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# The Effect of Chain Tacticity on the Thermal Energy Parameters of Isotactic and Syndiotactic Polypropylene

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**Keywords:**

Polypropylene; Tacticity; Melting point; Heat capacity; Thermal properties.

**Highlights:**

- The iso-tacticity index was examined using NMR.
- Glass transition temperature and melting point have been presented.
- Thermal conductivity and heat capacity have been related.

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**Abstract:** The thermal energy properties in any material affect the substance's capacity to store or transfer heat. This study investigated the effect of the polymeric chains' tacticity on the thermal properties of polypropylene related directly to the thermal power, i.e., the heat capacity and thermal conductivity. The study selected different commercial polypropylene groups with two steric modes: isotactic and syndiotactic. The aim is to determine the parameters: isotacticity index, degree of crystallinity, glass-transition temperature, melting point, heat capacity, and thermal conductivity. The data were collected using gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC). The results showed that methyl groups randomly distributed within the homo-polypropylene changed the overall content of meso diads, i.e., less isotacticity index. The differences between isotactic and syndiotactic polypropylene groups were 20-40% the degree of the crystallinity, 5-10°C the glass-transition temperature, and 10-20°C the melting point. Using suitable mathematical models, these parameters can be related directly to specific heat capacity and thermal conductivity.

# تأثير تكتيك السلسلة على معاملات الطاقة الحرارية للبولى بروبيلين ذو التموضع المتماثل والمتناوب

بيداء جابر نيهان، توفيق وسمي محمد، حارث حسون المعموري، لبنى غالب عبد الخالق

قسم هندسة المواد / الجامعة المستنصرية / بغداد – العراق.

## الخلاصة

ان الخصائص المتعلقة بالطاقة الحرارية في أي مادة هي تلك التي تؤثر على قدرة المادة على تخزين أو نقل الحرارة عبرها. تناولت هذه الدراسة تأثير تكتيك السلاسل البوليمرية على الخواص الحرارية لمادة البولي بروبيلين المرتبطة مباشرة بالقدرة الحرارية، وهي السعة الحرارية والتوصيل الحراري. اختارت الدراسة ست مجاميع من البولي بروبيلين مع طريقتين من التموضع، وهما المتماثل والمتناوب. الهدف هو تحديد المعلمات التالية: مؤشر التماثل، ودرجة التبلور، ودرجة حرارة التحول الزجاجي، ونقطة الانصهار، والسعة الحرارية، والتوصيل الحراري. تم جمع البيانات باستخدام نظام التصوير للهلام (GPC)، والرنين المغناطيسي النووي (NMR)، والمسعرات التفاضلية (DSC). أظهرت النتائج أن توزيع مجموعات الميثيل بشكل عشوائي داخل البوليمر المتجانس يغير المحتوى الكلي للديادات المتوسطة، مما يعني انخفاض مؤشر التماثل. بشكل عام، ينتج عن الاختلاف بين مجموعتي البولي بروبيلين متماثل التموضع والمتناوب اختلاف بنسبة ٢٠-٤٠٪ في درجة التبلور، وفرق ١٠-٥ درجة مئوية في درجة حرارة التزجج وفرق ١٠-٢٠ درجة مئوية في نقطة الانصهار. يمكن أن ترتبط هذه المعلمات مباشرة بالسعة الحرارية النوعية والموصلية الحرارية باستخدام نماذج رياضية مناسبة.

**الكلمات الدالة:** البولي بروبيلين، التكتيك، درجة الانصهار، السعة الحرارية، الخصائص الحرارية.

## 1. INTRODUCTION

Polymer's characteristics and corresponding thermo-physical and mechanical properties are mainly affected by their chains' structure and types of components and bonded groups [1-3]. Tacticity is the relative regularity of adjacent chiral centers inside the macromolecule. This regularity influences the polymer's structure to become rigidly crystalline with long-range order chains or amorphous with disorder chains [4, 5]. Polymers are classified according to their tacticity into isotactic, syndiotactic, and atactic. Regular substituents on the same side of the macromolecular backbone comprise isotactic polymers. The substituents in syndiotactic have various places throughout the chain, yet they are nonetheless properly sequenced. The substituents in atactic macromolecules are randomly distributed throughout the chain. However, the polymer may have the three modes of tacticity together [6, 7]. The isotactic mass fraction is commonly used to measure the polymer's tacticity degree and is denoted by the "isotacticity index" [8, 9]. The tacticity of a polymer is influenced mainly by the catalyst system used, the solvent, Lewis acids, polymerization temperature, and pressure [10-13]. Many methods have been tested to adjust certain tacticity modes, such as Ziegler-Natta catalysts [14], stereoselective catalytic polymerization [15], and microwave activation [16]. To investigate the influence of tacticity on the polymer's morphology and relate that to the thermo-physical properties, researchers studied simple structure polymers, such as polypropylene and polystyrene. Polypropylene (PP) is a common polymer usually proposed for house-holding manufacturing. It is introduced as grains with different sizes, standards, and tacticity modes depending on how it polymerizes. The tacticity essentially affects many of the polymer's characteristics related to the thermo-physical and mechanical properties [17-22]. The

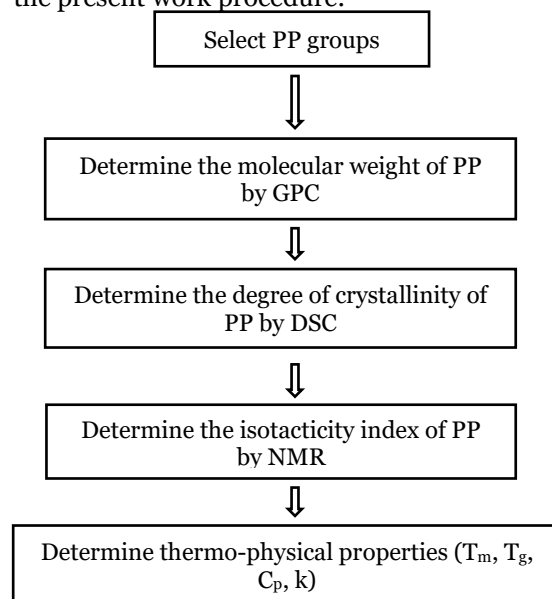
tacticity impact on polypropylene features was of interest in many works, as reported in many previous studies [23-34]. The researchers studied many polypropylene types, such as homopolymer or copolymer, with three categories based on tacticity: isotactic polypropylene "iPP," atactic polypropylene "aPP," and syndiotactic polypropylene "sPP." The methyl group (-CH<sub>3</sub>) is equally positioned throughout the chain of isotactic polypropylene. It is oppositely oriented for syndiotactic polypropylene and randomly oriented for atactic polypropylene. The investigations in this topic have mostly emphasized the relationships between stereo-regularity, chain microstructure, and polymerization characteristics. The studies state that the properties of PP are considerably impacted by the compound effect of steric chains and crystalline structure, and the modification in polypropylene features can be adjusted during the polymerization step by controlling the molar mass and chain regularity. Furthermore, the catalyst system during the polymerization affects the final product. The studies also revealed that raising the polymerization temperature enhanced the isotactic mode in the polymer. It has been stated that variations in molecular weight are related to variations in tacticity, affecting the polypropylene characteristics. The tacticity of PP is crucial for crystallization, melting behavior, and thermo-physical characteristics, such as expansion and degradation [35, 36]. In most cases, crystallization occurs in isotactic or syndiotactic structures, where most atactic polymers do not crystallize and stay amorphous due to the chain irregularity [37]. Regular chains might pack snugly and effectively to generate highly ordered crystalline structures. Hence, a high degree of chain tacticity might aid the crystallization process of manufacturing highly refined PP fibers, primarily determined

by the connection between tacticity and fiber diameter [38]. On the other hand, the distribution of component groups along the chains impacts the polymer's crystallinity to be crystalline, semi-crystalline or amorphous. The higher the isotacticity, the greater the crystallinity, which may affect corresponding thermal properties, such as glass-transition temperature ( $T_g$ ) and melting point ( $T_m$ ) [39-43]. This work introduces a study to link the tacticity index of PP (as well as the degree of crystallinity) with thermal calorimetric properties (melting point and glass-transition temperature) and heat transfer parameters (thermal conductivity and heat capacity). The tacticity analysis for different polypropylene groups was performed using nuclear magnetic resonance (NMR). Differential scanning calorimetry (DSC) obtains the resultant degree of crystallinity and corresponding thermal calorimetric properties. The molecular weight was estimated using gel permeation chromatography (GPC). These properties can be related to the isotacticity index using suitable mathematical models.

## 2. MATERIALS AND METHODS

The present study collected several PP granular materials from the local market. Only six groups have been selected with various molecular weights (MW). Polypropylene used was rigid, white, neat, and virgin homopolymeric material. The polypropylene under study was either isotactic or syndiotactic. However, commercial PP usually has 0.8-0.95 isotacticity with a degree of crystallinity ranging between 0.2-0.7 [24, 44, 45]. The MW was analyzed by gel permeation chromatography (GPC) of the ISOGEN PROXIMA 16 PHI brand. To determine the isotacticity index and analyze the steric orders, a spectroscopic technique by nuclear magnetic resonance (NMR) of the brand AGILENT 500 MHz was used. The  $^{13}C$ -NMR was used to determine the polymer composition in each mode of tacticity, i.e., stereo-regularity of polymeric chains [46]. Differential scanning calorimetry (DSC) of the brand SHIMADZU DSC-60 was used to obtain the degree of crystallinity and corresponding thermal properties. The most popular method of determining the polymers' crystallinity degree is by measuring the specific enthalpy of fusion (heat of melting) and comparing this value to the standard value of a fully crystalline polymer. For fully crystalline isotactic polypropylene, an average value of standard heat of fusion has been stated as 207 J/g [47-49]. The experimental measurements were done in several locations, where the GPC and the NMR were conducted at the Chemical Analysis Center-Mustansiriyah University. In contrast, the DSC tests were conducted at the Laboratory of Packing Materials-Ministry of

Industry and Minerals (MOIM). Fig. 1 shows the present work procedure.



**Fig. 1** Flow Chart Showing the Methodology of the Present Work.

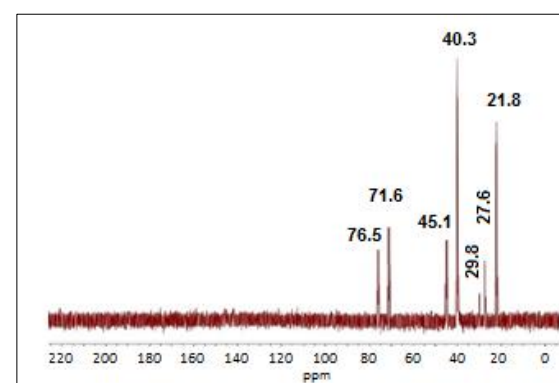
## 3. RESULTS AND DISCUSSION

It is essential to mention that the present results are limited to six groups of homopolypropylene samples. The selected samples were virgin and neat products with high crystallinity. The groups covered a range of molecular weights (extracted from the GPC test) between 71,000-183,000 g/mol, as shown in Table 1, representing low to medium molecular weight scales.

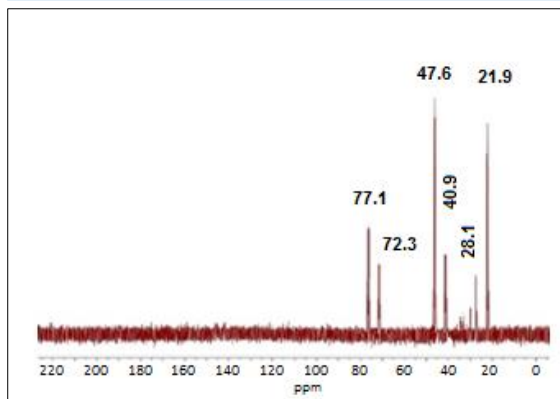
**Table 1** Molecular Weights of Polypropylene Groups Measured by GPC.

Group	Type	MW(g/mol)
1	Isotactic propylene (iPP)	183,000
2	Isotactic propylene (iPP)	165,000
3	Isotactic propylene (iPP)	92,000
4	Syndiotactic propylene (sPP)	122,000
5	Syndiotactic propylene (sPP)	98,000
6	Syndiotactic propylene (sPP)	71,000

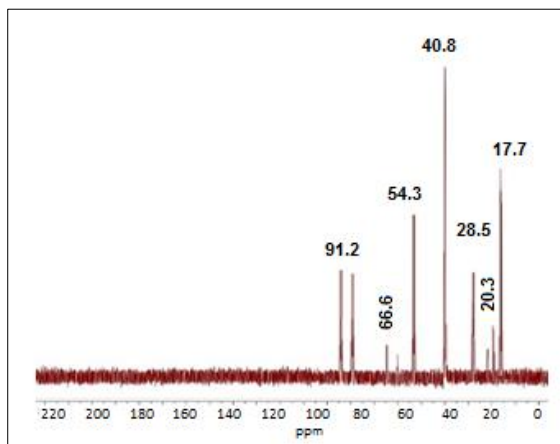
The groups of PP were exposed to  $^{13}C$ -NMR spectroscopic scanning to determine the peaks and configure the chains' stereo-regularity, as shown in Figs. 2-7.



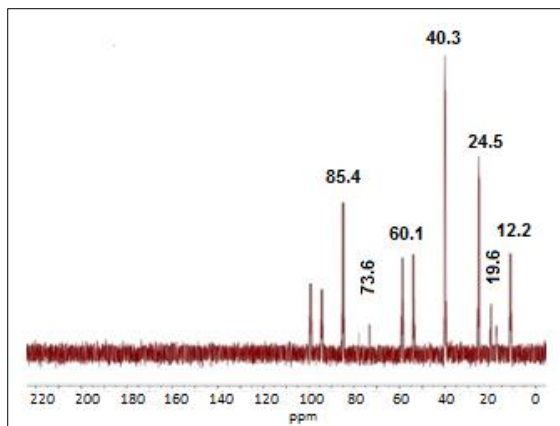
**Fig. 2** NMR Spectroscopic for Group No. 1.



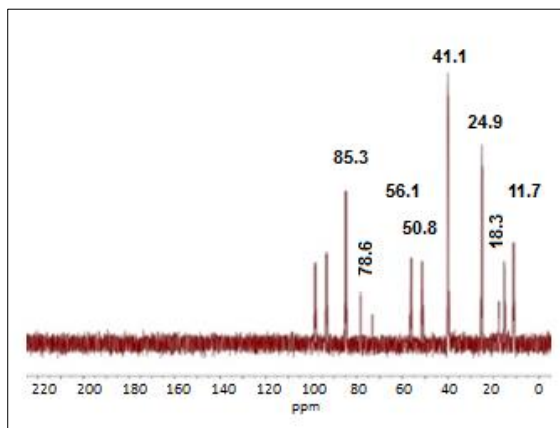
**Fig. 3** NMR Spectroscopic for Group No. 2.



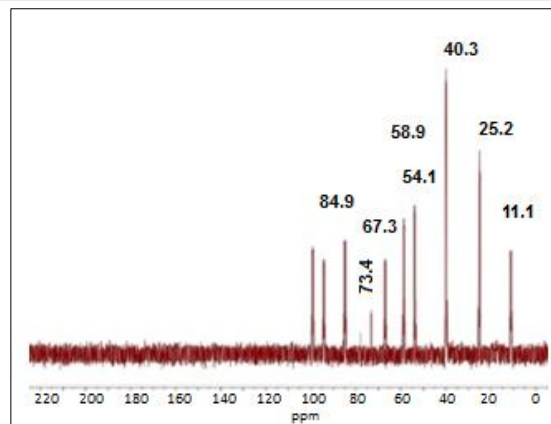
**Fig. 4** NMR Spectroscopic for Group No. 3.



**Fig. 5** NMR Spectroscopic for Group No. 4.



**Fig. 6** NMR spectroscopic for group No. 5.



**Fig. 7** NMR Spectroscopic for Group No. 6.

The number of peaks and corresponding repeats can be calculated to find the type of chain arrangement, where the present study assumed pentad distributions to analyze the tacticity of PP groups more accurately than tetrads or triads. The spectrum study revealed sensitivity to monomer insertion along macromolecular chains, and resonance of this intruder resulted in various chemical changes within the microstructure. Some variations in pentad analysis might be attributed to inaccurate peak assignment and overlapping. Extracting pentad distribution depends on the extent of peaks and shifts that appear in the NMR image, where each shift has specific values within a certain range. For example, the arrangement *rmrr* is within the range of 20 to 21 ppm, and so on. This procedure can be applied to the entire peaks to calculate each arrangement's frequency. According to the analysis based on random methyl groups in the polymeric chains, various arrangement shifts can be noticed. Thus, different steric orders for selected groups were obtained, as shown in Table 2. More details about calculating pentad assignments based on NMR spectroscopic are explained in [12, 30, 50]. The corresponding shifts and the change in the peaks mean increasing the bonding with different molecular groups, which resulted in more disorder in the polymeric chain's isotacticity. For statistical reasons, the macromolecule's stereochemistry is regarded as a Bernoullian process, which is simpler than the Markov sequence hypothesis. Therefore, the composition sequence may be deduced from the likelihood of discovering meso diads. The following relations can be utilized to compute corresponding meso indices for pentad sequences [12]:

$$mm = mmmm + mmmr + rmmr \quad (1)$$

$$mr = mrrm + mmrr + rrrm + rrrr \quad (2)$$

$$rr = mrrm + mrrr + rrrr \quad (3)$$



**Table 2** Ratios of Steric Orders for Selected Polypropylene Groups (mol%).

G.	mmmm	mmmr	rmmr	mmrr	mmrm	rrmr	rmmr	rrrr	mrrr	mrrm
1	55.6	24.1	13.4	1.2	2.1	1.1	0.9	0.3	0.6	0.7
2	54.5	24.2	13.5	1.1	2.2	0.9	1.1	0.4	1.1	1
3	53.1	23.9	13.6	1.6	1.5	1.6	1.4	0.8	1.1	1.4
4	51.2	22.8	14.4	1.5	1.9	1.9	1.5	1.5	1.8	1.5
5	49.9	22.5	14.8	1.1	1.4	1.6	2.7	1.9	1.6	2.5
6	47.7	21.7	14.4	1.8	1.6	1.9	3.3	2.6	2.1	2.9

**Table 3** Isotacticity Index for Each Polypropylene Group.

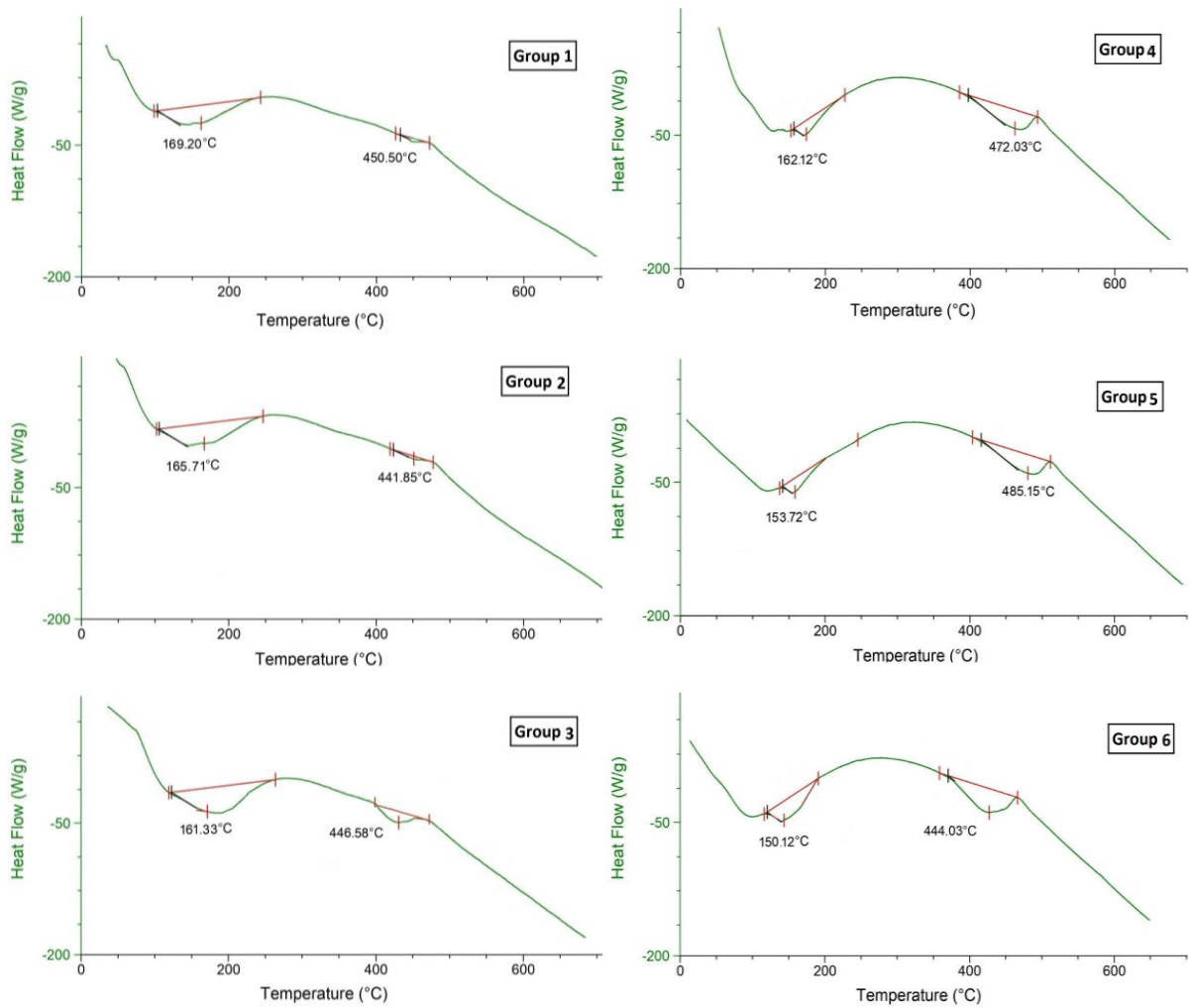
Group	mm (%)
1	93.1
2	92.2
3	90.6
4	88.4
5	87.2
6	83.8

**Table 4** Thermal Calorimetric Properties of Polypropylene Groups.

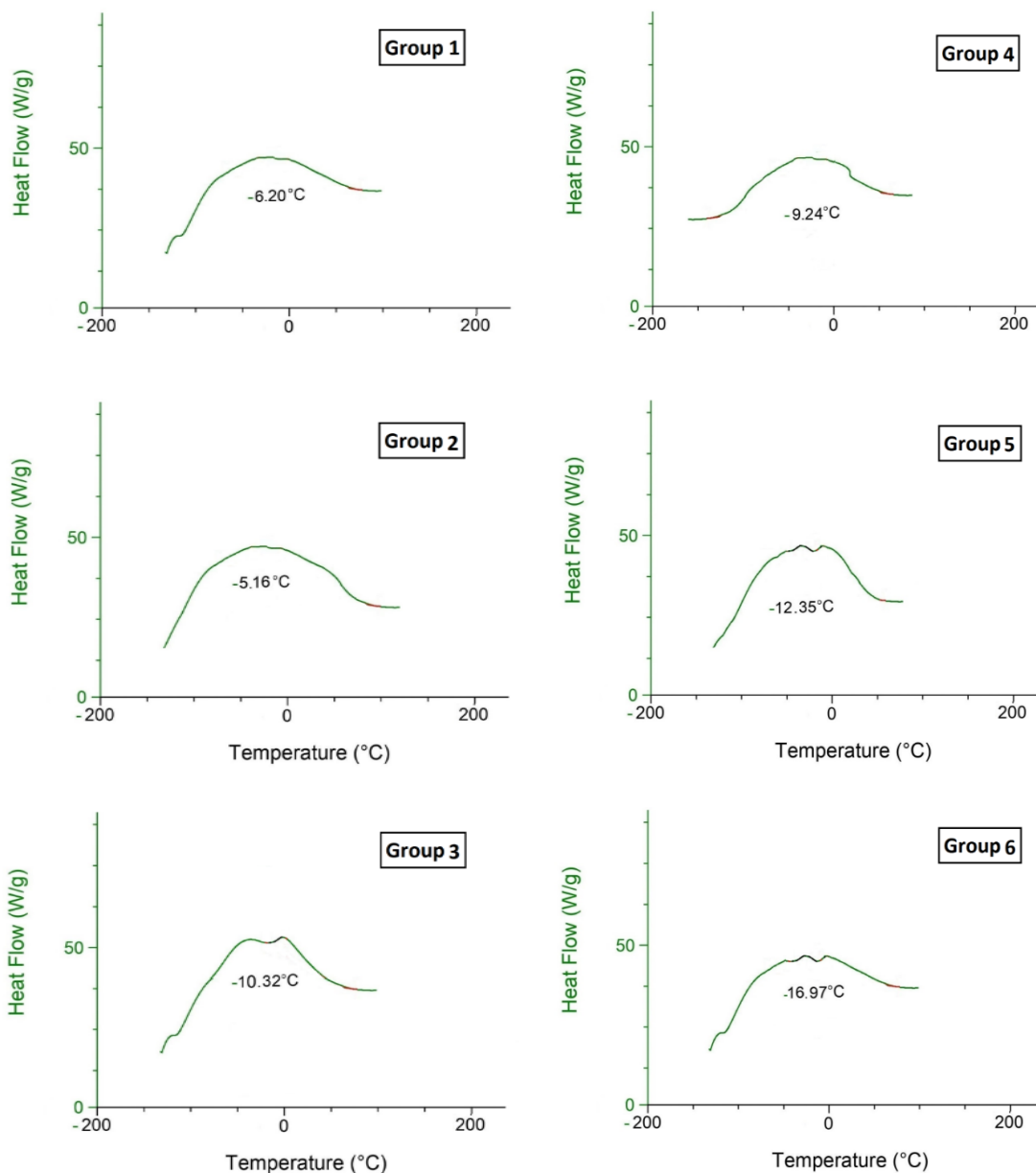
Group	X <sub>c</sub> (%)	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
1	62	-6	169
2	57	-5	166
3	41	-10	161
4	46	-9	162
5	38	-12	154
6	29	-17	150

The isotacticity index (mm) has been calculated for the whole group (by statistical processes) and presented in Table 3. According to stereoregularity, groups 1 to 3 had a high isotacticity index, i.e., between 90 and 93%. Less isotacticity index was observed for groups 4 to 6 due to higher (mr-) or (rr-) content, leading to an extra dis-ordinary in the structural chains within these groups. The crystallinity degree (X<sub>c</sub>) determined by the DSC analyzer showed dissimilar values for each group, where the values ranged between 29-62%, as shown in Table 4. The highest (X<sub>c</sub>) values were recorded for the highest tacticity index groups, due to more tightened and packed chains of isotactic propylene than the syndiotactic mode. It showed fewer crystalline portions or lamellae [39-43]. Moreover, the thermal properties of the polypropylene group (T<sub>g</sub> and T<sub>m</sub>) also showed harmonic variation, as shown in Figs. 8 and 9. These temperatures' behavior was rather complex due to the overlapping of peaks. However, the difference in the glass-transition temperature (T<sub>g</sub>) value of syndiotactic and isotactic polypropylene groups lies in the 5 to 10°C. For example, for group 3, the variation in T<sub>g</sub> value was only 5°C, whereas, for group 6, the variation was about 10°C. The influence of tacticity on the glass-transition temperature was less noticeable for isotactic groups with few substituent groups. The melting point of polypropylene was calculated by determining the maximum temperature reached in the DSC test. Melting values of the most significant isotacticity PP groups ranged from 160 to

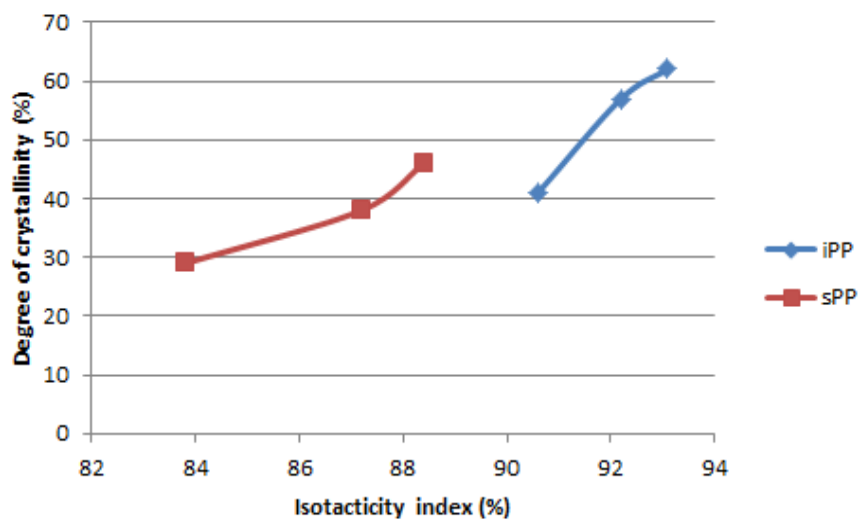
170°C. Less isotactic PP had a lower melting point than isotactic PP. Syndiotactic PP with high crystallinity had a melting point of 150 to 162°C. Thus, syndiotactic PP tends to have low crystallinity, glass transition, and melting point, where fewer stereoregular chains hinder the crystallization of the polymer and cause lower crystallization temperature [24, 26, 51]. The increase in the crystallization temperature increased melting and glass-transition points [52, 53]. In this context, Van Leeuwen [54] has mentioned that isotactic PP with almost fully regular chains melted at 166°C or even higher. Furthermore, the results showed that molecular weight had less effect on the thermal properties than the tacticity, except for the range when the degree of crystallinity became similar in isotactic and syndiotactic polypropylene, which may be attributed to the low range of molecular weights of the selected samples, where the dominant parameter will be the crystallinity, which is also mentioned by Paukkeri [24], who also referred that the tacticity of the chains increased directly proportional to the molecular weight when the values were less than 200,000 g/mol. For higher values, the tendency to increase dropped. From another perspective, when the isotacticity decreased that means more crosslinking. Due to the increased entanglement of chains with increased molecular weight, the polymer gets a higher glass-transition temperature, which makes the polymer's processing difficult. Overall, the isotacticity index directly affected the polypropylene's thermal properties. The random groups in the homo-polymer decreased polymer isotacticity, thus reducing its crystallinity and lowering the melting point of the glass transition temperature. Figs. 10-12 show the variation of thermal properties with the isotacticity index for selected PP groups. It can be said that the degree of crystallinity increased with the isotacticity index due to the high consistency of polymeric chains, less branching, and less crosslinking [55-57]. Furthermore, the polymer's melting behavior tended to decrease when the degree of crystallinity dropped because the crystalline structure offered rigidity and greater chemical resistance, which requires extra heat for melting [24, 29, 52].



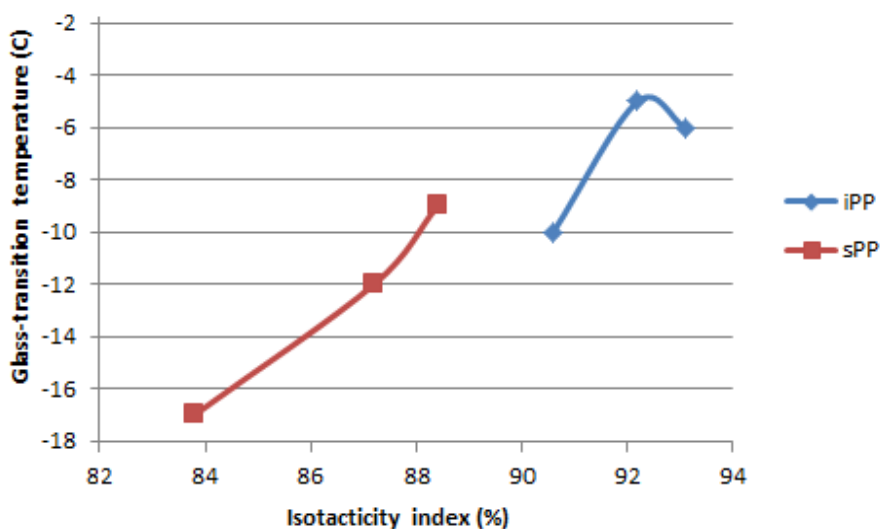
**Fig. 8** DSC Curves of Melting Behavior for Different Groups.



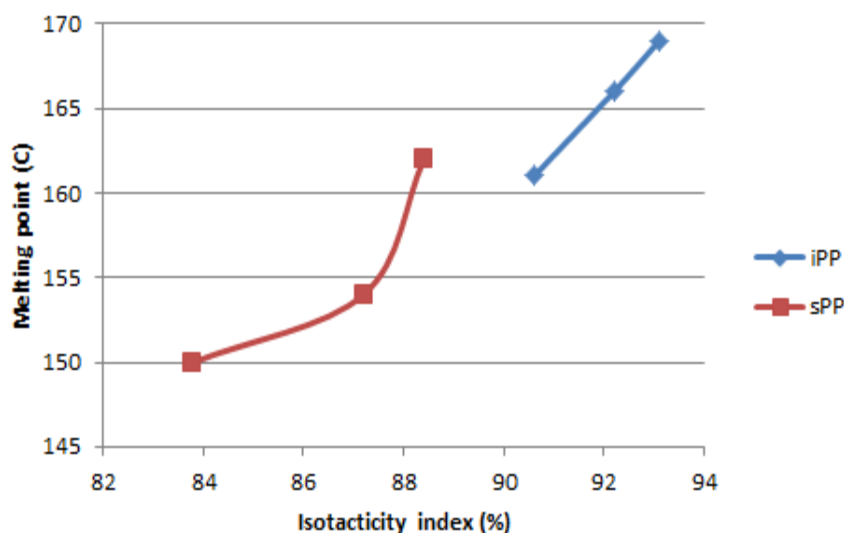
**Fig. 9** DSC Curves of Glass-Transition Behavior for Different Groups.



**Fig. 10** Variation of Degree of Crystallinity with the Isotacticity Index.



**Fig. 11** Variation of Glass Transition Temperature with the Isotacticity Index.



**Fig. 12** Variation of Melting Point with the Isotacticity Index.

Further calculations can be considered to determine other thermal properties, such as thermal conductivity and heat capacity. These properties can be referred to as thermal energy parameters since they are related to heat transfer and energy storage in materials. These properties can be linked directly to the degree of crystallinity ( $X_c$ ) for PP as follows [5]:

$$k = (0.8 + 0.2 X_c) k_c \quad (4)$$

$$C_p = (1.2 - 0.2 X_c) C_{pc} \quad (5)$$

where  $k_c$  is the thermal conductivity of fully crystalline polypropylene (0.22 W/m.K [40]), and  $C_{pc}$  is the heat capacity of fully crystalline polypropylene (1800 J/kg.K [40]). Table 5 shows the calculated values for different propylene groups. It can be noticed that the thermal conductivity decreased from 0.203 W/m.K for Group 1, which had the highest tacticity index, to 0.189 W/m.K for Group 6, which had the lowest tacticity index. This reduction was about 7%. On the other hand, the

heat capacity showed a reciprocating behavior, increasing in the less tacticity mode by 10%.

**Table 5** Thermal Energy Properties for Selected Polypropylene Groups.

Group	Thermal conductivity (W/m.K)	Heat capacity (J/kg.K)
1	0.203	1924
2	0.201	1975
3	0.194	2037
4	0.196	2009
5	0.192	2052
6	0.189	2106

#### 4. CONCLUSIONS

The effect of the homo-polypropylene chain's isotacticity was studied to observe several thermo-physical properties' behavior, such as glass-transition temperature, melting point, heat capacity, and thermal conductivity. By comparing the results of six PP groups, it was revealed that the isotacticity directly influenced the values of the selected properties due to the change in the proportion of random methyl groups in the polymer. It is noticed that by



decreasing the isotacticity for a certain limit, the degree of crystallinity decreased by 33%, also the glass-transition temperature and melting point decreased by 10 and 20°C, respectively. Furthermore, the reduction in the chain order decreased the k-value by 7% and increased the Cp-value by 10%.

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