contents of the films as well as the peaks reflecting the orientation of the films were investigated over the temperature range from 120-170°C. Temperature cycle was also applied. Moreover, the films were investigated after application of additional stress at 120°C for various durations.

The crystallinity and orientation of the films are affected significantly when the films were analyzed at higher temperature (>150°C). The crystallinity content of the film

recovers after returning back to room temperature whereas orientational loss are permanent.

**Keywords: Polypropylene, FT-IR, Dichroism, XRD, Raman Spectroscopy, Phase Transition, and Temperature Effect**

## ÖZET

### FT-IR, XRD, RAMAN TEKNİKLERİNİ KULLANARAK SICAKLIK DEĞİŞİKLİĞİNE BAĞLI OLARAK POLİPROPİLEN FİMLERİNDE KRİSTALLİNİTE VE YÖNLENMENİN İNCELENMESİ

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İyi mekanik ve bariyer özelliklerine sahip olan polipropilen endüstride geniş bir şekilde kullanılmaktadır. Polipropilenin kristallinitesinin ve yönlenmesinin bu özellikleri ile ilişkili olduğu bilinmektedir. Polipropilen filmi ısıtmanın kristallinitesi ve yönlenmesi üzerine önemli bir etkisi vardır. Bu çalışmanın amacı sıcaklığa bağlı olarak kalıp ve çift yönde çekilmiş polipropilen filmlerinde ki kristallinite ve yönlenme değişikliklerini daha iyi anlamaktır. Bu değişiklikler özellikle yerinde (in-situ) FT-IR , dikroizm ve XRD, Raman spektrokopi kullanılarak incelenmiştir.

Bu amacın doğrultusunda, değişik sıcaklıklara ulaşabilen yerinde (in-situ) düzenek geliştirilip FT-IR'e adapte edildi. Böylece, 120-170°C aralığında ki sıcaklıklarda amorf ve kristalin kısımlarına karşılık gelen piklerde olan değişmeler ve yönlenme hakkında bilgi veren piklerdeki değişmeler incelenmiştir. Ayrıca aynı filmler tekrar ısıtılarak bir devir yapılmıştır. Bundan başka, çeşitli sürelerde 120°C'de ilave stress uygulanan filmlerde incelenmiştir.

Yüksek sıcaklıklarda filmler ısıtılırken ( $>150^{\circ}\text{C}$ ) filmlerin kristallinitesi ve yönelmesi önemli ölçüde değişmektedir. Oda sıcaklığına geri dönüldüğünde, filmlerin kristallinitesi eski haline geri dönerken yönelme kaybı sabit olarak kalmaktadır.

**Anahtar Kelimeler: Polipropilen, FT-IR, Dikroizm, XRD, Raman Spektroskopisi, Faz Geçişi, ve Isı Etkisi**

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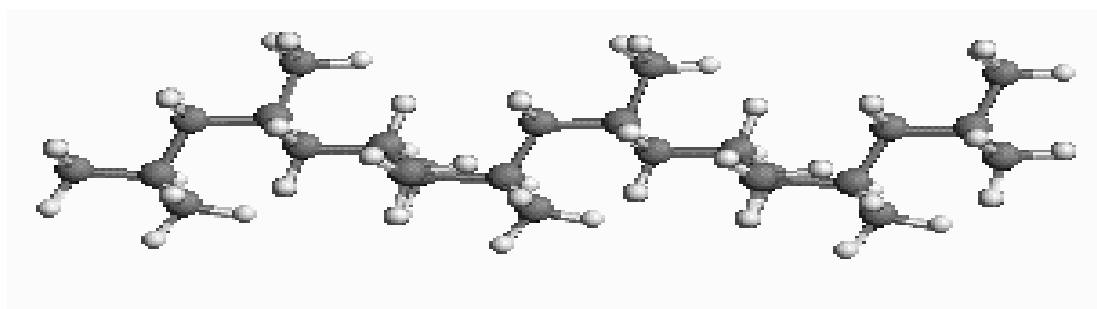
# 1. INTRODUCTION

## 1.1. Polypropylene and Its Properties

### 1.1.1. Polypropylene

Paul Hogan and his fellow research chemist Robert Bank, in 1951, invented crystalline polypropylene. In 1954, it was synthesized by G. Natta who discovered a new polymerization mechanism, in which a transition metal compound bears a metal-carbon bond able to carry out a repeated insertion of olefin units. By this way, the random structural arrangement of non-crystallizable polymers could be transformed into structures having high chemical and geometrical regularity. Many types of catalysts were improved to get polypropylene. Nowadays, metallocenes are widely used as catalysts, because these catalysts provide enhanced control over the molecular make up of polypropylene and grades with extremely high isotacticity [1].

Polypropylene, a thermoplastic material, is produced by polymerizing propylene molecules into long polymer molecules, as exhibited in scheme.1. It is linear hydrocarbon chain containing no unsaturation [2].



**Scheme.1:** Structure of polypropylene.

Polypropylene, density of which is  $0.905\text{g/cm}^3$ , is the lightest polymer. It is the semicrystalline polymer including both crystalline and amorphous phases. Its crystalline melting point, depending on the grade and the frequency/heat rate, is between  $160\text{-}170^\circ\text{C}$ . Due to its lower thermal conductivity, it can be used in insulation applications such as food packaging. As other plastics, polypropylene has considerably higher thermal expansion coefficient than metals. It thus leads to internal stresses and stress concentrations. The mechanical properties of polypropylene depend strongly on the molecular weight. Decreasing molecular weight leads to a reduction in tensile strength, stiffness, and hardness of polypropylene. This effect of molecular weight on polypropylene is contrary to most plastics. Moreover, it is an excellent electrical insulator, as can be expected from a non-polar hydrocarbon. Due to this property, it is used in insulating power cable, particularly for telephone wires. Polypropylene granules are white and translucent. However, the last appearance of the material changes from hard and colored to flexible and transparent depending on processing. When required, transparency can be improved by moulds or dies [3, 4].

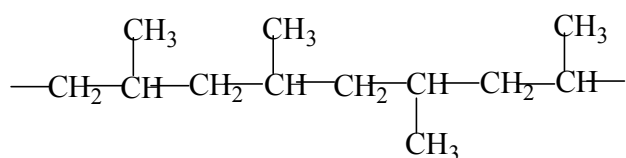
Density	$0,905\text{ g/cm}^3$
Melting Point	$160\text{-}170^\circ\text{C}$
Maximum Continuous Use Temperature	$100^\circ\text{C}$
Tensile Strength	$33\text{Mpa}$
Temperature of Deflection under load (18MPa)	$55^\circ\text{C}$
Temperature of Deflection under load (0.45MPa)	$85^\circ\text{C}$
Thermal Expansion Coefficient	$1,35 \times 10^{-4}$
Volume Resistivity ( $\Omega\text{cm}$ )	$10^{17}$

**Table.1:** Basic Properties of Polypropylene

As a non-polar hydrocarbon, it has extraordinary chemical resistance to organic and inorganic reagents. Indeed, there is not any solvent to dissolve polypropylene at room temperature. In addition, it is not affected by most concentrated acids and bases. However, it is vulnerable to oxidizing agents such as pure fuming nitric acid and sulphuric acids. Polypropylene is accepted as a non-toxic and non-carcinogenic material. Also, it does not have a nutrient medium for microorganism attacking [3].

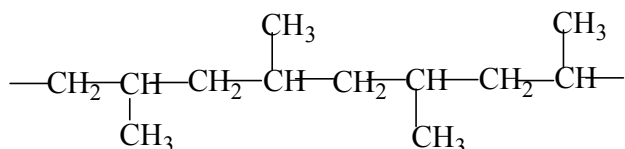
### 1.1.2. Types of Polypropylene

According to the steric arrangement of methyl groups attached to CH group in the chain, the character of polypropylene is different. In scheme.2, the structure where methyl groups are substituted randomly on the polymer chain is the atactic form in which polypropylene is an amorphous material and its strength is low.



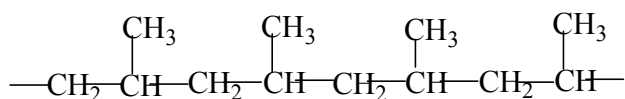
**Scheme.2:** Atactic-polypropylene

If a methyl group is bonded to CH group in one side and the other one is bonded to CH group in opposite direction like in scheme.3, this polypropylene is known as syndiotactic.



**Scheme.3:** Syndiotactic-polypropylene

If all methyl groups attached to chain are on the same side, as indicated in scheme.4, this polypropylene is named as isotactic. In addition, isotacticity word means the measure of the percentage of side methyl groups on only one side. For industrial use, isotacticity of polypropylene varies between 85% and 95%.



**Scheme.4:** Isotactic-polypropylene

TYPE	PROPERTY
Isotactic-Polypropylene	Its melting point varies between 160-170°C. It is strong and hard with excellent resistance to stress, cracking, and chemical reaction. It has high crystalline content.
Syndiotactic-Polypropylene	Its melting point varies between 125-130°C. It is softer than isotactic polypropylene, and also is tough and clear. It is stable to gamma radiation. It has lower crystalline content according to isotactic polypropylene.
Atactic-Polypropylene	Its melting point is above 0°C. It is really soft polymer and has little strength. It has almost only amorphous content.

**Table.2:** Basic Properties of Isotactic, Syndiotactic, and Atactic Polypropylene

In table.2, basic properties of atactic, syndiotactic, and isotactic polypropylene are illustrated. However, only isotactic polypropylene among them has the proper properties needed for a good and useful plastic material due to its greater stiffness, hardness, tensile strength and modulus [3].

### **1.1.3. Advantages of Polypropylene**

Especially, compared to polyethylene, it has higher stiffness at lower density and resistance to higher temperatures. In addition, good chemical resistance, environmental stress cracking resistance, good hardness, contact transparency, ease of machining and cheapness can be said as other positive sides of polypropylene [3].

### **1.1.4. Disadvantages of Polypropylene**

Compared to other thermoplastics, higher mould shrinkage, lower impact strength and higher thermal expansion are disadvantages of polypropylene. Moreover, it has poor UV resistance in the presence of certain metals. The tertiary carbon atom in the chain gives a possibility for oxidation so that polypropylene has low stability compared to polyethylene. Other shortcomings of polypropylene are poor flammability, difficult solvent and adhesive bonding, and troubles in frictional applications [3,5].

### **1.1.5. Application Fields**

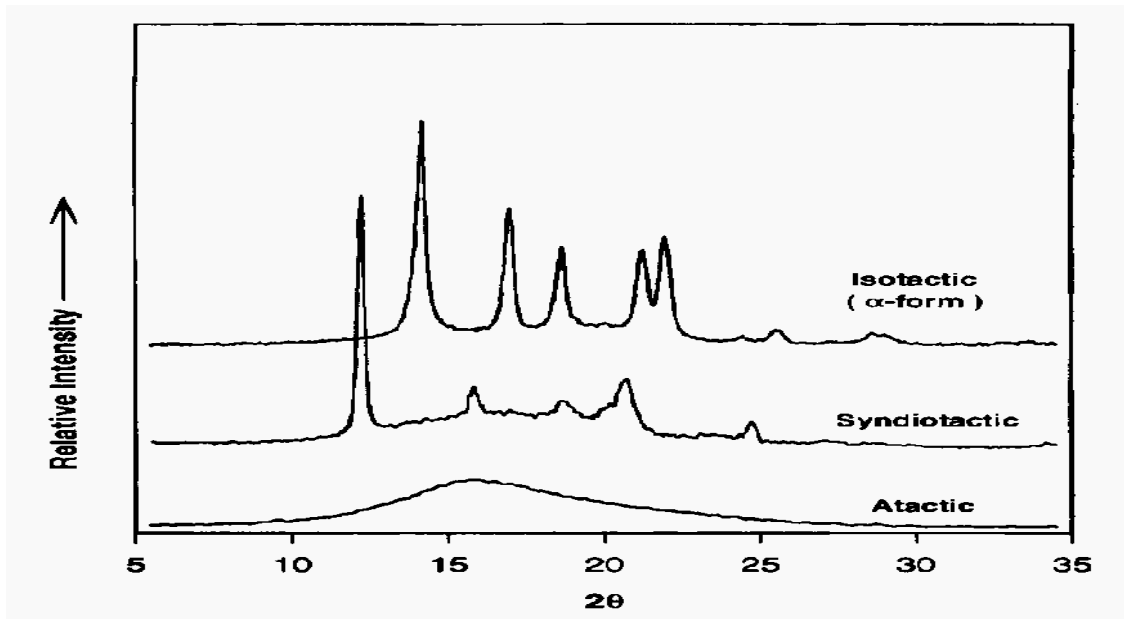
Polypropylene has been one of the most important plastics for the last four decades. After polyethylene and polyvinylchloride, it is third largest plastic consumed. Polypropylene is used in video cassettes, luggage, toys, radiator expansion tanks, bumper covers, wheel covers, battery cases, artificial sport surfaces, monofilaments for rope and cordage, packaging sacks, staple fibres, coarse fibres, filament yarns, microwave oven cabinet, refrigerator parts, margarine tubs, disposable food trays, blister packaging, hot wire reservoirs, heat exchangers, pressure pipes etc [1,2,6,7].

### **1.1.6. Crystallinity**

An amount of crystalline and amorphous phases in polymer depends on structural and stereochemical characteristics of chains and how are performed the fabrication such as extrusion, thermal history or molding. Thermal history of polymers is a significant point for the degree of crystallinity of them. Whereas rapid quenching gives high crystalline product, annealing and slow cooling causes low crystalline product. High crystallinity leads to increase in hardness, strength, wear resistance. Low crystallinity causes good processibility, better transparency. The linearity of the molecular chains in polypropylene provides them packing ability in an ordered crystal structure. Branching in the chain causes decreasing regularity of the structure. The tacticity of the chain governs the degree of crystallinity of polypropylene. High tacticity means that the presence of long and uninterrupted sequences. The greater tacticity means that the greater crystallinity.

The stereochemistry of the polypropylene chain strongly affects the crystallinity. Fig.1 shows that wide angle XRD patterns of isotactic, syndiotactic and atactic polypropylene.

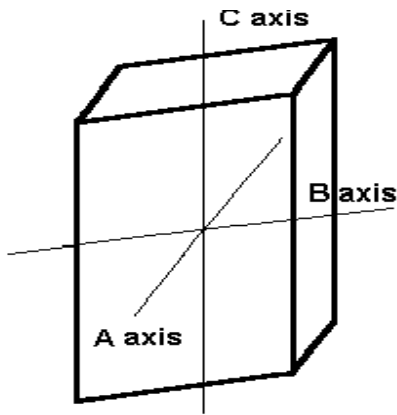
Whereas polypropylene chain for isotactic and syndiotactic give crystalline reflections, there is a very broad scattering observed in atactic polypropylene [1, 2].



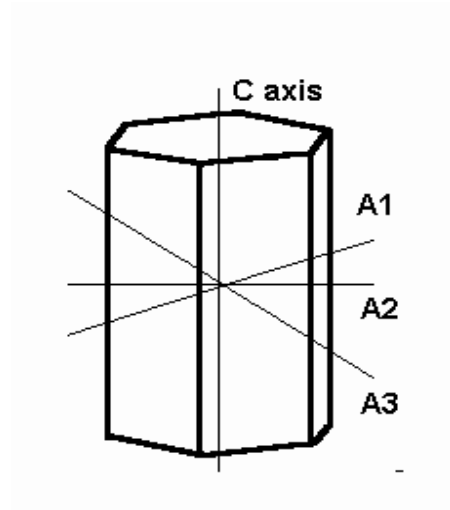
**Fig.1:** Wide angle X-ray scattering patterns of isotactic, syndiotactic and atactic PP.

#### 1.1.6.1. $\alpha$ and $\beta$ crystalline forms

In the crystalline state, isotactic-polypropylene can be found in several different forms. These forms denote different crystallographic symmetries. All of the different crystalline forms are constituted from chains in a  $3_1$  helical conformation with a common repeat distance (approximately  $6.5\text{\AA}$ ), but differentiate in unit cell symmetry, structural disorder and inter-chain packaging. The  $\alpha$ -form is superior to other forms. It is arranged on a monoclinic unit cell, which is illustrated in fig.2.



**Figure.2:** Monoclinic form.



**Figure.3:** Hexagonal form.

In monoclinic form, all the axes are different lengths. Two of them, the A and C axes, meet at  $90^\circ$ , but the third one does not. For monoclinic form of polypropylene, unit cell parameters are assigned as  $a=6.6\text{\AA}$   $b=20.8\text{\AA}$   $c=6.5\text{\AA}$  [1, 8].

$\beta$  crystalline form, which is rare compared to  $\alpha$ -form, is stacked on hexagonal unit cell as shown in fig.3. Numerous unit cell structures of  $\beta$ -form were reported and there is controversial debate about assigning unit cell parameters in literature [9-11]. The simplest satisfactory model for  $\beta$ -form is smaller trigonal or hexagonal unit cell with  $a=b=11.03\text{\AA}$  and  $c=6.49\text{\AA}$ . The formation of  $\beta$  crystallinity leads to a unit cell structure with lower density, lower melting point, metastability compared to the  $\alpha$ -form. These display a lower degree of order in the crystalline state of the  $\beta$ -form with respect to that of the  $\alpha$ -form [1].

### **1.1.7. Preparation of PP Films**

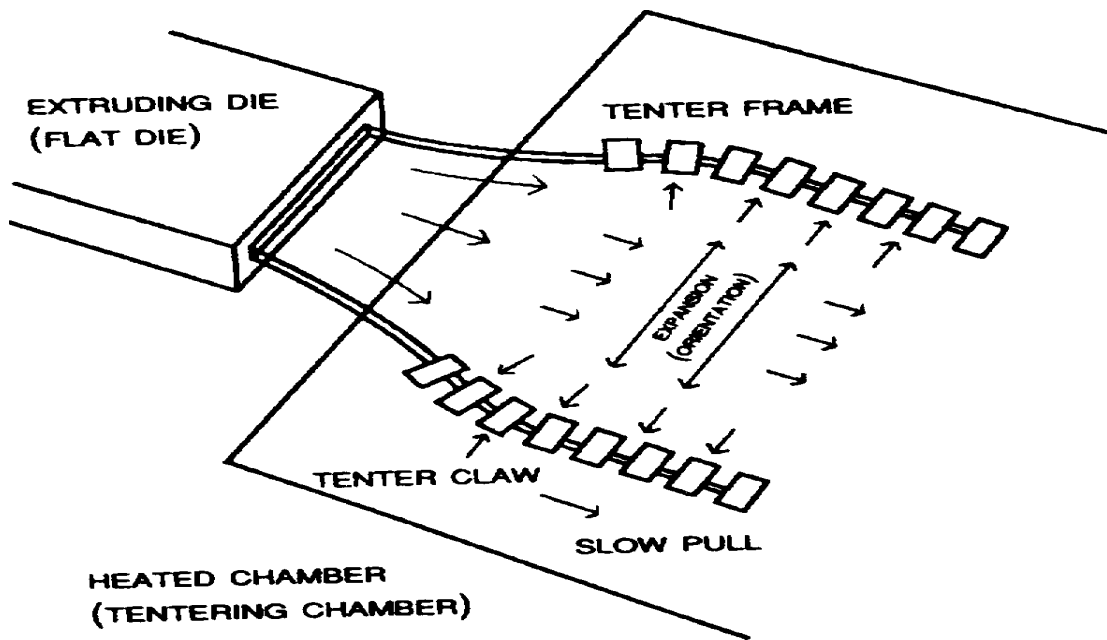
#### **1.1.7a. Cast Film (CPP)**

In cast film producing processes, extruding of polypropylene through a die onto chill roll or water quench techniques is used. The film thickness is controlled by the gap between the die slips or by the rotational speed of the chill roll. Unorientation and softness are basic properties of cast film [6].

#### **1.1.7b. Biaxially Oriented Film (BOPP)**

As illustrated in figure.4, the film itself is stretched in one or two directions with a tentering frame, a device that keeps the edges in clamps that move outward to stretch the sheet in the cross-machine direction. In production of biaxially oriented film, extruded sheet is drawn firstly in machine direction and then in the transverse direction. Draw ratios of 4 X 7 and 6 X 10 are common.

Stretching the film under controlled temperatures can improve certain properties of polypropylene. By the biaxial stretching of film, deformation resistance of film increases. Table.3 states that after stretching, material has a considerably greater tensile strength and lower elongation at break in the stretching directions [3].



**Figure.4:** The representation of stretching of polypropylene.

Property	Cast Film	Biaxially Oriented
Tensile Strength - Machine Direction (MPa)	39	180
Tensile Strength - Transverse Direction (MPa)	22	152
Elongation at break – machine direction (%)	425	80
Elongation at break – transverse direction (%)	300	65

**Table.3:** Comparison of Cast and Biaxially oriented films

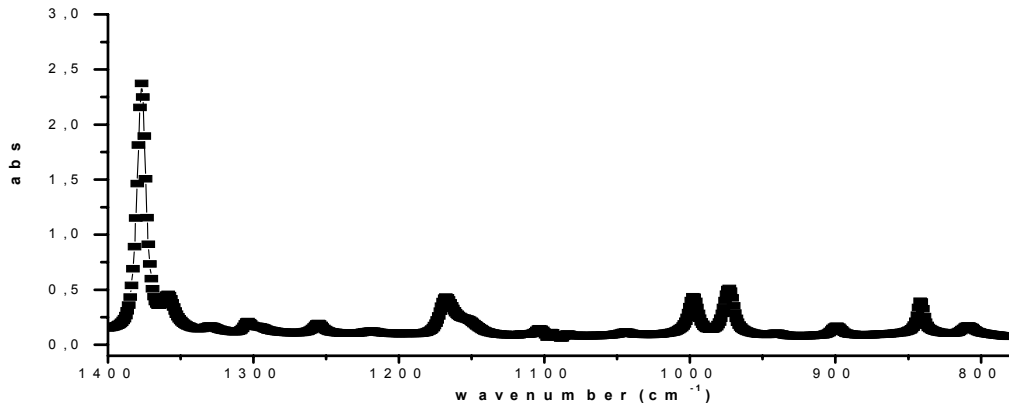
## **1.2. Tools for Studying Properties of Polypropylene**

### **1.2.1. Infrared Spectroscopy**

Infrared spectroscopy relies on an alteration in the permanent dipole moment of the chemical bond with vibrational normal mode in order to produce absorption. Infrared spectroscopy, rapid and sensitive with sampling techniques that are easy to use, is one of the most commonly used spectroscopic methods. A list of application areas of IR in polymers can be roughly said as measuring the concentration of end groups, determining the reaction order and chemical processes, investigating the structural changes produced by chemical reactions, characterizing copolymers, measuring stereoregularity, conformation, and branching, characterizing polymer blends, measuring morphological units in polymers, and investigating crystallinity and orientation etc. For various studies in polypropylene, IR spectroscopy is already highly recommended for determining the orientation of polypropylene films [12-15].

#### **1.2.1a. Infrared Spectrum and Bands of Polypropylene**

The mid-infrared spectrum of isotactic polypropylene has been studied extensively during last five decades. Many types of vibrations, such as C-C chain stretching, CH<sub>3</sub> rocking, CH<sub>2</sub> rocking occur at the mid-infrared spectrum of polypropylene. Typical infrared spectrum of polypropylene film and the assignment of bands are as shown below.



**Figure.5:** Infrared absorption spectrum of a 20µm unoriented polypropylene film (CPP).

<i>Frequency</i>	<i>Phase</i>	<i>Angle</i>	<i>Assignment</i>
809 cm <sup>-1</sup>	Crystalline	⊥	CH <sub>2</sub> rocking, C-C chain stretching, C-CH stretching
841 cm <sup>-1</sup>	Crystalline		CH <sub>2</sub> rocking, C-CH <sub>3</sub> stretching
899 cm <sup>-1</sup>	Crystalline	⊥	CH <sub>3</sub> rocking, CH <sub>2</sub> rocking, CH bending
941 cm <sup>-1</sup>	Crystalline	⊥	CH <sub>3</sub> rocking, C-C chain stretching
973 cm <sup>-1</sup>	Amorphous		CH <sub>3</sub> rocking, C-C chain stretching
998 cm <sup>-1</sup>	Crystalline		CH <sub>3</sub> rocking, CH <sub>2</sub> wagging, CH bending
1045 cm <sup>-1</sup>	Crystalline		C-CH <sub>3</sub> stretching, C-C chain stretching, CH bending
1104 cm <sup>-1</sup>	Crystalline	⊥	C-C chain stretching, CH <sub>3</sub> rocking, CH <sub>2</sub> wagging
1168 cm <sup>-1</sup>	Crystalline		C-C chain stretching, CH <sub>3</sub> rocking, CH bending
1220 cm <sup>-1</sup>	Crystalline	⊥	CH <sub>2</sub> twisting, CH bending, C-C chain stretching
1256 cm <sup>-1</sup>	Crystalline& amorphous		CH bending, CH <sub>2</sub> twisting, CH <sub>3</sub> rocking
1377 cm <sup>-1</sup>	Crystalline& amorphous	⊥	CH <sub>3</sub> symmetric bending, CH <sub>2</sub> wagging

**Table.4:** Assignment for absorption bands of polypropylene.

### 1.2.1b. Infrared Dichroism

Vibrational analysis of oriented polymers provides a method of determining independently the molecular orientation both in crystalline and amorphous phases of polymers [16-18]. Infrared spectroscopy is a particularly useful method for orientation studies when bands from each phase are observed. In addition, surface and bulk orientation can be investigated separately [19, 20]. It can be utilized from calculating chain orientations of the different polymers in a blend [21, 22].

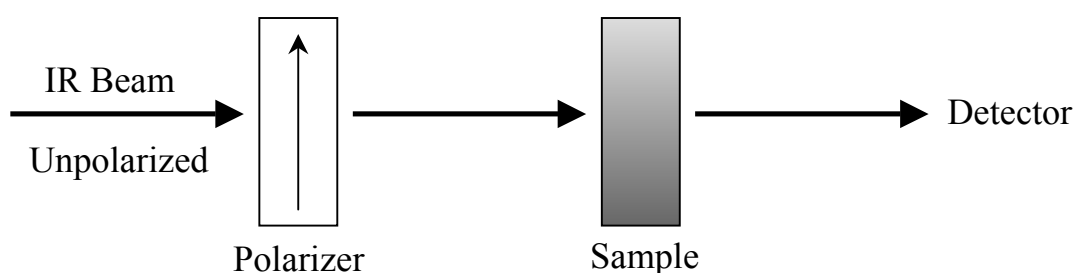
IR absorption for gases and liquids is independent of the polarization of the incident beam, because the random orientation of the molecules produces a random orientation of the resultant transition moment vector. However, the direction of transition moment in solid molecules is fixed. Therefore, two important concepts exist here, one of them is the transition moment vector of molecule in a given mode, the other is the electric field vector of the incident beam at the absorbing frequency. If the angle between these two vectors is  $\alpha$ , the absorbance is proportional to  $\cos^2 \alpha$ . It means that if the electric field vector of incident beam is exactly perpendicular to the transition moment vector of any given mode, there will be no absorbance.

The electric field vector can be linearly polarized into two perpendicular directions. The absorbance of a given infrared band changes depending on both the direction of the transition moment vector of the particular normal mode with respect to the molecular axis and the polarization of the electric vector of the incident radiation. In a drawn polymer, the macromolecular chains are preferentially oriented in the direction of strain. When measurements are made with the parallel or perpendicular to this preferred direction, a dichroic ratio arises;

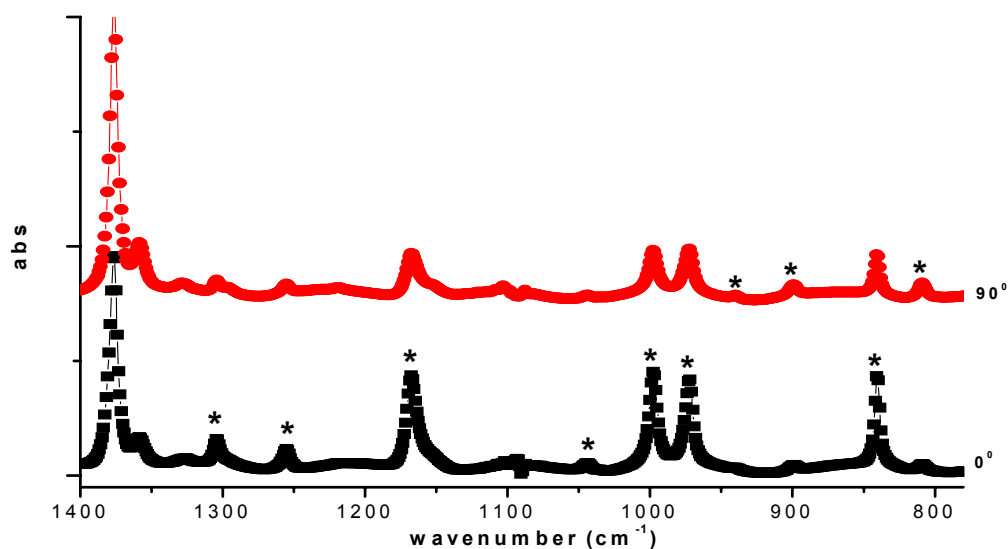
### Dichroic Ratio: $A_0 / A_{90}$

$A_0$  is the absorbance for the linearly polarized light parallel to the chain axis,  $A_{90}$  is the absorbance for the linearly polarized light perpendicular to the chain axis. This ratio can change from zero to infinity. For an unoriented polymer, no dichroism occurs and also the ratio is equal to 1 [23].

A schematic description of using of polarizer is given in figure.6 and figure.7 depicts the infrared absorption spectra of polypropylene recorded with two different polarizers. The dichroism sensitive bands are denoted by \*.



**Figure.6:** Schematic representation of polarizer in FTIR



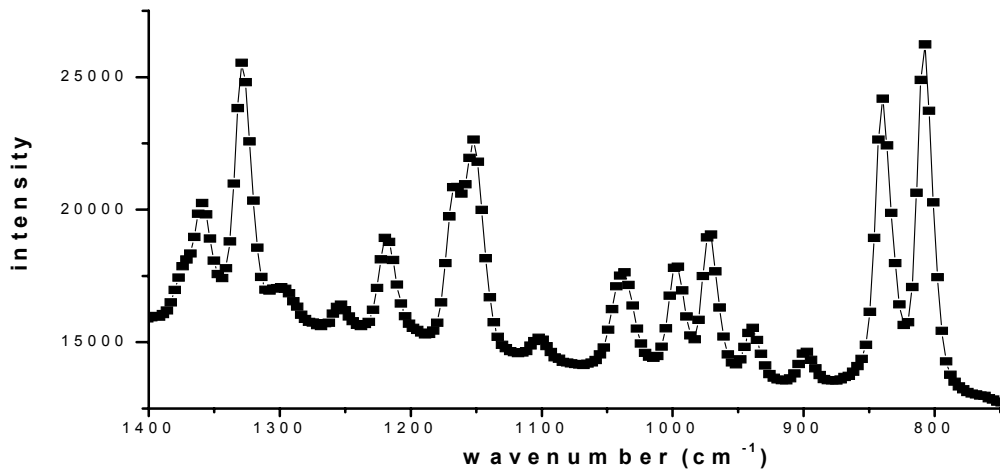
**Figure.7:** Infrared spectra of BOPP with using  $0^\circ$  and  $90^\circ$  polarizers.

### 1.2.2. Raman Spectroscopy

Raman spectroscopy, which is a complementary technique to infrared spectroscopy, also measures the vibrational energy levels. It is based upon a change in the induced dipole moment or polarization to produce Raman scattering. When a beam of light strikes a molecule, it can be either absorbed or scattered. Most of the photons are scattered elastically, and this is termed as Rayleigh scattering. A few of the photons ( $1$  in  $10^8$ ) are scattered inelastically, and this is named as Raman scattering. These Raman scattered photons, having different frequencies, constitute the Raman spectrum of the molecule.

Due to the high sensitivity of the Raman effect for certain non-polar groups like C-C bonds, Raman spectroscopy is used for analysis of chemical composition and structure

of polymers. Moreover, it can be utilized for determining of the configuration, tacticity and conformation of polymer chains [12, 24].



**Figure.8:** Raman Spectrum of Polypropylene Film.

### 1.2.3. XRD

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction. XRD is used to identify crystalline phases and orientation. In addition, it can be exploited to determine atomic arrangement and structural properties. For measuring the thickness of thin films and multi-layers, XRD is useful method.

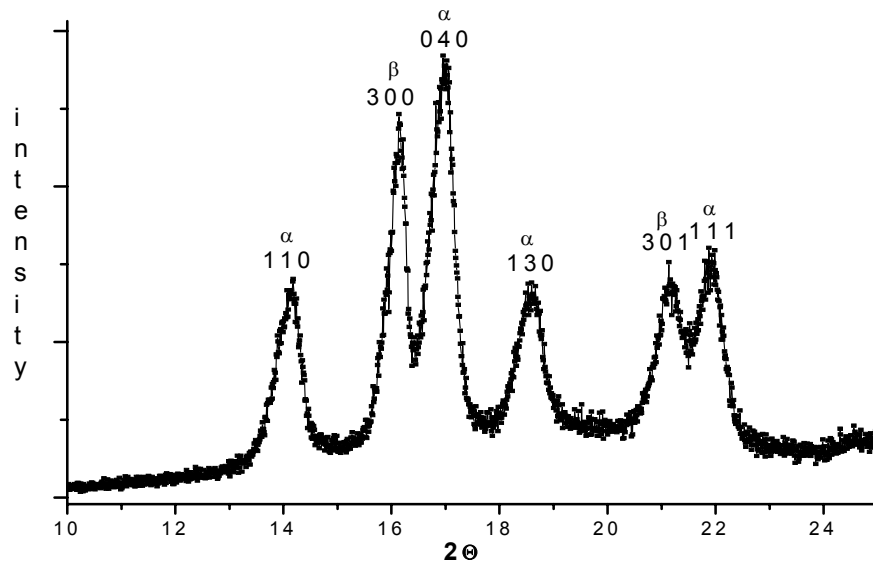
Since many plastic polymers are crystalline or semicrystalline, they can be identified and studied by X-ray diffraction methods. In fact, the percent crystallinity in a polymer can be determined due to the fact that it has variable crystallinity degree. Polymers, for instance polypropylene, have generally polymorphic forms, for which  $\alpha$ ,  $\beta$ ,  $\gamma$  and mesomorphic forms can be stated. Since phase transformations among them can be

existed with increasing temperature or changing other parameters, these transformations can be determined using XRD [1, 25, 26].

The corresponding unit cells for observed lines and typical XRD pattern of polypropylene, including  $\alpha$  and  $\beta$  phases, are illustrated in table.3 and figure.8 respectively [27-33].

<b>2<math>\theta</math></b>	<b>Unit Cell</b>	<b>Crystalline form</b>
14.0 <sup>o</sup>	(110)	$\alpha$
16.0 <sup>o</sup>	(300)	$\beta$
17.0 <sup>o</sup>	(040)	$\alpha$
18.5 <sup>o</sup>	(130)	$\alpha$
21.2 <sup>o</sup>	(301)	$\beta$
21.5 <sup>o</sup>	(111)	$\alpha$

**Table.5:** XRD peaks of polypropylene and corresponding unit cells.

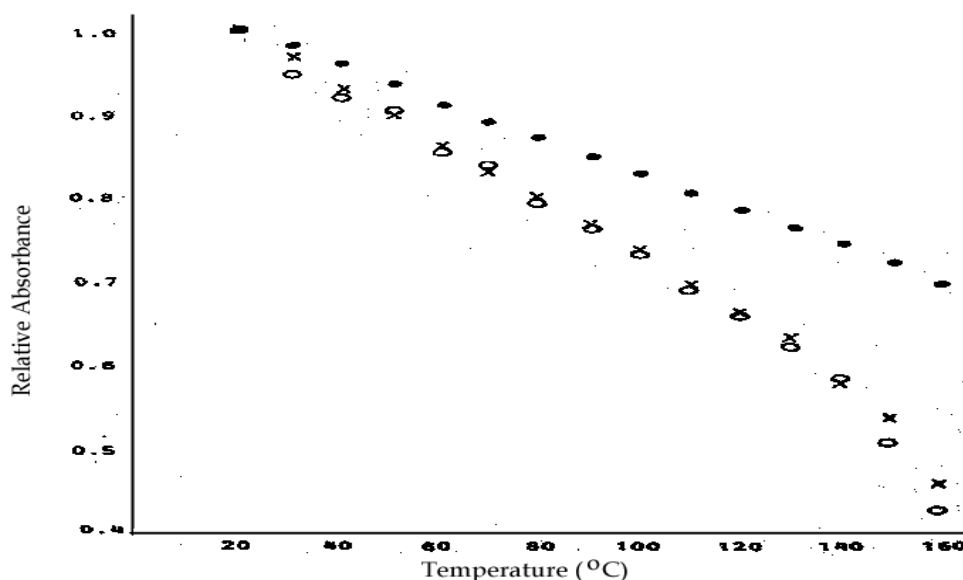


**Figure.9:** Typical XRD pattern of polypropylene.

### 1.3. Effect of Temperature on the Crystallinity and Orientation

A heat treatment may lead to changes in structure and morphology of the material on different scales, such as macromolecular chain, lamellea structure and bulk [34]. Heating of polypropylene has a strong influence on its crystallinity and orientation. Infrared spectroscopy has been oftenly used to understand this relation. The infrared spectrum of i-PP has a number of bands depending on the conformations of the individual chains. These bands, 1330, 1303, 1220, 1167, 1100, 998, 940, 900, 841, and 808  $\text{cm}^{-1}$ , are called regularity bands. In addition, all of them are crystalline bands. Hendra *et al.* [35] observed that considerable changes occur in high crystalline polypropylene at about 130-135°C. Hendra scaled the peak absorbance as a function of temperature for several

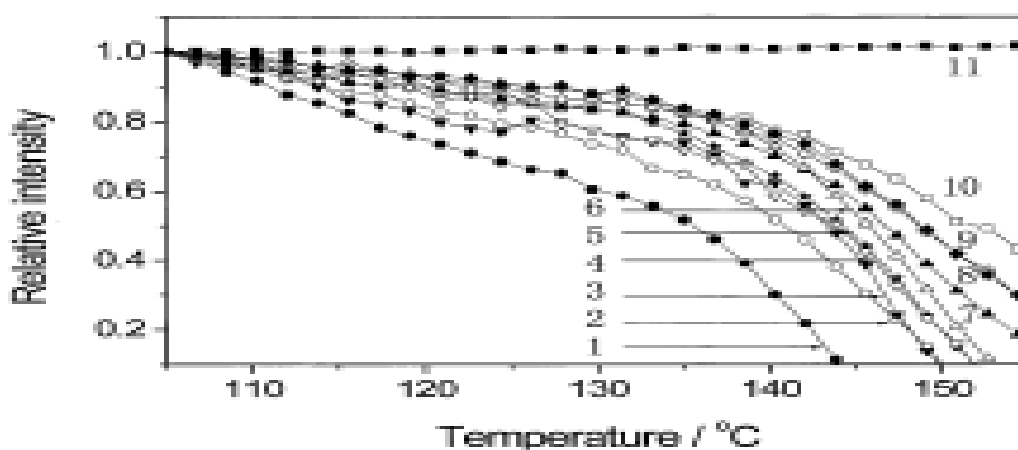
infrared regularity bands. In the figure.10, 900 and 1220  $\text{cm}^{-1}$  (crystalline bands), 973  $\text{cm}^{-1}$  (amorphous band), are compared according to increasing temperature. The absorption of regularity bands, 900 and 1220  $\text{cm}^{-1}$ , decreases much more rapidly beyond 130° C. However, there is still a linear decrease of absorbance at 973  $\text{cm}^{-1}$ , non-regularity band, beyond 130° C. Similar decreases in absorbance of 841 and 1167 $\text{cm}^{-1}$  were observed by Lamberti [36]. Yan *et al.* [37] stated that there is a great decrease in the intensity of 841, 998 and 1220  $\text{cm}^{-1}$  bands at above 170.5°C.



**Figure.10:** Temperature dependence of infrared bands, cross, filled circle, unfilled circle refer to 900, 973 and 1220  $\text{cm}^{-1}$  respectively.

Later, Yan *et al.* [38] tried to elucidate this change at 135°C using almost all regularity bands. In figure.11, with increasing the temperature, firstly, the intensity of 940  $\text{cm}^{-1}$

bands decreases much more rapidly, then the 1220, 1167, 1303, 1330, 841, 998, 900, 808, and 1100  $\text{cm}^{-1}$ . The intensity of 973  $\text{cm}^{-1}$  does not change appreciably. They stated that the longer helix length of isotactic sequence leads to faster intensity decrease of the correspondent band.



**Figure.11:** Temperature dependence of regularity bands: (1) 940  $\text{cm}^{-1}$ , (2) 1220  $\text{cm}^{-1}$ , (3) 1167  $\text{cm}^{-1}$ , (4) 1303  $\text{cm}^{-1}$ , (5) 1330  $\text{cm}^{-1}$ , (6) 841  $\text{cm}^{-1}$ , (7) 998  $\text{cm}^{-1}$ , (8) 900  $\text{cm}^{-1}$ , (9) 808  $\text{cm}^{-1}$ , (10) 1100  $\text{cm}^{-1}$ , (11) 973  $\text{cm}^{-1}$ .

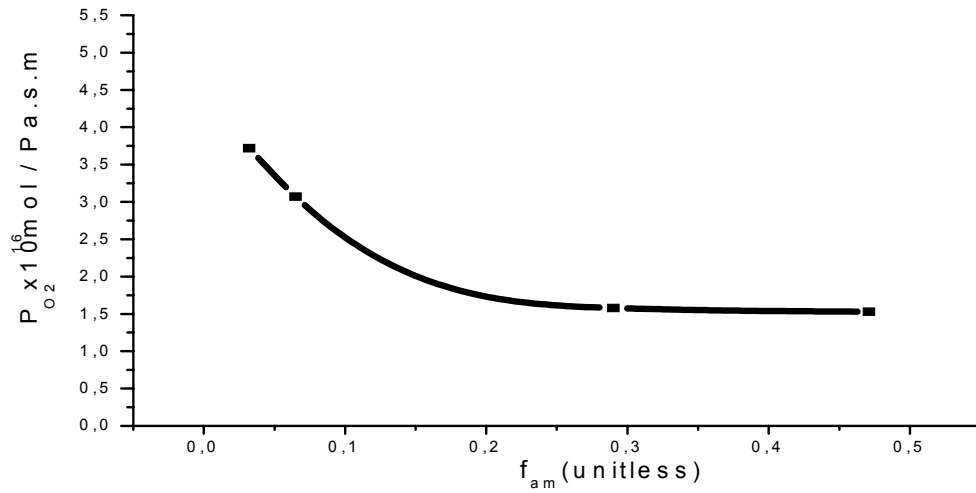
Zhu *et al.* [39] also tried to show that there is a relationship between heating and orientation. Based on polarization infrared spectroscopy, they performed in-situ measurement of orientation change of macromolecular chains in uniaxially stretched i-PP upon heating. In their study, during heating, dichroic ratio of 1220  $\text{cm}^{-1}$  (crystalline band) and 2725  $\text{cm}^{-1}$  (amorphous band) decreased to approximately 1, it means that orientation disappeared.

#### **1.4. Shifts in IR bands**

Painter *et al.* [40] observed that differences in frequencies of i-PP having different degrees of crystallinity. They assigned  $973\text{ cm}^{-1}$  band as the superposition of two close peaks, one of them is located at  $972\text{ cm}^{-1}$  (crystalline) and the other is located at  $974\text{ cm}^{-1}$  (amorphous). In that study,  $973\text{ cm}^{-1}$  band was observed at  $974\text{ cm}^{-1}$  for polypropylene which was prepared by quenching into ice-water producing smectic phase. However, this band was detected at  $973\text{ cm}^{-1}$  for polypropylene prepared by annealing which gives monoclinic form. In addition to this study,  $975\text{ cm}^{-1}$  in amorphous phase of the quenched sample shifted to  $972\text{ cm}^{-1}$  in the ordered phase of the annealed sample.

#### **1.5. Permeability of Polypropylene**

Whereas polypropylene is impermeable to water and other liquids, gases penetrate through it. Mechanical and barrier properties of polypropylene are continuously tried to make better, since it plays a crucial role in packaging industry. At this stage, its crystallinity and orientation are paid attention, due to the fact that there is a strong relation between gas permeability and crystallinity/orientation. Vries indicated, in figure.12, increasing of molecular orientation of amorphous phase in polypropylene leads to decreasing of gas permeability [41].



**Figure.12:** Representation of relation between gas permeability and orientation.

In addition, humidity and oxygen permeability of CPP (unoriented) and BOPP (oriented) were measured by Polinas A.C. In table.6 and 7, humidity and oxygen permeability of BOPP is low compared to humidity.

Humidity Permeability (gr/m <sup>2</sup> per day)	1.measurement	2.measurement	Average
CPP (unoriented)	9.82	9.84	9.83
BOPP (oriented)	3.66	3.56	3.61

**Table.6:** Humidity permeability of CPP and BOPP films.

Oxygen Permeability (gr/m <sup>2</sup> per day)	1.measurement	2.measurement	Average
CPP (unoriented)	2825	2937	2881
BOPP (oriented)	1235	1126	1181

**Table.7:** Oxygen permeability of CPP and BOPP films.

### 1.6. Aim of the Present Study

In the present study, we have set at three aims. Firstly, we try to understand better crystallinity & orientation changes in polypropylene, because oxygen permeability and shelf-life are important issue related to crystallinity and orientation of polypropylene films.

Secondly, we determined phase transition (from  $\beta$  form to  $\alpha$  form) in CPP film using both XRD and FT-IR with increasing the temperature. Our purpose was to determine this phase transition using FT-IR, which is a more practical and common instrument.

Thirdly, since infrared spectroscopy is one of the most frequently used spectroscopic technique; our objective is to apply IR as both fast and practical method on measuring crystallinity-amorphous content, detecting phase transitions and orientation changes.

## **2. EXPERIMENTAL**

### **2.1. Materials**

The polymers, which were used in our experiments, were received from Polinas A.Ş. These polymers were prepared as thin film. Those used polymers in this work are listed below.

- a) CPP (cast polypropylene) has 28 $\mu$ m thickness.
- b) BOPP (biaxially oriented polypropylene) has 28 $\mu$ m thickness. It was drawn five times along machine direction and then ten times along transverse direction.
- c)  $\beta$ -CPP (cast polypropylene) has  $\beta$ -crystallinity. It has a higher thickness compared to polypropylene films having no  $\beta$ -form.
- d)  $\beta$ -MPP (mono oriented polypropylene) has  $\beta$ -crystallinity. Its thickness is higher relative to polypropylene films having no  $\beta$ -form.

We reduced the thickness of polypropylene films having  $\beta$ -form to be able to record their infrared spectra. We did not make additional process on films such as purification.

### **2.2 Tools**

We mainly utilized FT-IR and Raman spectrometer, X-Ray Diffraction and equipments related with heating. Table.8 indicates tools and their models in our experiments.

<b>Tool</b>	<b>Model</b>
Thermocouple	J-Type
Heater/Controller	Harrick 1600
FTIR Spectrometer	Bomem 102 MB
X-Ray Diffractometer	Rigaku Miniflex diffractometer high power Cu-K <sub>α</sub> source operating at 30kV/15mA
Raman Spectrometer	Jobin Yvon Labram 5/203 IM

**Table.8:** Type of instruments and tools.

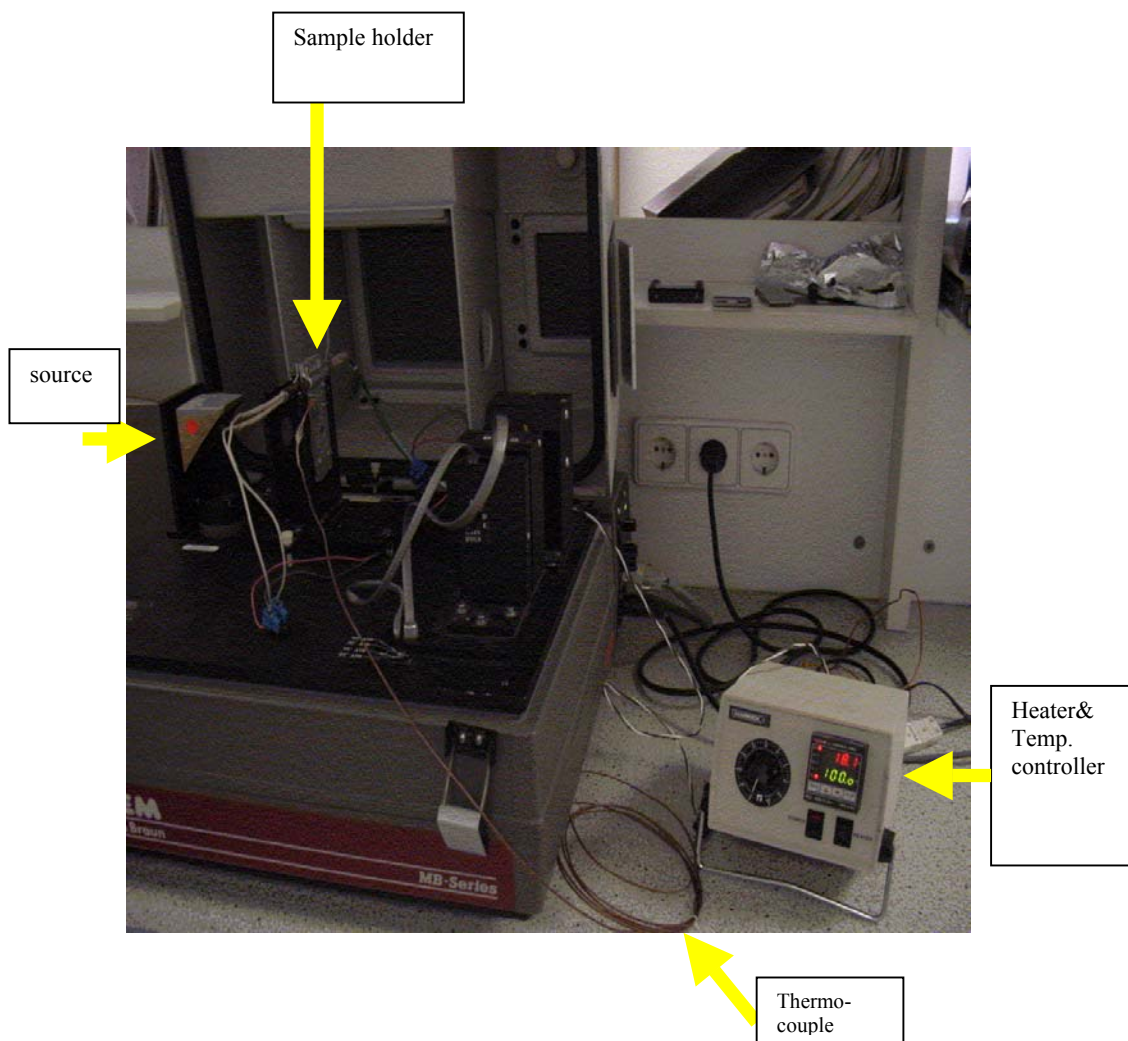
### **2.2.1. Temperature Controller and Its Calibration**

Our digital temperature controller and its accompanying thermocouple provide temperature regulation over an extensive temperature range (for J type thermocouples from -73 to 760°C). Since temperature used in this study was not higher than 175°C, indium was selected for calibration of the temperature controller because melting point of indium is 156.6°C. Our measurement value was determined as 156.2±0.5 which was satisfactory for our purpose. To heat the sample, 40% of output voltage is generally used. To reach above 170°C, this output voltage was increased to 50%.

### **2.2.2. In-situ FT-IR Spectrometer**

In-situ FT-IR analysis is widely used in this study. When measuring the orientation using polarized-FT-IR, we often performed experiments in-situ. In-situ technique means that heating the sample and recording the spectrum occur simultaneously. It gives us an important knowledge about the changes during heating. A schematic

representation of our system for in situ analysis of polymers is presented in fig 13. The FT-IR spectra of all polypropylene films were recorded in the range of 4000-400 $\text{cm}^{-1}$  with 4 $\text{cm}^{-1}$  resolution and 128 scans. For recording small shifts in the bands to follow phase transitions, the spectrum of film was recorded with 2 $\text{cm}^{-1}$  resolution and 64 scans.



**Fig.13:** Experimental set up

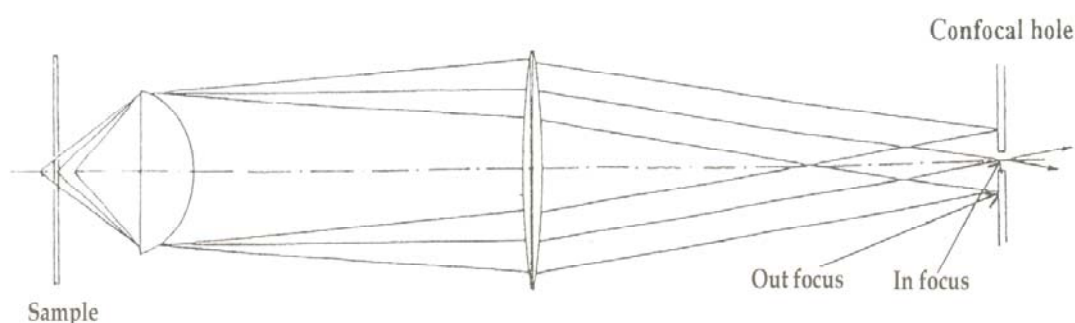
### 2.2.3. XRD

X-ray diffraction patterns were recorded using Rigaku Miniflex diffractometer with high power  $\text{Cu-K}_\alpha$  source operating at 30kV/15mA. Polypropylene films were

placed on a glass lamella. XRD patterns of these films were collected with a scan rate of 10 degree/min in the range of 10-40°. Duplicate measurements were done to ensure reproducibility.

#### 2.2.4. Raman Spectrometer

We used Raman spectrometer with 632.81nm as excitation wavelength supplied by an internal He-Ne 20mW laser. Before recording Raman spectrum of a sample, the instrument must be calibrated. Without the laser light, the position of peak must be positioned to zero should be exactly at zero and the intensity of this peak must be maximized. Firstly, 10x objective is used to focus the light. Raman spectra of CPP and BOPP films are collected with 100x objective, 1100 $\mu\text{m}$  hole, 200 $\mu\text{m}$  slit interval, and 600 grooves/mm grating. The range of 200-1600 $\text{cm}^{-1}$  is scanned 10 times and duration of each scan is 10 seconds. To record spectra in machine and transverse directions of films, sample holder can be rotated by 90°. The width of confocal hole can be reduced from 1100 $\mu\text{m}$  to 200 $\mu\text{m}$  for extracting information about depth profile. As depicted in figure.14, with increasing the confocal hole, the deeper of sample can be focused. Also, the higher intensity can be obtained from the wider confocal hole, because most of the scattered light is in focus.

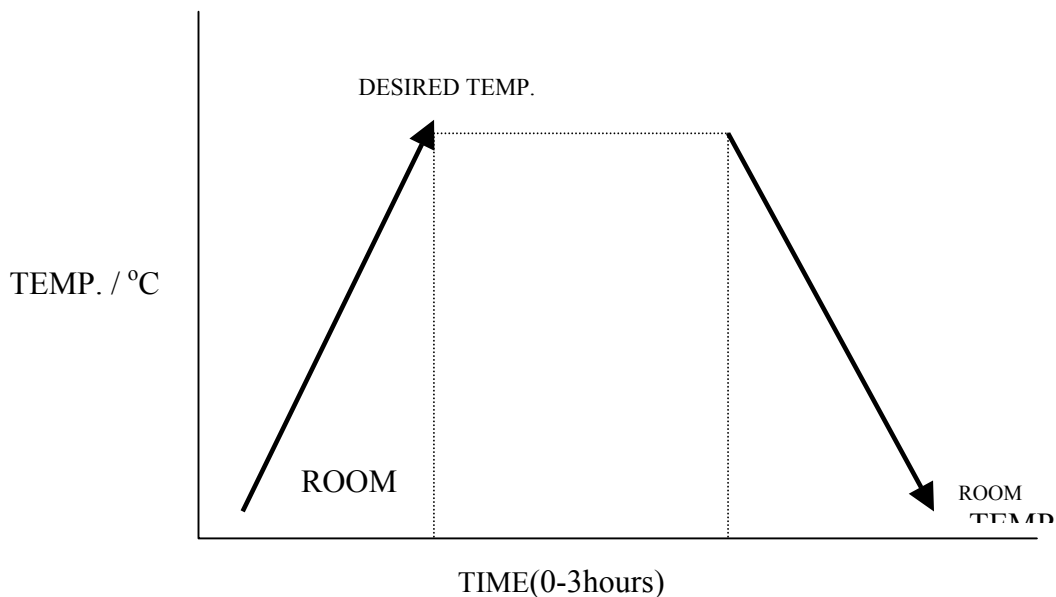


**Figure.14:** The representation of scattered light from sample on confocal hole.

### 2.3. Procedure

In a typical experiment, we followed the pathway described below.

- Alignment of source and background are recorded.
- The polypropylene film is placed on top of a silicon wafer in the sample holder and its close contact with the wafer is ensured by the screws if studied above 150°C. Below 150°C, silicon wafer is not needed.
- For orientation measurements, polarizer is put in front of sample.
- Heater/temperature controller and thermocouples are connected to the sample holder properly.
- At room temperature and during heating, infrared spectrum of the sample is recorded. Once the desired temperature is reached, spectra are recorded for 3 hours in 30 minutes intervals for the crystallization experiments, for one hour in 20 minutes time intervals in the orientation experiments. A schematic representation of the temperature profile is depicted in fig 15.



**Figure.15:** The representation of heat profile.

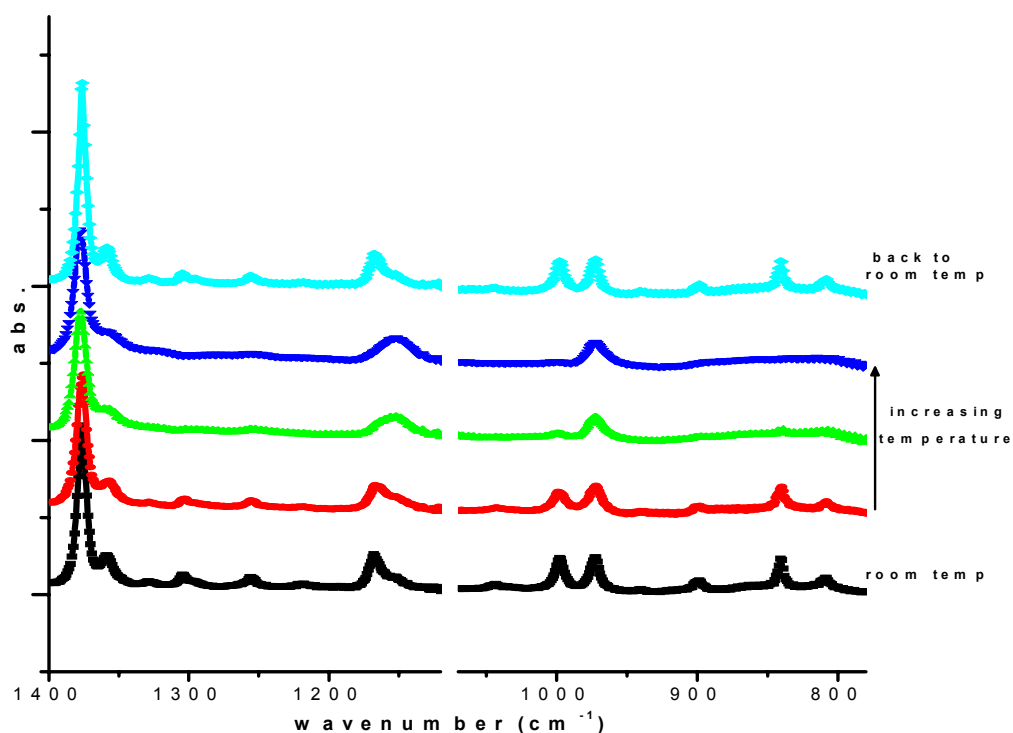
### 3. RESULTS AND DISCUSSION

#### 3.1. Crystallinity Studies

Changes in crystallinity as a function of temperature were investigated by interpreting the alterations in the infrared bands of polypropylene. A set of spectra at various temperatures as a spectroscopic fingerprint of the crystallinity is depicted in fig.16. When temperature increases, the intensity of 809, 841, 899, 998, 1045, 1220, 1168, and 1256  $\text{cm}^{-1}$  bands, belonging to crystallinity phase, weaken and then disappear. However, 973 and 1153  $\text{cm}^{-1}$  bands, belonging to amorphous phase, remain unchanged. 1377  $\text{cm}^{-1}$  band, having partially amorphous character, does not change significantly. This is the indication that crystallinity decreases with increasing temperature similar to previous studies[37, 38]. We have paid attention to what happens after polypropylene films were cooled to room temperature. Furthermore, the crystallinity bands reappear after cooling to room temperature is completed. Yan *et al.* [42] reported that a similar crystallization occurred in both cooling to room temperature at a rate of 20° C/min for non-isothermal crystallization and cooling to 120°C for isothermal crystallization.

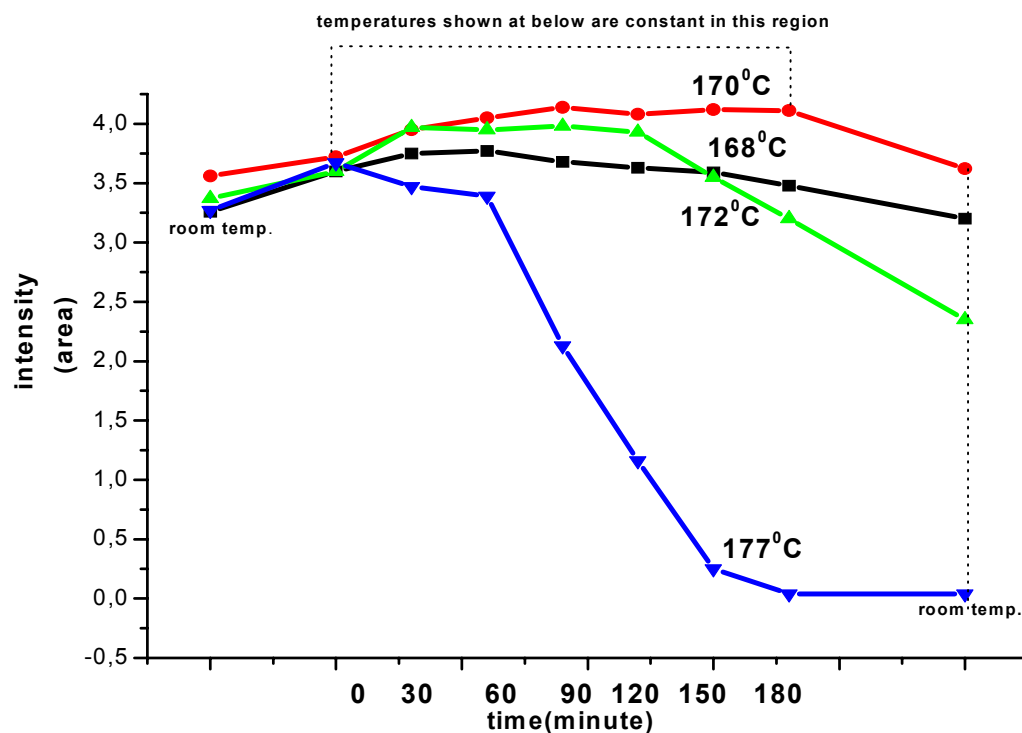
We selected the 973 $\text{cm}^{-1}$  (amorphous) and 998 $\text{cm}^{-1}$  (crystalline) bands to follow the crystallinity changes in detail. Interpretation of fig.17 and 18 is a good way to understand the crystallinity behavior of polypropylene with respect to temperature. As shown in fig.17, there is no significant change in absorbance of 973  $\text{cm}^{-1}$  band during heating-cooling process. Although there are small fluctuations for heating to 168, 170, and 172°C, they do not lead to significant changes on the intensity of this band. The reason for 973  $\text{cm}^{-1}$  band which has almost same intensity during this process is due to its amorphous character. During waiting at 177°C, there is a great

decrease in intensity of this band, because of the destruction of helical sequences of polypropylene. However, fig.18 depicts that  $998\text{ cm}^{-1}$  band does not behave like  $973$



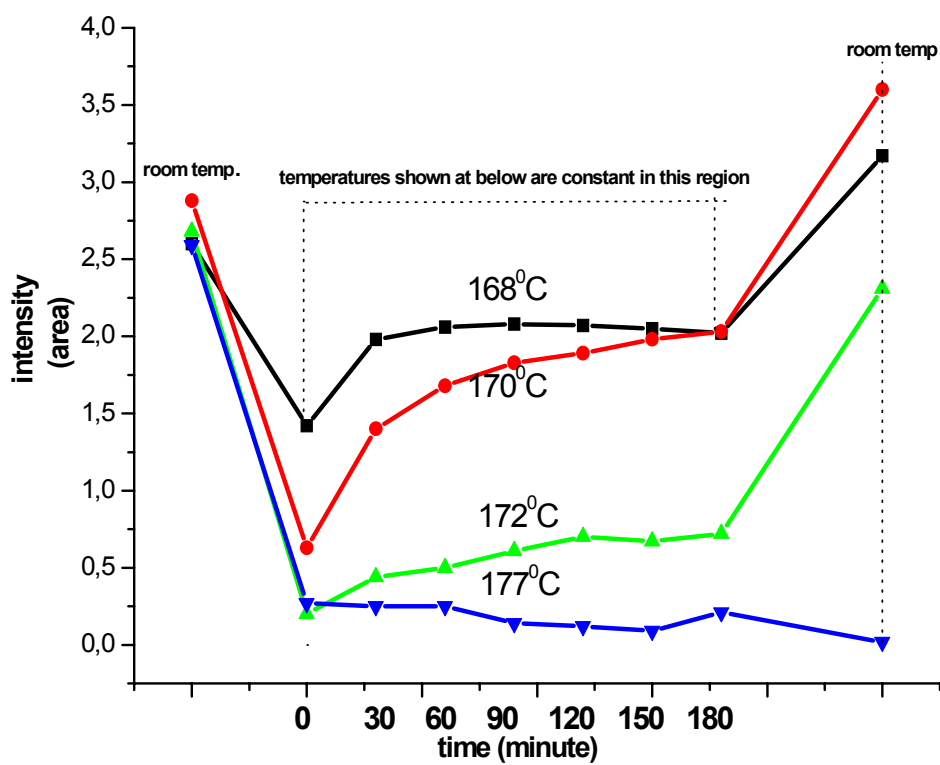
**Figure.16:** Effect of increasing temperature on the bands of polypropylene.

$\text{cm}^{-1}$  band at all. Especially, as temperature increases initially, there is a significant decrease in the absorbance of  $998\text{ cm}^{-1}$  band. For  $168, 170, 172^\circ\text{C}$ , area of this band decreases to 1.4, 0.7, and 0.25 respectively. Due to the fact that  $998\text{ cm}^{-1}$  is a typical crystalline band, this band loses its intensity with increasing temperature. During the waiting period, there is an increase in the absorbance of this band. After returning back to room temperature, there is a sharp increase in the absorbance except  $177^\circ\text{C}$ . Due to the destruction of helix at  $177^\circ\text{C}$ , the band cannot reach its initial value.



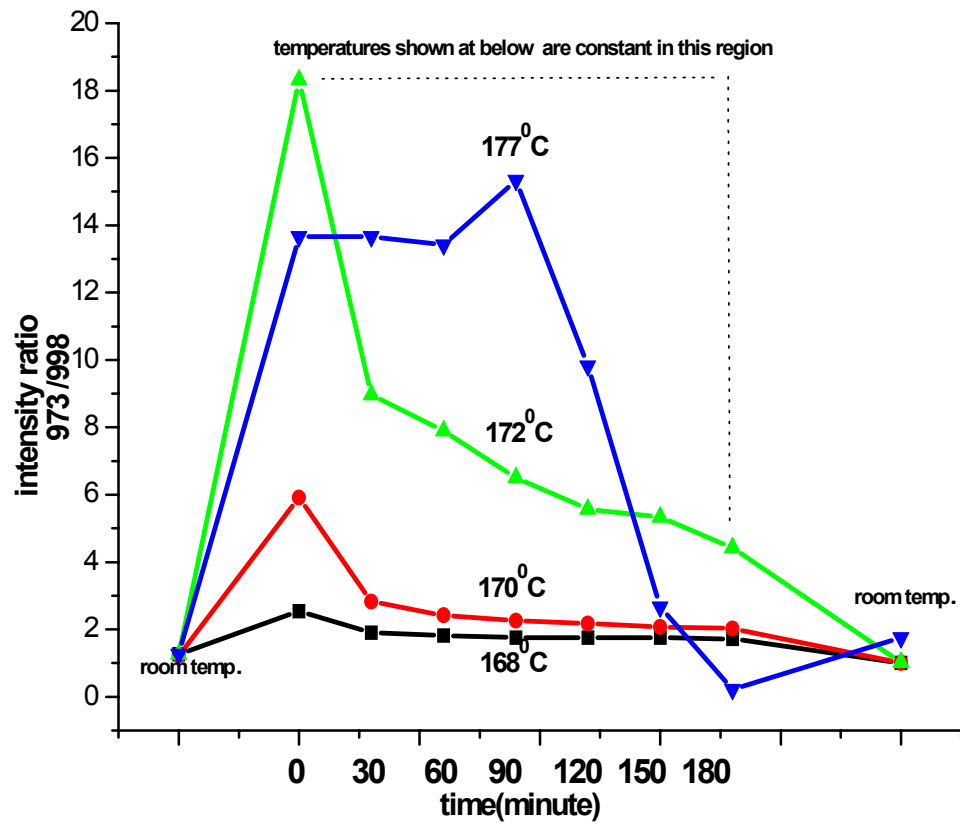
**Figure.17:** Intensity plot of CPP films for  $973\text{cm}^{-1}$  band during heating-cooling process.

Fig.19 gives the ratio of the intensity, as determined from the areas of the peaks, of  $973\text{ cm}^{-1}$  to  $998\text{ cm}^{-1}$  during heating-cooling process of CPP film. It can be easily observed that amorphous/crystallinity ratio increases initially from room temperature to  $168$ ,  $170$ ,  $172$  and  $177^\circ\text{C}$ , but the ratio steadily decreases during the waiting period for  $168$ ,  $170$ , and  $172^\circ\text{C}$ . The ratio at  $172^\circ\text{C}$  is higher than ratio at  $170^\circ\text{C}$ , and the ratio at  $170^\circ\text{C}$  is higher than at  $168^\circ\text{C}$ . After returning back to the room temperature, amorphous/crystallinity ratio drops back to approximately the initial value.



**Figure.18:** Intensity plot of CPP films for  $998\text{cm}^{-1}$  band during heating-cooling process.

It can also be observed from fig.19 that intensity ratio of  $973\text{ cm}^{-1}$  to  $998\text{ cm}^{-1}$  bands at  $177^\circ\text{C}$  is constant for about sixty minutes. Therefore, it can be said that the amorphous/crystallinity ratio can be controlled to some extent. However, as shown in figure.19, the ratio of  $973/998$  decreases after the end of first hour and cannot return its initial value which is an indication that polypropylene starts decompose at and above this temperature.



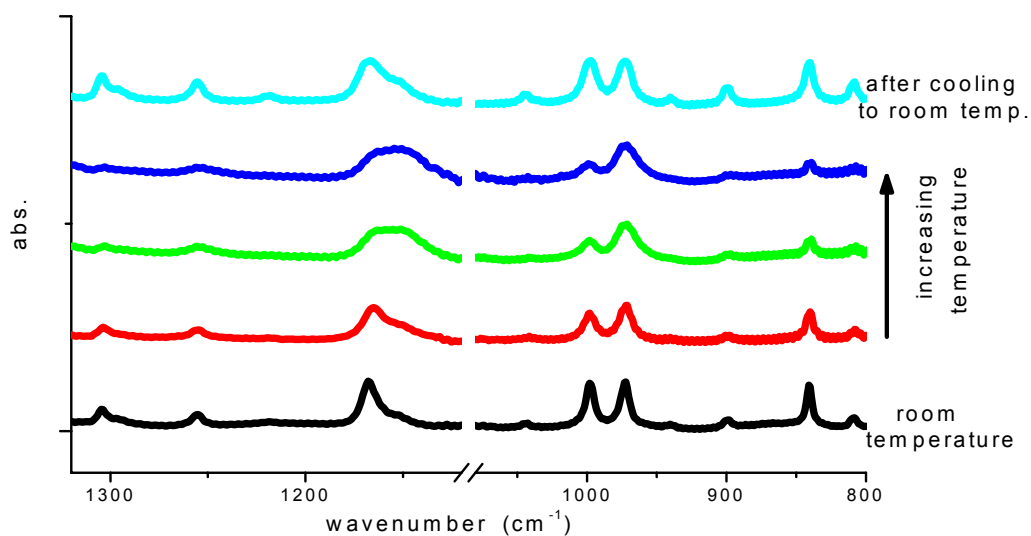
**Figure.19:** This plot shows that  $973\text{cm}^{-1}/998\text{cm}^{-1}$  ratio in heating-cooling process of CPP films.

We observed that heating-cooling process leads to a slight increase of the crystallinity in CPP film. As listed in table.9,  $973/998$  ratio decreases slightly from about 1.25 to about 1.00 after the process completed. Waiting for three hours at 168, 170,  $172^{\circ}\text{C}$  results nearly same amorphous/crystallinity ratio.

Temperature	Ratio of 973/998 (Before heating-cooling process)	Ratio of 973/998 (After heating-cooling process)
168°C	1.26	1.01
170°C	1.23	1.01
172°C	1.26	1.02

**Table.9:** Amorphous/Crystallinity ratio of CPP film before and after heating-cooling process.

We observed a similar trend in BOPP film with increasing temperature. Similarly, crystalline bands weaken and disappeared as shown figure.20. From this similar behavior of BOPP film to CPP film, it can be stated that the heating-cooling process of BOPP and CPP film affects the crystallinity and amorphous character similarly. Small differences between CPP and BOPP films in  $973/998\text{ cm}^{-1}$  can also be observed. Before heating-cooling process, this ratio is about 1.25 for CPP film and 1.00 for BOPP film as shown in table.10. By regarding this ratio, it can be stated that BOPP film has a slightly more crystalline content than CPP film at their initial state. There is an increase in the amorphous/crystallinity ratio to about 1.25 at 160°C. We would like to touch on a point for the values of this ratio between initial and final room temperatures. In spite of the fact that this ratio decreases from 1.25 to 1.00 for CPP film, it remains about 1.00 for BOPP film. This must be related with the crystallinity of BOPP film. It can be said that this process does not appreciably affect the amorphous and crystalline content of BOPP film.

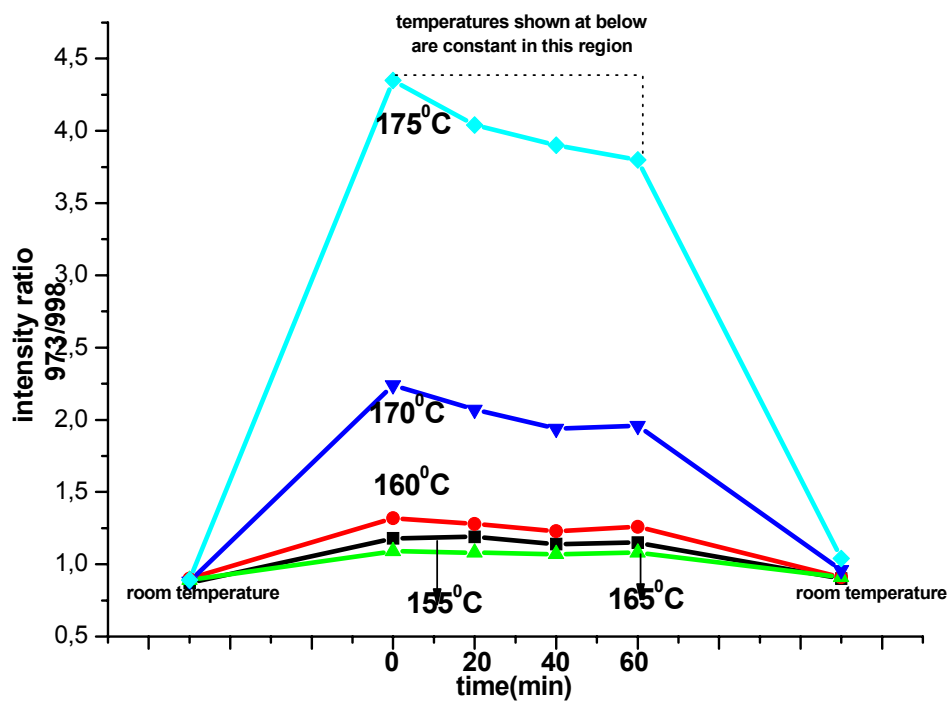


**Figure.20:** The effect of increasing temperature on the bands of BOPP film in FT-IR.

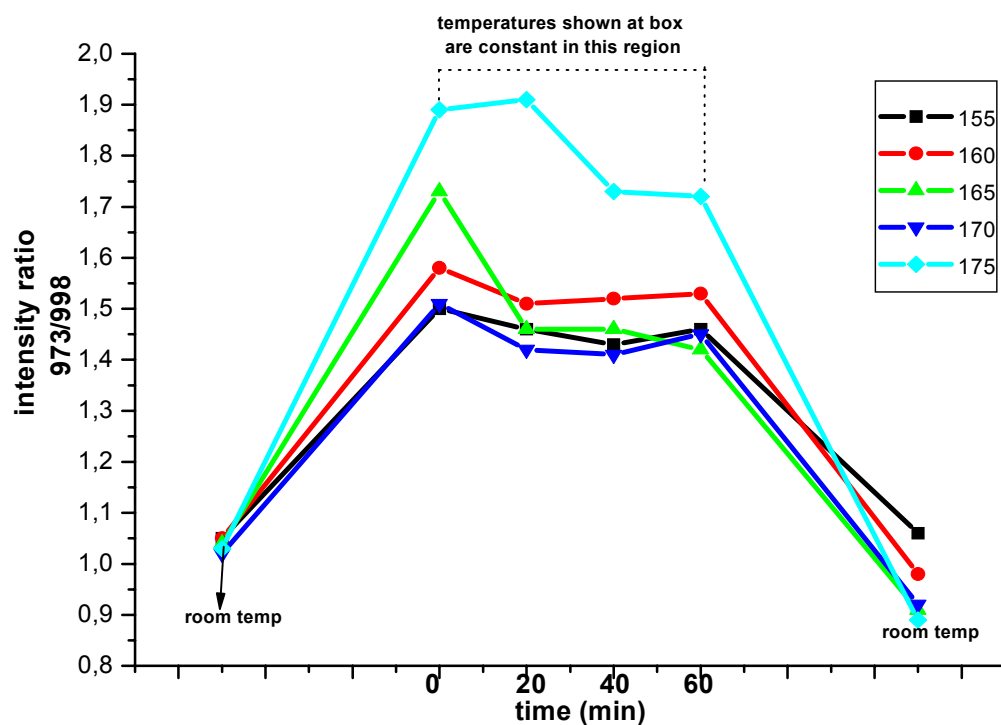
	1.Measurement	2.Measurement	3.Measurement	4.Measurement
Before heating-cooling process	1.01	1.02	1.00	1.02
At about 160°C	1.28	1.27	1.26	1.24
After heating-cooling process	1.00	1.03	1.02	1.02

**Table.10:** 973/998 ratio in BOPP film with respect to temperature changes.

Figure.21 and figure.22 show that changes in crystallinity of BOPP films. The initial increase of the temperature leads to an increase in amorphous/crystallinity ratio, which is generally greater for higher temperatures. During waiting period, a gradual decrease in this ratio is observed which return to initial values after returning back to the room temperature. All of these lead us to conclude that the crystallinity behavior of BOPP and CPP film is similar.



**Figure.21:** This plot shows that  $973\text{cm}^{-1}/998\text{cm}^{-1}$  ratio in heating-cooling process of BOPP films with using  $0^\circ$  polarizer.

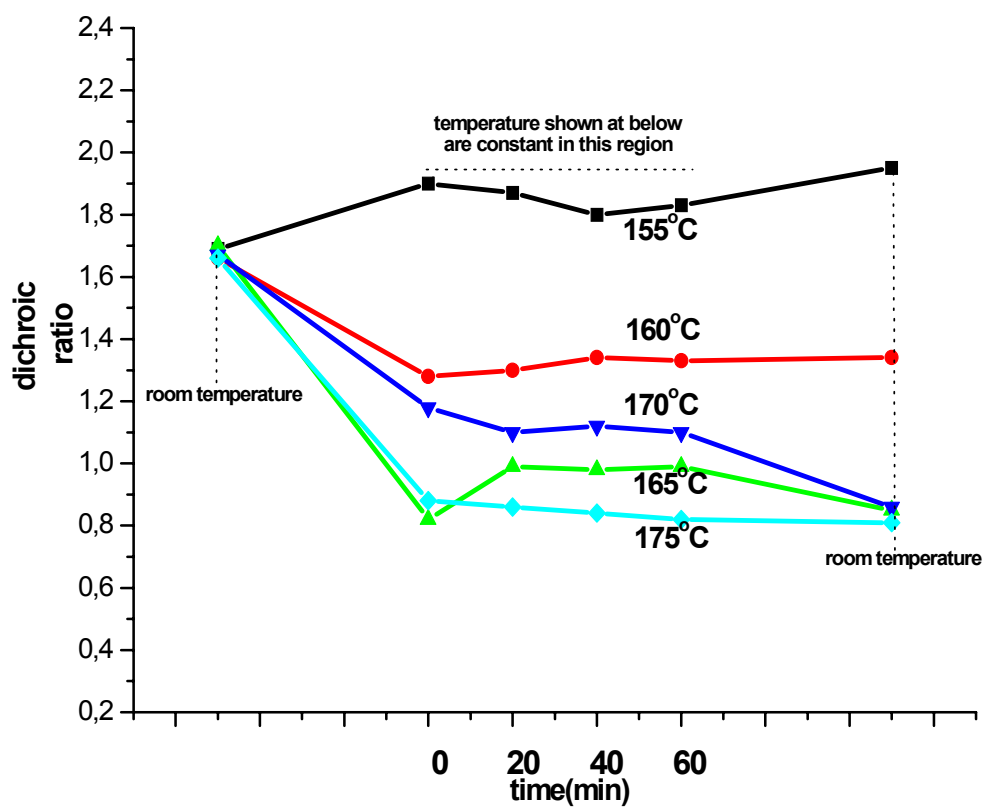


**Figure.22:** This plot shows that  $973\text{cm}^{-1}/998\text{cm}^{-1}$  ratio in heating-cooling process of BOPP films with using  $90^\circ$  polarizer.

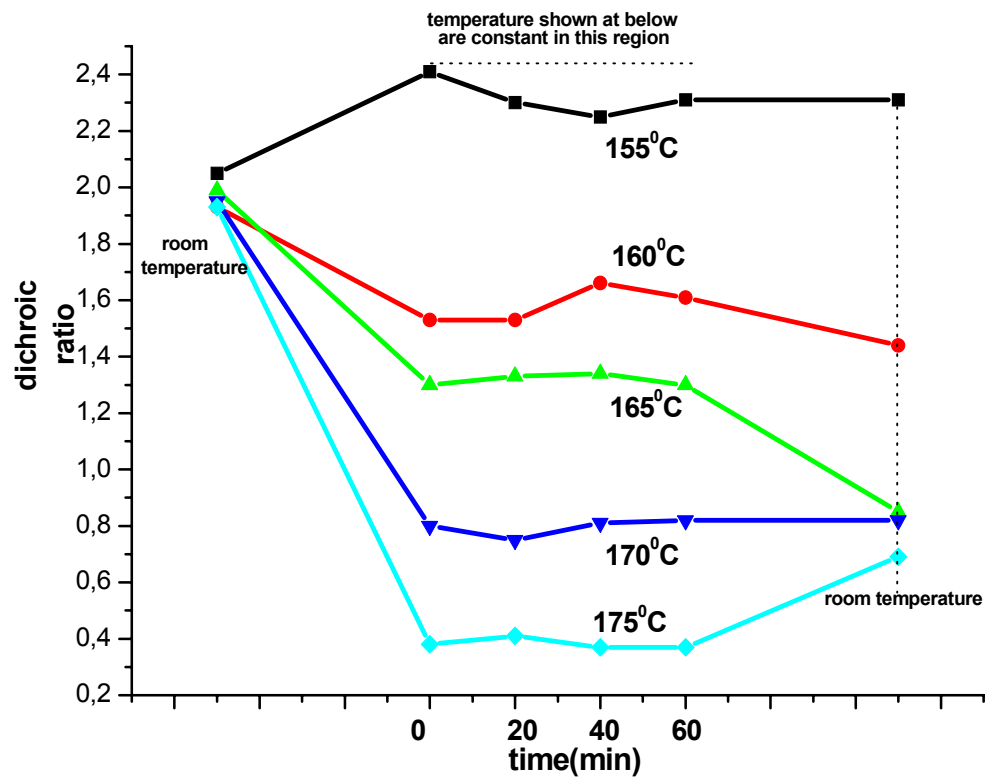
### 3.2. Orientation Studies

We investigated the changes in the orientation of the films with temperature by recording dichroic ratio of  $973$  and  $998\text{ cm}^{-1}$  bands. Fig.23 and 24 give information about dichroism for  $973$  and  $998\text{ cm}^{-1}$  bands during heating-cooling process. As shown in fig.23, the dichroic ratio is approximately 1.7 at room temperature. This ratio is slightly higher for  $155^\circ\text{C}$ , but for  $160$ ,  $165$ ,  $170$ , and  $175^\circ\text{C}$  dichroic ratio is lower. It can be easily inferred that dichroism does not change appreciably during waiting period for these temperatures. After returning back to the room temperature, dichroic ratio of  $973\text{ cm}^{-1}$  band cannot return to its initial value. As indicated in

fig.24, dichroic ratio of  $998\text{ cm}^{-1}$  band at  $155^\circ\text{C}$  is higher than that of  $998\text{ cm}^{-1}$  band at room temperature. Dichroic ratios at 160, 165, 170, and  $175^\circ\text{C}$  are lower than that at room temperature.



**Figure.23:** Dichroism for  $973\text{ cm}^{-1}$  band in heating-cooling process of BOPP.

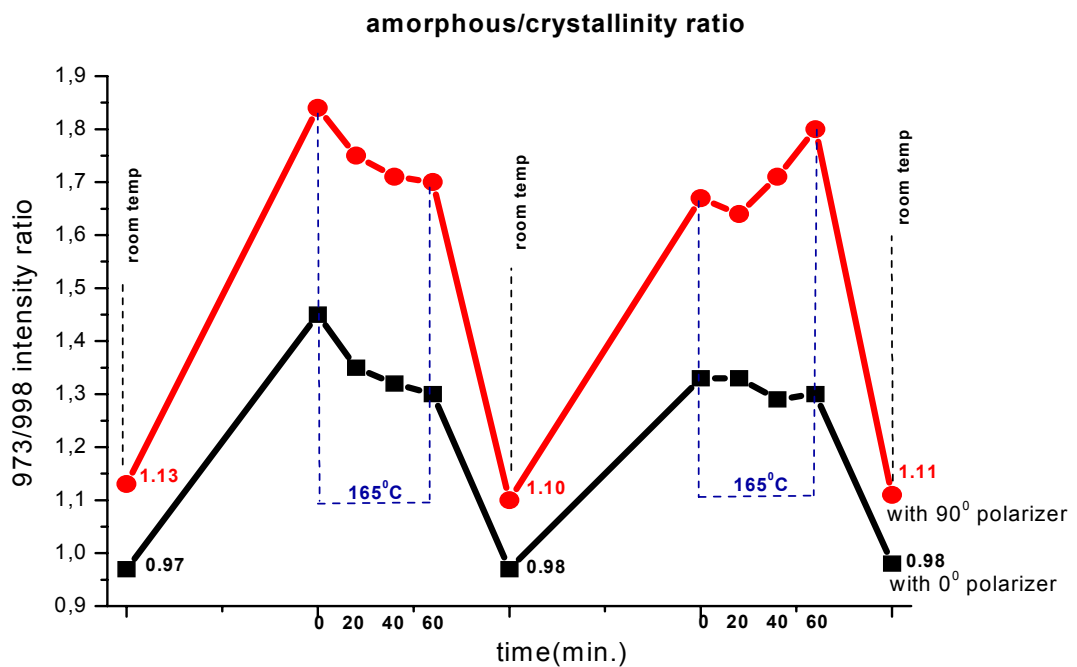


**Figure.24:** Dichroism for  $998\text{ cm}^{-1}$  band in heating-cooling process of BOPP films

### 3.3. Heat Cycle

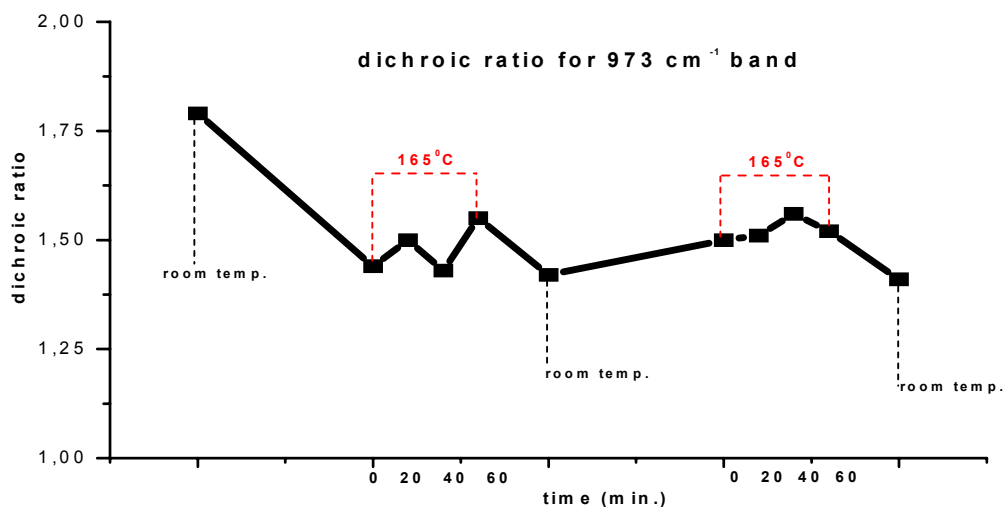
The cycle of the heating-cooling process was performed to investigate additional changes. In the process, BOPP film was heated to  $165^{\circ}\text{C}$  and kept at this temperature during one hour and this process is repeated one more time. As shown in fig.25, there is a great similarity between first and second heating processes. After second heating to  $165^{\circ}\text{C}$ , amorphous/crystallinity ratio increases to nearly same value as first heating. At  $165^{\circ}\text{C}$ ,  $973/998$  ratio fluctuates in the interval 1.7-1.85 for both first and second heating with  $90^{\circ}$  polarizer. This value with  $0^{\circ}$  polarizer is about 1.35-1.45. Moreover, amorphous/crystallinity ratio at room temperature is the same for the first

and the second cooling to room temperature. This ratio is 0.97 at room temperature, and 0.98 at after first and second cooling to room temperature with using 0° polarizer. With using 90° polarizer, this ratio is approximately 1.1 for room temperatures.



**Figure.25:** Amorphous/crystallinity ratio of BOPP film during the cycle process.

Fig.26 exhibits that dichroic ratio value does not change after first reaching to 165°C. Orientation decreases after heating to 165°C, and it does not change by cycle process. From these results, we can say multiple heating does not cause additional orientation and crystallinity changes.



**Figure.26:** Dichroic ratio of 973cm<sup>-1</sup> band in BOPP film during the cycle process.

### 3.4. Shifts in IR Bands

We have also investigated the positions of the bands to follow the crystallinity and orientation changes. By increasing the temperature, a shift in the 973cm<sup>-1</sup> band is observed in CPP films, while there is no change in the 998 cm<sup>-1</sup> band. Moreover, we did not observe shift at both 973 and 998cm<sup>-1</sup> of BOPP films with respect to temperature changes.

Experiment	CPP	BOPP
<b>I)</b> Room temperature	973.48	973.10
<b>I)</b> After heated to 60 <sup>0</sup> C and cooled to room temp.	973.48	973.12
<b>II)</b> Room temperature	973.46	972.85
<b>II)</b> After heated to 100 <sup>0</sup> C and cooled to room temp.	973.21	972.92
<b>III)</b> Room temperature	973.49	973.00
<b>III)</b> After heated to 130 <sup>0</sup> C and cooled to room temp.	973.08	973.07

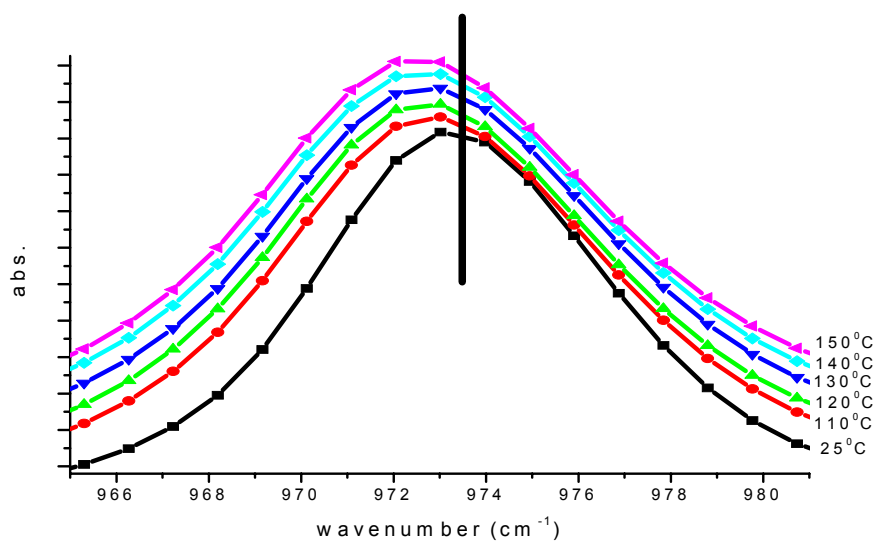
**Table.11:** This table shows the effect of temperature increase on 973cm<sup>-1</sup> band.

Experiment	CPP	BOPP
<b>I)</b> Room temperature	997.67	997.69
<b>I)</b> After heated to 60 <sup>0</sup> C and cooled to room temp.	997.69	997.76
<b>II)</b> Room temperature	997.74	997.68
<b>II)</b> After heated to 100 <sup>0</sup> C and cooled to room temp.	997.71	997.71
<b>III)</b> Room temperature	997.68	997.54
<b>III)</b> After heated to 130 <sup>0</sup> C and cooled to room temp.	997.75	997.74

**Table.12:** This table shows the effect of temperature increase on 998cm<sup>-1</sup> band.

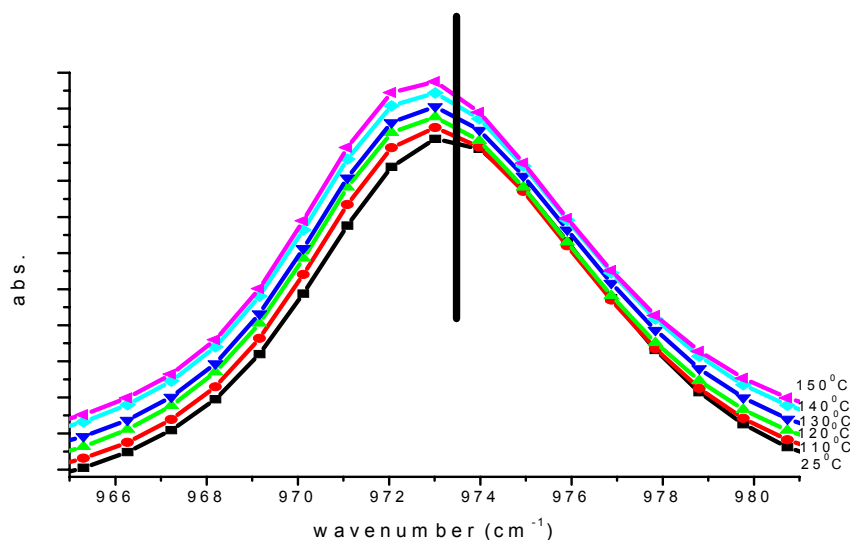
As exhibited in table 11, the difference is approximately 0.4-0.5 cm<sup>-1</sup> between CPP and BOPP for the 973 cm<sup>-1</sup> band. After heating to 60°C and cooling to room temperature, this difference still remains. At 100°C, this difference decreases to 0.3 cm<sup>-1</sup> but disappears at 130°C. Table 12 displays that there is no difference at 998 cm<sup>-1</sup> band between CPP and BOPP. This band is observed at about 997.6 - 997.7 cm<sup>-1</sup> for these two samples.

To investigate shift at 973 cm<sup>-1</sup> band in CPP film in detail, the film was heated to 110, 120, 130, 140 and 150°C, as indicated in fig. 27. The center of this band is observed at 973.50 cm<sup>-1</sup> for room temperature. At 150°C, its center shifts to 972.80 cm<sup>-1</sup>. The shifting of the band is proportional to increasing temperature. At 110 °C, its center is approximately seen at 973.10 cm<sup>-1</sup>.



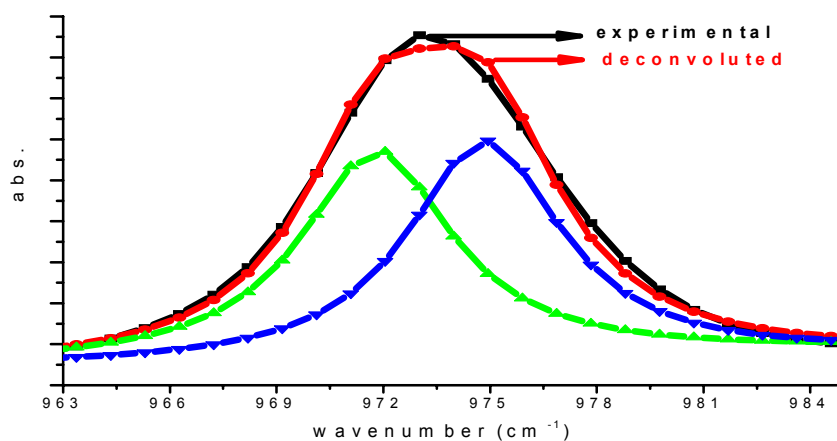
**Figure.27:** The representation of shift at  $973\text{ cm}^{-1}$  band with increasing temperature.

After cooling back to room temperature, this band returns to its initial position. As shown in fig.28 for heating to  $150^{\circ}\text{C}$  and cooling, its center was detected at  $973.1\text{ cm}^{-1}$ , it means that there is still shift. For lower temperatures, the center of this band is closer to  $973.5\text{ cm}^{-1}$ .

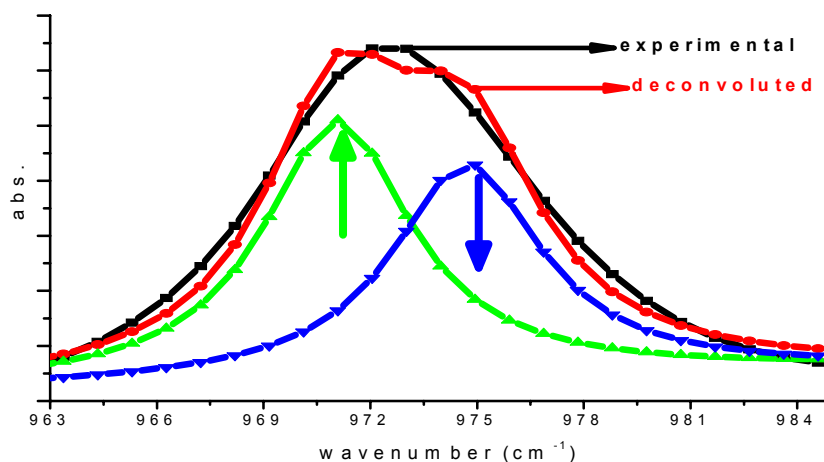


**Figure.28:** The representation of shift at  $973\text{ cm}^{-1}$  band.

These shifts might be related to changes in crystallinity of the film. Remembering that  $973\text{ cm}^{-1}$  band is the superposition of two close peaks,  $972\text{ cm}^{-1}$  (crystalline) and  $974\text{ cm}^{-1}$  (amorphous) [40], we deconvoluted  $973\text{ cm}^{-1}$  band into  $972$  and  $974\text{ cm}^{-1}$  bands. As illustrated in fig.29 , at room temperature, intensity of these bands are nearly same. At  $150^{\circ}\text{C}$ , in fig.30 , whereas the intensity of  $972\text{ cm}^{-1}$  increases, that of  $974\text{ cm}^{-1}$  decreases. It is consistent with the shifting of the center of this band from  $973.5\text{ cm}^{-1}$  to  $972.8\text{ cm}^{-1}$ .

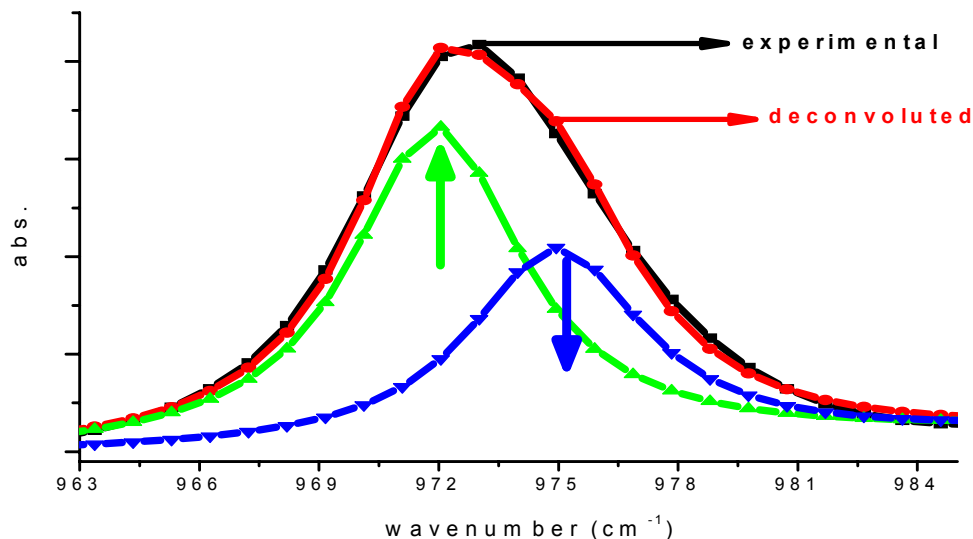


**Figure.29:** Deconvolution of  $973\text{cm}^{-1}$  into  $972$  and  $974\text{cm}^{-1}$  for room temperature.



**Figure.30:** Deconvolution of  $973\text{cm}^{-1}$  into  $972$  and  $974\text{cm}^{-1}$  for  $150^{\circ}\text{C}$ .

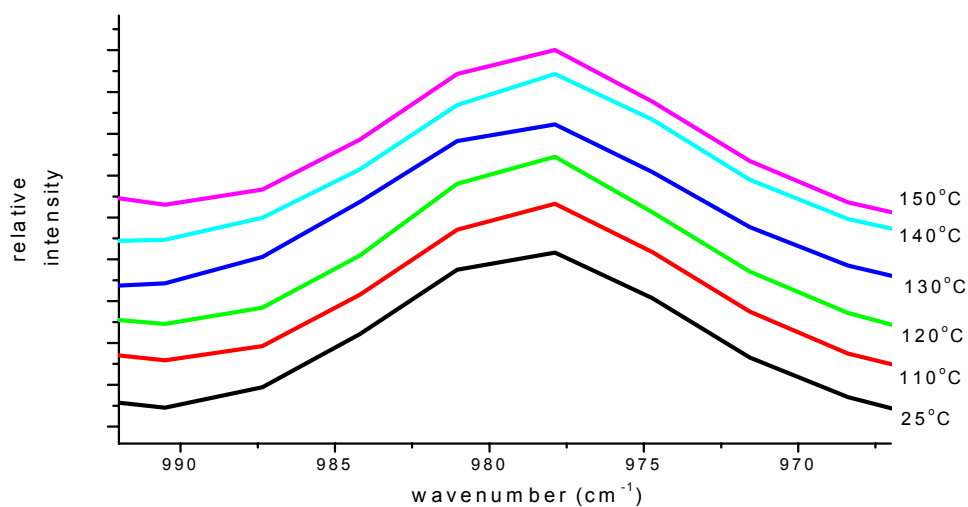
After heating-cooling process is completed, the difference in the intensities of these bands slightly increases as depicted in fig.31. As a result, it can be stated that heating leads to decreasing of  $974\text{ cm}^{-1}$  and increasing of  $972\text{ cm}^{-1}$  bands.



**Figure.31:** Deconvolution of  $973\text{cm}^{-1}$  into  $972\text{cm}^{-1}$  and  $974\text{cm}^{-1}$  for after returning to room temp.

Remembering that the amorphous/crystallinity ratio decreases from 1.25 to 1.00 for CPP film after heating-cooling process is completed, we would like to state that there may be a relation between this ratio and the shift of this amorphous band on the side of  $972\text{ cm}^{-1}$  band (crystalline). The increase in the crystallinity character is illustrated two ways.

We tried to observe this shift by using Raman spectroscopy as shown in fig.32. At room temperature, the center of this band is observed at  $978.45\text{cm}^{-1}$  as listed in table.13. After CPP film was heated to 110, 120, 130, 140 and  $150^{\circ}\text{C}$ , the center of this band is close to this value. Although some fluctuations about this value are recorded, we could not determine a consistent change in this band by using Raman.



**Figure.32:** Raman Spectra of CPP film after heated to shown temperature and cooled.

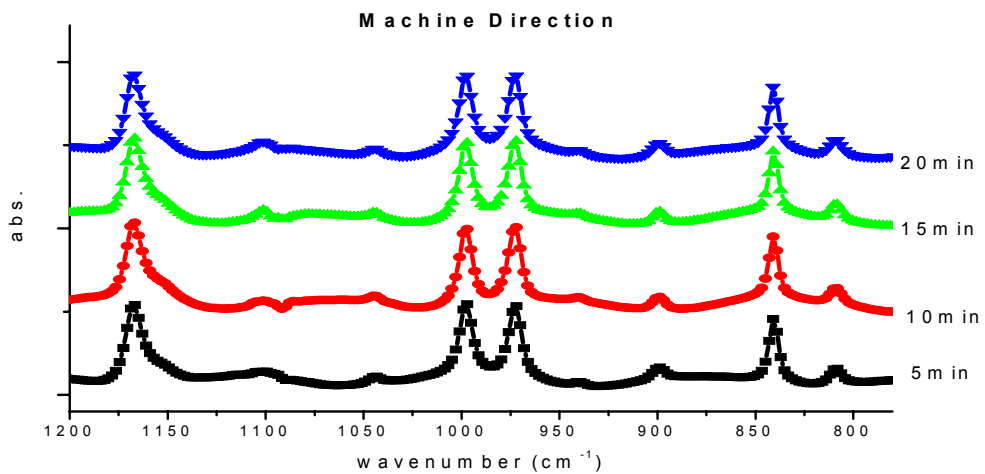
	Center
Before heating-cooling.	978.45
After heated to 110°C and cooled.	978.32
After heated to 120°C and cooled.	978.33
After heated to 130°C and cooled.	978.60
After heated to 140°C and cooled.	978.20
After heated to 150°C and cooled.	978.44

**Table.13:** The center of investigated band with respect to heating to different temperature.

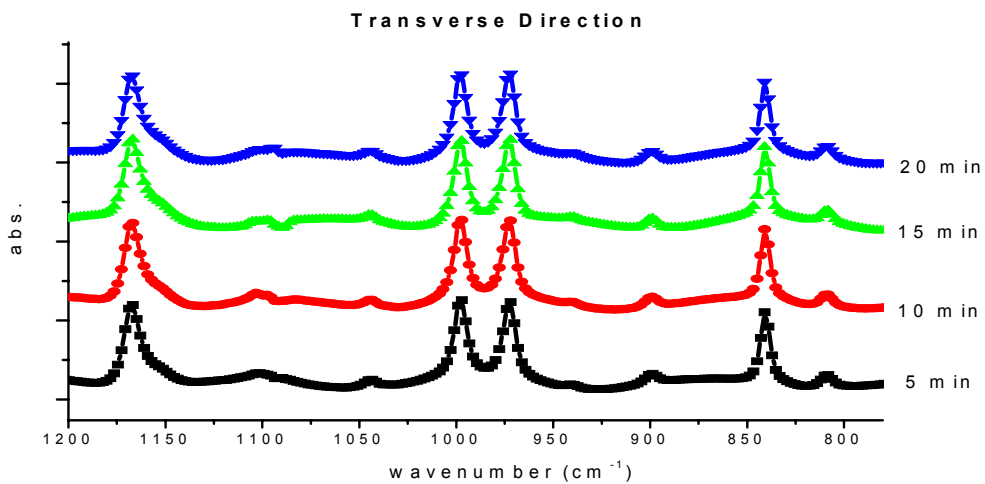
### 3.5. Direction of Stretching Analysis by FT-IR

We investigated the stretching directions of BOPP film which is heated at 120°C in oven during 5, 10, 15, 20 minutes. This process is performed for measuring the amount of shrinkage of the film along machine and transverse direction. Industrially,

shrinkage of the film exceeding over %2 is not desired. By using FT-IR, it was studied whether two different stretching directions are affected differently from this process or not. Infrared spectra of these directions are almost same as illustrated in fig.33 and 34. Moreover, there is no difference for 5, 10, 15, and 20 minutes waiting at 120°C in both machine and transverse directions.

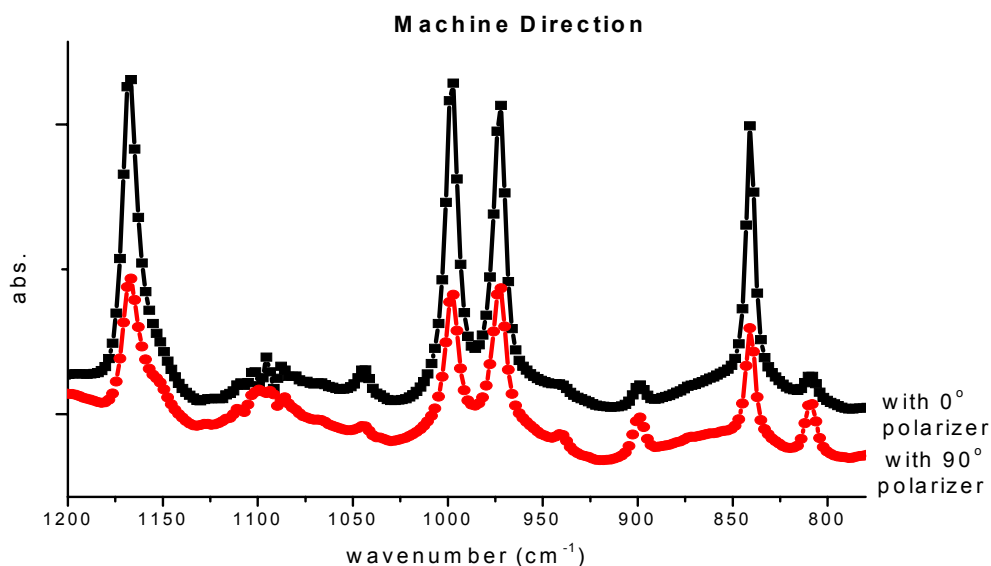


**Figure.33:** FT-IR spectra of BOPP film along machine direction after heated at 120°C in different waiting times.



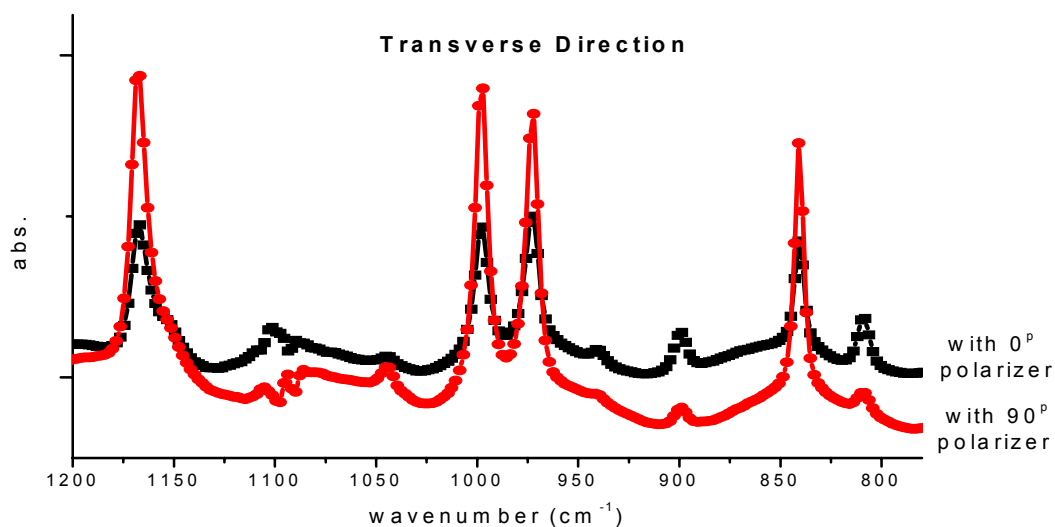
**Figure.34:** FT-IR spectra of BOPP film along transverse direction after heated at 120°C in different waiting times.

By using polarized FT-IR, machine and transverse directions can be identified. In machine direction, polymer absorbs generally light from  $0^\circ$  polarizer more than  $90^\circ$  polarizer as given in figure.34.  $841$ ,  $973$ ,  $998$ ,  $1045$ , and  $1167\text{cm}^{-1}$  has higher intensity with  $0^\circ$  compared to  $90^\circ$  polarizer.  $809$ ,  $900$ , and  $941\text{cm}^{-1}$  has higher intensity with  $90^\circ$  polarizer. However, in transverse direction, polymer absorbs widely light from  $90^\circ$  polarizer more than  $0^\circ$  polarizer as illustrated in figure.36. Whereas  $841$ ,  $973$ ,  $998$ ,  $1045$ , and  $1167\text{cm}^{-1}$  absorbs more with  $90^\circ$  polarizer,  $809$ ,  $900$ , and  $941\text{cm}^{-1}$  absorbs more with  $0^\circ$  polarizer.



**Figure.35:** Polarized-FT-IR spectra of BOPP film along machine direction after heated at  $120^\circ\text{C}$  in 20 minutes.

We investigated the dichroic ratio of  $973$  and  $998\text{ cm}^{-1}$  bands for machine and transverse direction of BOPP film which was heated at  $120^\circ\text{C}$  in the duration of 5, 10, 15, and 20 minutes. However, although there is a slight decreasing in machine direction for dichroic ratio of  $973\text{ cm}^{-1}$ , we did not see significant effect of time on dichroic ratio as given in table.14 and table.15. In transverse direction, dichroic ratio is lower than 1, since it absorbs light more with  $90^\circ$ .



**Figure.36:** Polarized-FT-IR spectra of BOPP film along transverse direction after heated at 120°C in 20 minutes.

Machine Direction	973cm <sup>-1</sup>	998cm <sup>-1</sup>
5min.	1.86	2.08
10min.	1.83	2.30
15min.	1.75	2.18
20min.	1.56	1.91

**Table.14:** Dichroic ratio values of 973 and 998 cm<sup>-1</sup> bands along machine direction.

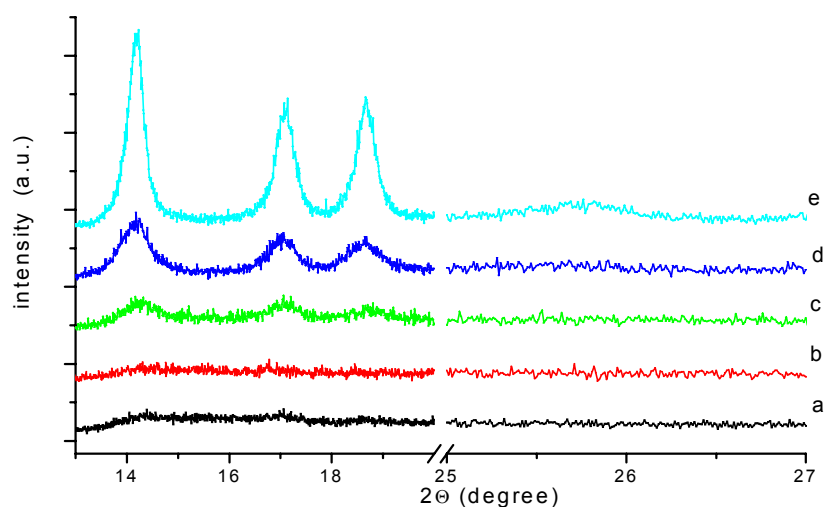
Transverse Direction	973cm <sup>-1</sup>	998cm <sup>-1</sup>
5min.	0.53	0.39
10min.	0.58	0.50
15min.	0.58	0.46
20min.	0.57	0.47

**Table.15:** Dichroic ratio values of 973 and 998 cm<sup>-1</sup> bands along transverse direction.

## 3.6. XRD Studies

### 3.6.1. Temperature effect

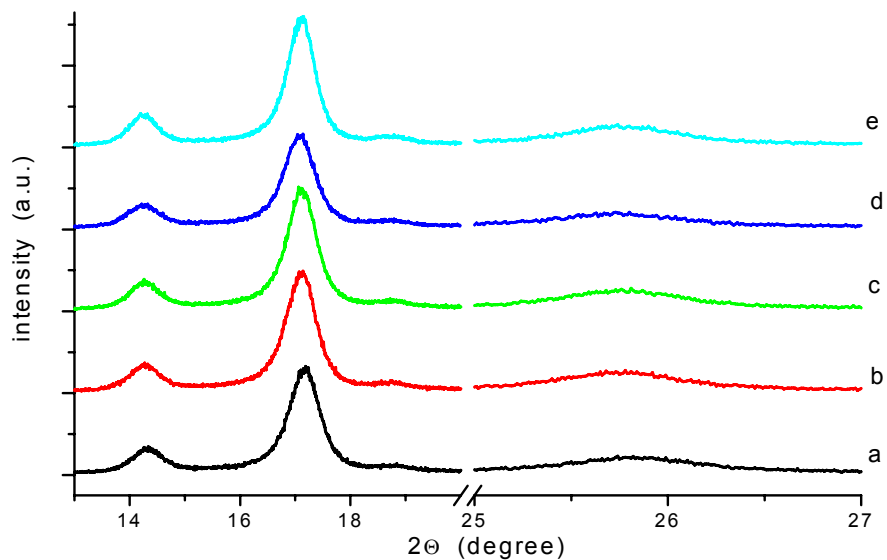
Temperature effect on polypropylene can be mostly easily followed by XRD. Zhu *et al.* [39] determined that while temperature is higher than 100°C, the crystallinity of uni-axially stretched isotactic polypropylene increases by using wide-angle X-ray diffraction. We also detected a significant increase in crystallinity in CPP film with heating. As in fig.37, new strong lines are observed at 14, 17, and 18.5° at about 130-140°C.



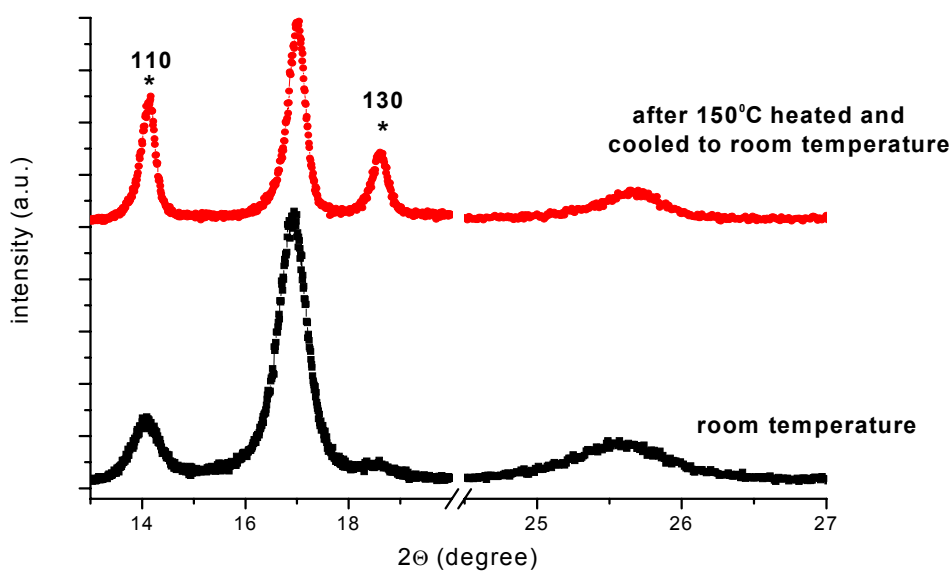
**Figure.37:** XRD pattern of CPP films. *a* at room temperature, *b*, *c*, *d*, *e* were heated to 60, 100, 130, 140°C respectively and then cooled to room temperature.

X-ray diffraction patterns of CPP and BOPP film are affected differently with respect to heating. Heating effect on BOPP is low compared to CPP film. As indicated in fig.38, heating of BOPP film to 60, 100, 130, 140°C does not induce appreciable changes in the XRD patterns. However, peak (130) has considerable higher

intensity at 150°C compared to room temperature as given fig.39. This peak is located at 18.5° belonging to  $\alpha$ -phase. The intensity of peak (110) at 14.0° increases slightly with heating.



**Figure.38:** XRD pattern of BOPP films. *a* at room temperature, *b, c, d, e* were heated to 60, 100, 130,140°C respectively and then cooled to room temperature.

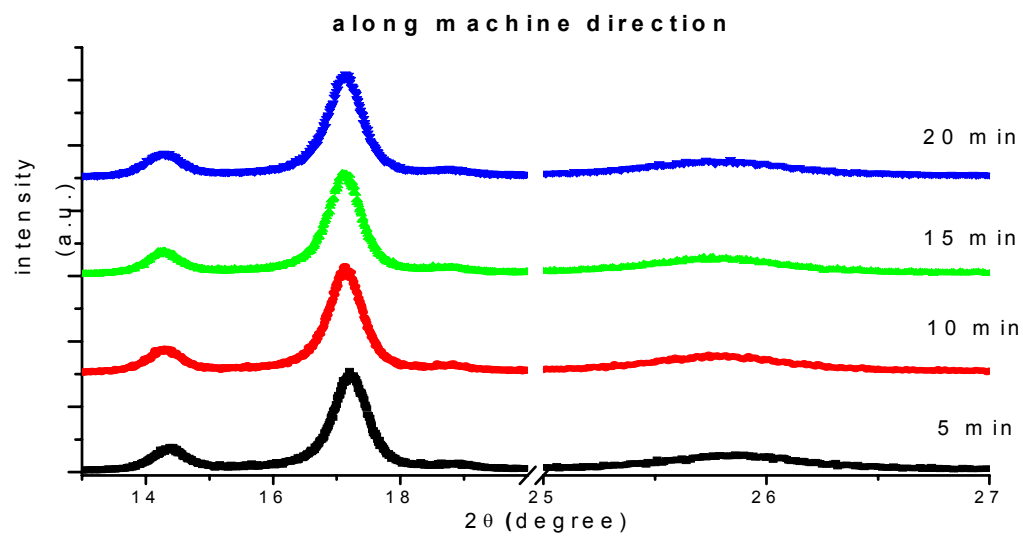


**Figure.39:** The representation of heating to 150°C on BOPP film.

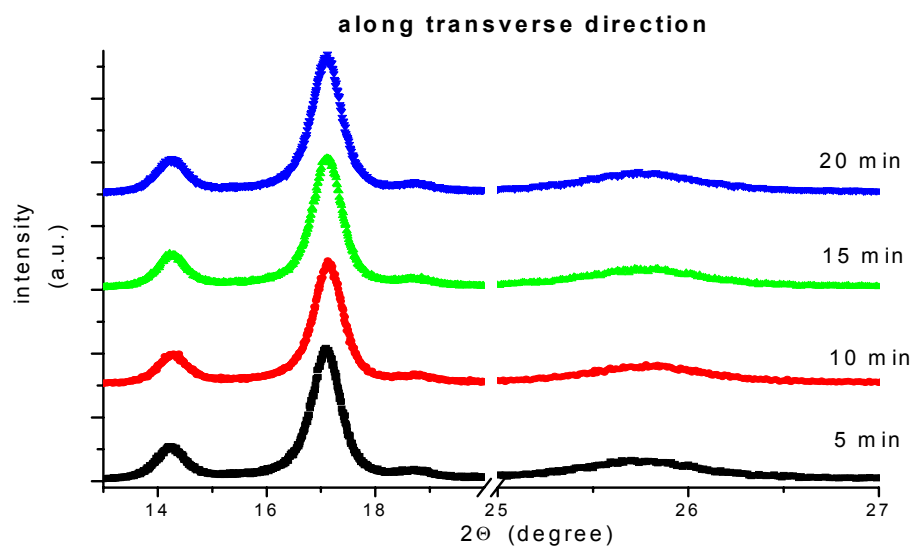
When temperature increases, the sharpness and intensity of these peaks increases. The peaks of CPP film at 140°C are located at same angle like the location of peaks of BOPP film. In BOPP film the peak at 17.0° has higher intensity and in CPP film the peaks at 14.0° has higher intensity relative to other peaks. At room temperature, there are great differences between X-ray diffraction patterns of CPP and BOPP films mostly due to the fact that BOPP films have higher crystallinity content than CPP films. Moreover, stretching may have contribute to diffraction pattern of BOPP film having more and stronger peaks.

### **3.6.2. Direction of Stretching**

We also carried out studies on whether there is a difference between stretching directions or not by using XRD. In this study, films prepared for measuring the amount of shrinkage were also used. Fig.40 and 41 demonstrate XRD patterns of assigned machine and transverse directions of BOPP film at room temperature. There is no difference in the XRD patterns between stretching directions and unassigned BOPP film. In addition, heating time has no any contribution on X-ray diffraction pattern. No difference between machine and transverse directions could be detected.

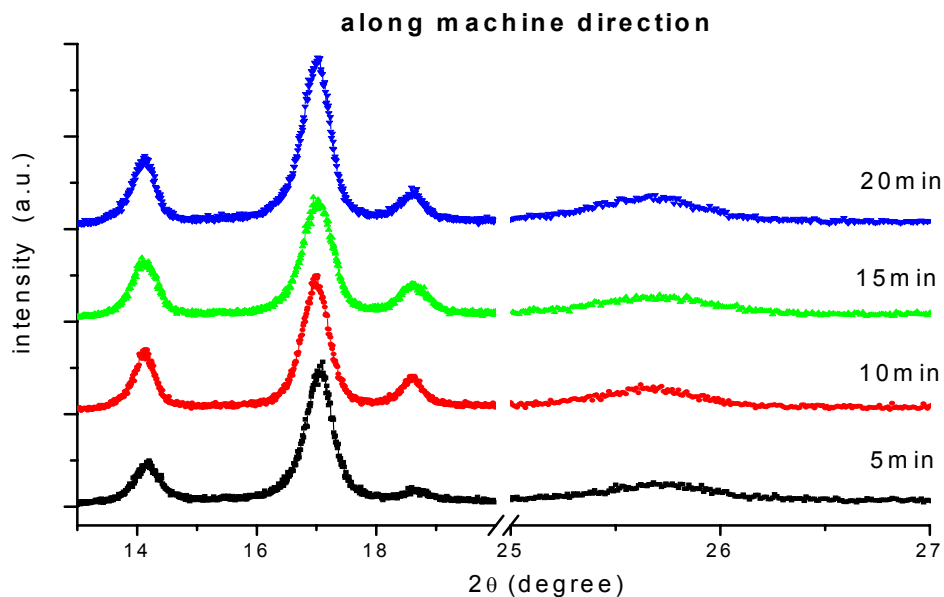


**Figure.40:** XRD pattern of machine direction of BOPP films heated at 120°C

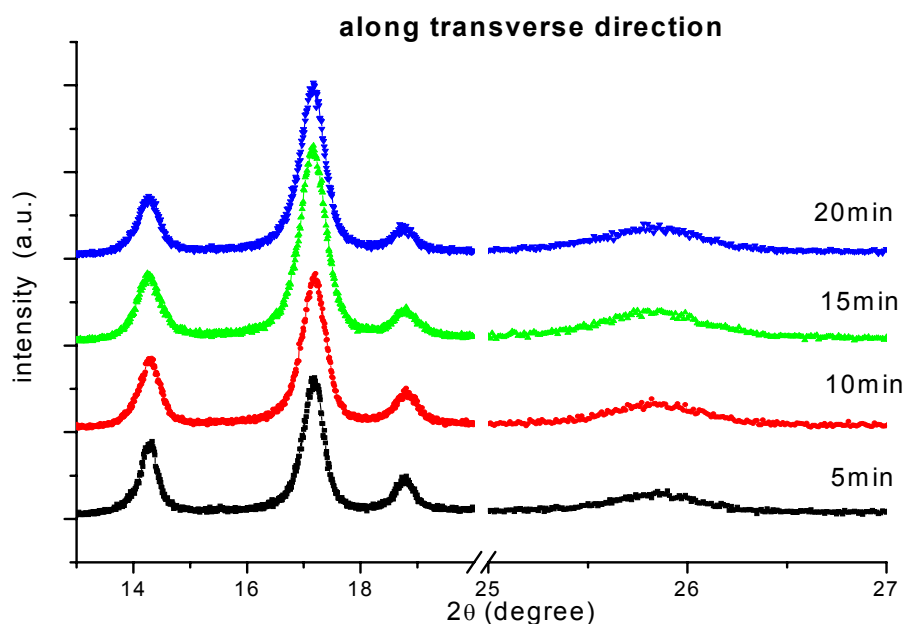


**Figure.41:** XRD pattern of transverse direction of BOPP films heated at 120°C.

We heated the BOPP films, stretching directions of which are assigned, to 150°C to see whether any difference between them arises. Heating to 150°C effects samely the stretching directions of these BOPP films. As denoted in fig.42 and 43, we observed peak (130) at 18.5°. We also detected the arising of the same peak with heating to 150°C for BOPP film in which stretching directions are unassigned. Moreover, we could not see a difference among 5, 10, 15, and 20 minutes waited films after heating to 150°C. These films have same peaks which have nearly same intensity.



**Figure.42:** XRD pattern of BOPP films stretched in machine direction after heated to 150°C and cooled.

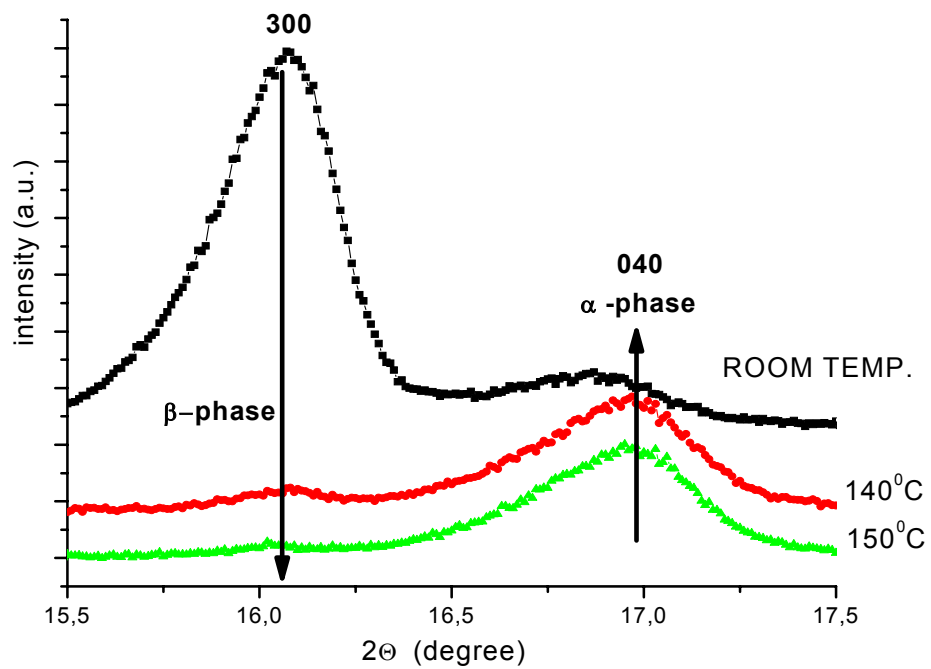


**Figure.43:** XRD pattern of BOPP films stretched in transverse direction after heated to 150°C and cooled.

### 3.6.3. Phase Transition

Since some polypropylene films have varying degrees of different phase ( $\alpha$  and  $\beta$ ), we followed the phase transition with temperature using X-ray diffraction. To investigate the change between these two phases, (300) reflection of  $\beta$ -crystalline phase at 16.0° and (040) reflection of  $\alpha$ -phase at 17.0° are paid attention. As shown in figure.44, after CPP film was heated to 140-150°C and cooled to room temperature, whereas  $\beta$ -phase content decreases sharply,  $\alpha$ -phase content increases. Due to the significant differences of unit cells of  $\alpha$  and  $\beta$  phases, the transition from  $\beta$ -phase to  $\alpha$ -phase is supposed to require a melt/recrystallization step. It was proposed that the temperature should be lowered to below critical temperature, which is in the range of 100-110°C, to occur recrystallization of  $\beta$ -phase to  $\alpha$ -phase. The

proposed mechanism is considered that after cooling below critical temperature, the formation of  $\alpha$ -form nuclei within  $\beta$ -spherulite occurs [1]. For this reason, these proposed views are consistent with our study in that heating at 140-150°C and cooling back to room temperature is adequate to see this transition in our sample having different phases.



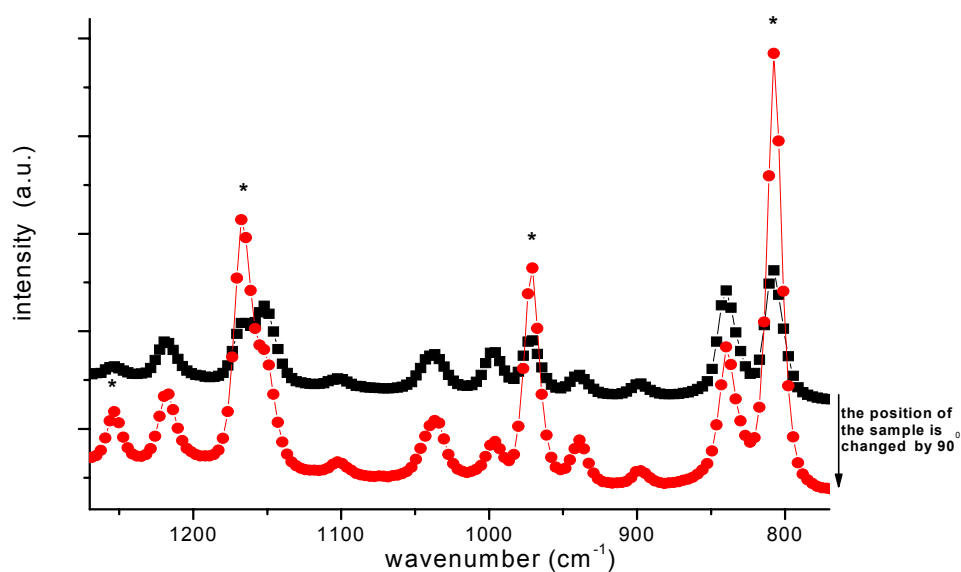
**Figure.44:** The representation of phase transition with increasing temperature.

### 3.7. Raman Studies

#### 3.7.1. General Investigation of CPP and BOPP Films

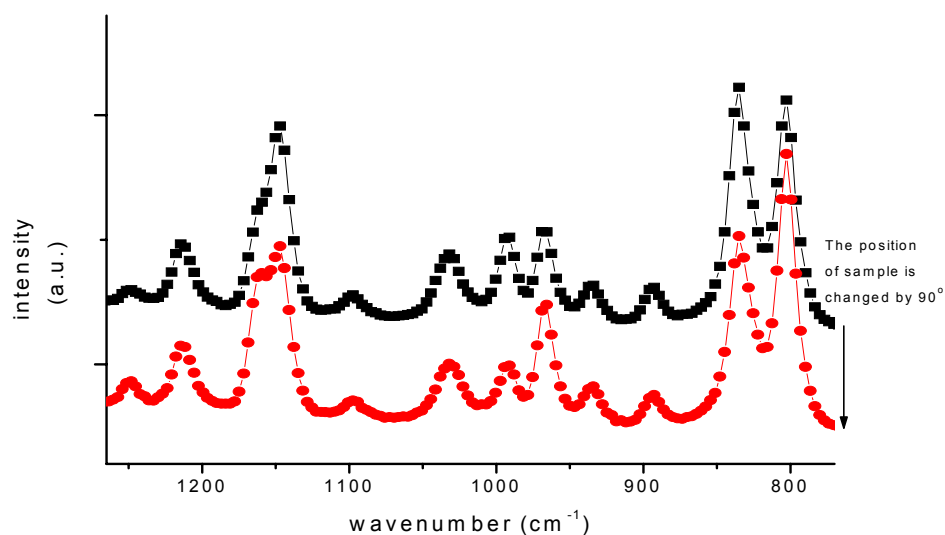
Since strong Raman scattering arises from nonpolar molecular groups, the vibrations of the carbon chains, such as C-C stretching modes, are very active.

Since Raman source is highly polarized, it can be utilized for orientation studies, we investigated the orientation of films by changing direction of the sample holder. We investigated the Raman spectra of CPP and BOPP films. Due to the fact that BOPP film is highly oriented, the changes in the spectra of this film occurs very drastically by rotating sample holder with  $90^\circ$ . There are larger enhancements in the intensity of  $809$ ,  $973$ ,  $1168$  and  $1256$   $\text{cm}^{-1}$  bands after the position of sample is changed to its perpendicular direction as illustrated in fig.45.



**Figure.45:** The Raman spectra of BOPP film.

A small change exists in the CPP film by rotating relative to the BOPP film, due most probably to their stress induced crystallinity differences. As shown in figure.46, there is a small change in 809, 841 and 973 $\text{cm}^{-1}$  bands.



**Figure.46:** The Raman spectra of CPP film.

The ratio of 809/841 and 973/998 demonstrate that changes in BOPP film is considerably greater than that in CPP film by rotation as listed in table.16.

Film Type	809/841	973/998
CPP	0.90	1.10
CPP rotating by 90°	1.16	2.67
BOPP	1.19	1.36
BOPP rotating by 90°	3.54	7.10

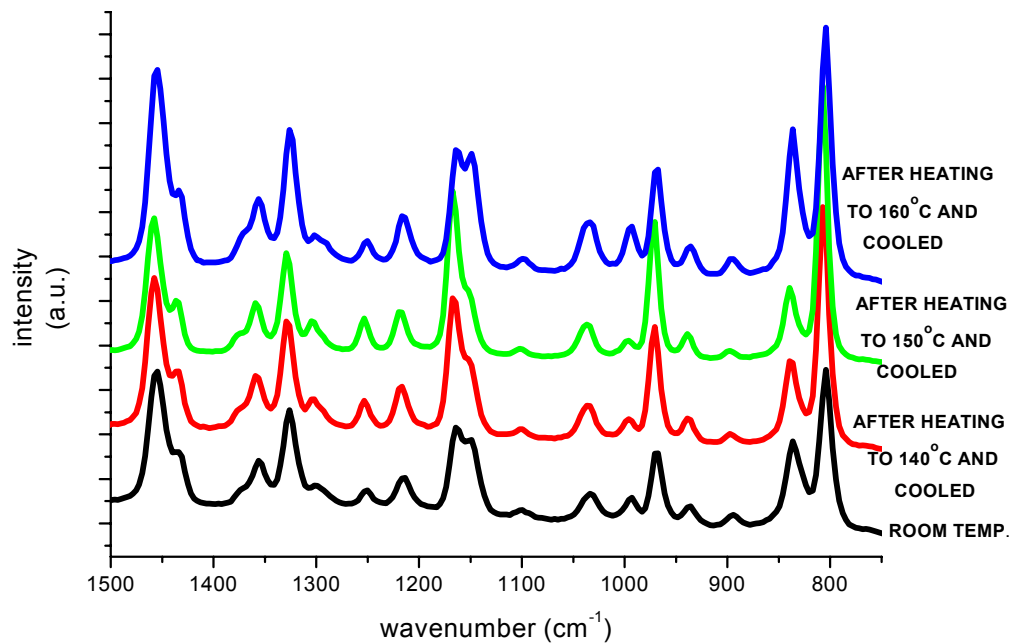
**Table.16:** 809/841 and 973/998 ratio of CPP and BOPP films before and after rotating.

### 3.7.2. Effect of Temperature

Hendra *et al.* [43] detected the peak broadening and disappearing of regularity bands at the interval of 185-210°C. Pyrz *et al.* [44] determined a quantitative relation between Raman scattering intensity and the crystallinity of polypropylene which is in melt and solid state by considering 808, 830 and 840  $\text{cm}^{-1}$ . In our studies, after CPP films were heated to 140, 150, and 160°C and then cooled to room temperature, their Raman spectra was recorded. However, we did not observe significant changes on their Raman spectra due to Raman spectrum could not be recorded as in-situ. As shown in figure.47, at room temperature, intensity of 1167 and 1153  $\text{cm}^{-1}$  bands are nearly equal. There is an increase in the intensity of 1167  $\text{cm}^{-1}$  band compared to 1153  $\text{cm}^{-1}$  after heating to 140 and 150°C and cooling back to room temperature. However, the intensity of 1167  $\text{cm}^{-1}$  is nearly same as the intensity of 1153  $\text{cm}^{-1}$  for the same heat treatment. Similar fluctuations in other bands can be seen.

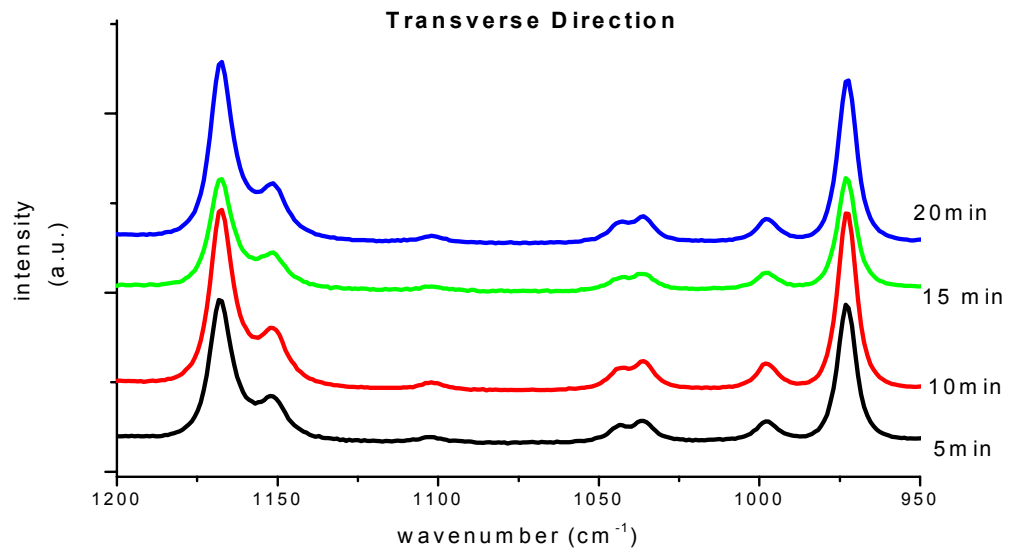
### 3.7.3. Direction of Stretching Analysis

Machine and transverse direction of BOPP films have different Raman spectra. As illustrated in figure.48, in transverse direction, the intensity of 1167  $\text{cm}^{-1}$  has higher than that of 1153  $\text{cm}^{-1}$  and the intensity of 998  $\text{cm}^{-1}$  is significantly lower than that of 973  $\text{cm}^{-1}$ .

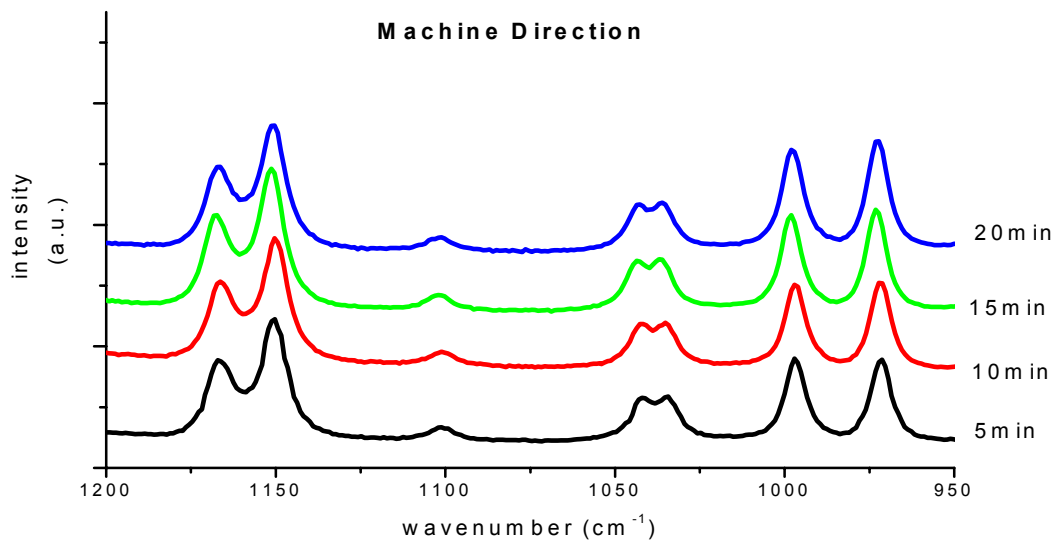


**Figure.47:** The Raman spectra of CPP films at room temperature, after heated to 140, 150, 160°C and cooled to room temperature.

In machine direction, the intensity of has 1153  $\text{cm}^{-1}$  higher than that of 1167  $\text{cm}^{-1}$  and intensities of 973 and 998  $\text{cm}^{-1}$  are nearly equal in fig.49. After assigned the stretching direction of these films, they were heated in 5, 10, 15, and 20 minutes at 120°C. However, we could state that the increasing waiting duration at 120°C has no effect on both Raman spectra of machine and transverse directions.



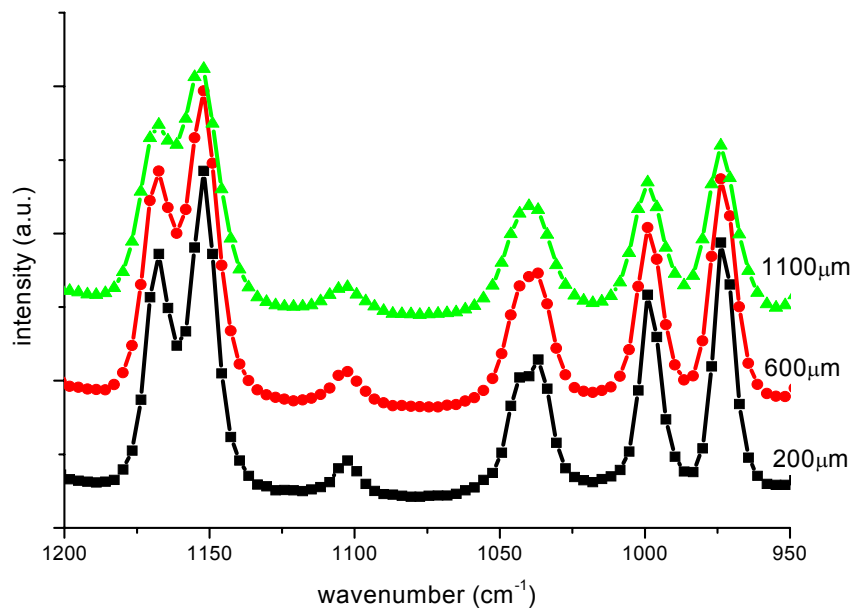
**Figure.48:** The Raman spectra of BOPP film in transverse direction



**Figure.49:** The Raman spectra of BOPP film in machine direction.

### 3.7.4. Depth Analysis

We have tried to obtain a depth profile of polypropylene films by changing the width of hole of the source. Our aim is to determine whether there is a difference between bulk and surface of the films or not. Figure.50 illustrates Raman spectra of BOPP film for the width of the hole 1100, 600, and 200  $\mu\text{m}$ . FWHM is about  $2\mu\text{m}$  for the width of confocal hole at 200  $\mu\text{m}$  and about  $5\mu\text{m}$  for 1100 $\mu\text{m}$  when using 100x objective. Although there is a slight increase in the separation between 1153 and 1167  $\text{cm}^{-1}$  bands when decreasing the width of hole, we were not able to establish that there is a significant difference in the Raman spectrum of BOPP film with respect to varying the width of the hole.



**Figure.50:** The Raman spectra of BOPP film with different width of hole.

## 4. CONCLUSION

We have tried to reevaluate the information obtainable using IR and Raman Spectroscopic and X-Ray Diffraction techniques for the analysis of industrially produced two polypropylene films (BOPP and CPP). The main emphasis was focused on changes of their crystallinity content and orientation as a function of temperature increase and/or heat exposure. This focus was dictated mainly by the fact that the amorphous/crystallinity content and orientation induced properties are crucial for the shelf-life and oxygen permeability of these films which are mainly employed for food packaging and other related areas. Moreover, we had specifically sought to apply the IR technique over the others due to its widespread availability and ease of use in industrial environment.

In order to follow changes as a function of temperature faithfully we developed an in-situ IR technique. Unfortunately, such in-situ technique was not adaptable to our Raman and XRD systems for which we could record data only at room temperature.

From these studies, we can now conclude that temperature effects significantly the crystallinity and orientation of the polypropylene films. With increasing temperature, the content of crystallinity decreases and loss of orientation takes place. After returning back to room temperature, crystallinity increases back to its initial value, but orientational loss stays permanent. The cycle of heating-cooling process does not lead to any additional changes.

XRD studies indicate that CPP film is more sensitive to temperature changes than BOPP. After CPP film is heated to 130-140°C, the sharp crystalline peaks appear. Phase transition can also be detected using X-ray diffraction from  $\beta$  to  $\alpha$  at 140-150°C. However, we could not detect this phase transition using FT-IR. This is

explained by the fact that while XRD measures the long-range or intermolecular order, but IR measures the short range or intramolecular order [12].

Using FT-IR we have determined a shift in the  $973\text{ cm}^{-1}$  band of the CPP films having mostly the  $\alpha$ -crystalline phase. With increasing temperature, a shift occurs from  $973,5\text{ cm}^{-1}$  to  $972,8\text{ cm}^{-1}$  which could be related with changes in crystallinity/amorphous content. Using Raman spectroscopy we could not see this shift with increasing temperature.

Although we could not detect that any difference when the films were subjected to additional stresses at  $120^{\circ}\text{C}$  along the machine and the transverse directions of polypropylene films using X-ray diffraction and FT-IR, difference in these directions can be observed using Raman spectroscopy due to its higher sensitivity on polarization.

As a final conclusion of work, we can state that although XRD is extremely sensitive to detect and study phase transitions, IR and Raman are insensitive. However, the amorphous/crystallinity content of films and changes in the orientation of biaxially orientated PP films can be followed using both IR and Raman techniques. Use of in-situ IR spectroscopy for investigation of the effect of temperature and/or heat exposure is a particularly attractive and easy-to use method.

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