

## CHAIN REGULARITY OF ISOTACTIC POLYPROPYLENE DETERMINED BY DIFFERENT THERMAL FRACTIONATION METHODS

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### Abstract

The chain regularity of isotactic polypropylene (iPP) homo- and random copolymers was characterized by different thermal fractionation methods in this study. Different stepwise temperature programs were applied in a calorimeter (DSC), in order to develop a method which is significantly faster than SIST and provides reliable information about the chain regularity of iPP. Our studies prove that self-seeding accelerates the crystallization process during annealing in SSA-DSC experiments (successive self-nucleation and annealing). Consequently, the time of isothermal steps can be shortened significantly in the SSA-DSC method. On the other hand we found that step time should not be too short if the goal of the measurement is the determination of average chain regularity. Our results clearly indicate that both the experimental conditions and the evaluation technique influence the obtained results. A standard experimental procedure is proposed for reliably determining the average chain regularity of iPP. The length of the SSA-DSC temperature program developed in this study is much shorter compared to that of the conventional SIST (stepwise isothermal segregation technique) measurements used recently for such experiments. The proposed SSA-DSC program makes the reliable characterization of a large number of samples on an acceptable timescale possible.

**Keywords:** Isotactic polypropylene, molecular structure, chain regularity, stepwise crystallization, SIST, successive self-nucleation and annealing (SSA-DSC)

## Introduction

### *Thermal fractionation of polymers*

The molecular structure of polymeric materials is an important question, because small differences in molecular structure may result in large changes in the properties of the polymer [1, 2]. Thermal fractionation is a versatile and widely used technique for the characterization of the chain structure of polymeric materials. The history and literature background of thermal fractionation of polymers is collected thoroughly in the review of Müller and Arnal [3]. The pioneering works in this area were done by Grey *et al.* [4] and Varga *et al.* [1, 5] on polyethylene. According to these early works, two classes of thermal fractionation methods can be distinguished. One is the stepwise crystallization from melt (SC) and the second is the successive self-nucleation and annealing (SSA) technique [3]. Both methods were applied frequently for the characterization of the chain structure of PE in the last few decades. The effect of co-monomer type and content on the chain structure and the characterization of side branches were frequently the major goal of these measurements [6-9] (see Table 2 in reference [3] for more examples on the application of thermal fractionation methods). The chain structure of isotactic polypropylene has frequently also been characterized by thermal fractionation methods. Virkkunen *et al.* [10, 11] proposed the SSA method for the fractionation of iPP in order to characterize the tacticity distribution of samples polymerized by different catalyst systems. Garoff *et al.* [12] developed a method for the quantitative determination of average chain regularity. They used an SC method for the fractionation of iPP called stepwise isothermal separation technique (SIST). They found acceptable correlation between chain regularity obtained by SIST and by temperature rising elution fractionation (TREF-NMR) measurements, which was confirmed by other studies as well [13]. Unfortunately, SIST experiments are very time consuming, thus their application has not been spread widely until now. The TREF-NMR technique can characterize both stereo- and region-defects independently, but the evaluation of NMR spectra is quite complicated. The major advantage of calorimetric techniques, both SC (SIST) and SSA, is that they are sensitive to any kind of defects, since these techniques do not measure the chemical structure of the PP chain directly. In addition, calorimetric techniques are simple measurements and their evaluation is easy, but they do not provide any information about the type of defects in the polymer.

### *The concept of the SIST technique*

SIST is an SC method, which is based on the simple assumption that at a given isothermal crystallization temperature ( $T_c$ ) only those chains crystallize in which the regular sequences are long enough to form lamellae with thickness proportional to  $T_c$ . If  $T_c$  is high enough lamella thickness will be limited by chain regularity. Accordingly, the most regular sequences will crystallize at the highest temperature, and the lower is the crystallization temperature the shorter regular sequences crystallize. Consequently, the fractionation of crystalline structure is possible with an appropriate stepwise crystallization (SC) program [12]. However, we should consider that the formation of the perfect structure achievable is essential for the proper estimation of chain regularity, otherwise the basic assumption of the technique will not be fulfilled. The dependency of melting temperature on the lamella is described by the well-known Gibbs-Thomson equation:

$$T_m = T_m^0 \left( 1 - \frac{2\sigma_e}{\rho_c \Delta H_m^0 \ell} \right) \quad (1)$$

Where  $T_m^0$  is the equilibrium melting point,  $\sigma_e$  is the free energy of the folding surface of the lamella,  $\rho_c$  is crystal density and  $\Delta H_m^0$  is the equilibrium heat of fusion of iPP.  $\ell$  is lamella thickness. The regular sequences can be calculated from lamella thickness according to Equation 2.

$$I = 3 \frac{\ell}{c} \quad (2)$$

Parameter  $I$  is the length of flawless regular sequence in monomer units, while  $c$  is the height of a unit cell, which can be found in the literature and its value is  $6.5 \text{ \AA}$  [14]. The multiplication by three comes from the  $3_1$  helix in the unit cell of iPP [15]. The weight average of  $I$  ( $I_{av}$ ) can be used for the characterization the chain regularity of iPP.

A careful SIST measurement requires 18-24 hours depending on the number and duration of the steps. Consequently, several attempts were made to calculate chain regularity from melting traces recorded after SSA crystallization, since the traces recorded after SIST and SSA crystallization, respectively, are similar [16, 17]. Although, differences in the chain structure of the polymer were revealed clearly in these studies, the chain regularity estimated is questionable because of the short step time ( $t_a = 15 \text{ min}$ ) used. The short  $t_a$  used by Chang *et al.* [16] and Kang *et al.* [17] was proposed earlier by Lorenzo *et al.* [18], but the latter article focused on the kinetics of self-nucleation and chain regularity was not calculated in that work.

Accordingly, our goal was to investigate the effect of experimental conditions and evaluation technique on the results of thermal fractionation experiments, with special focus on the estimation of average chain regularity ( $I_{av}$ ) from melting traces recorded after fractionated crystallization. One SC (SIST) and two SSA methods were applied for the determination of the chain regularity of iPP. We also intended to suggest an easy and relatively fast experimental procedure, which can be applied routinely for the determination of the chain regularity of iPP.

## Experimental

### Materials

The iPP grades studied were supplied by Borealis GmbH. The most important characteristics like MFR (230 °C, 2.16 kg of load), molecular mass ( $M_w$ ) and polydispersity ( $Pd = M_w/M_n$ ) are included in Table 1. “PP” refers to polypropylene, “N” to nucleation in the sample codes. The letter “r” appears in the code if the polymer is random ethylene-propylene copolymer.

### Methods

Crystallization was followed by polarized light microscopy. The measurements were carried out using a Zeiss Axioscop equipped by a Leica DMC 320 digital camera and a

Mettler FP82 type hot stage. The micrographs were recorded with the Leica IM50 software. The samples were placed between crossed polarizers and a  $\lambda$ -plate located diagonally was used to determine the optical character of the supermolecular units. The sample was heated to 220 °C and held there for 5 min in order to erase any thermal and mechanical prehistory. Subsequently the sample was cooled to 170 °C and held there for 180 min. After the first step the sample was cooled to the second step at 160 °C and held there for another 180 min. The steps were repeated until growth of the spherulites became visible.

**Table 1** The most important characteristics of the studied iPP grades

| Polymer             | MFR /dg min <sup>-1</sup> | M <sub>w</sub> /kg mol <sup>-1</sup> | Pd   | C2 content /% |
|---------------------|---------------------------|--------------------------------------|------|---------------|
| PP1 <sup>a</sup>    | 2.3                       | 607                                  | 8.4  | -             |
| PP2                 | 0.2                       | 765                                  | 3.7  | -             |
| NPP1 <sup>b</sup>   | 2.5                       | 223                                  | 4.7  | -             |
| NPP2 <sup>a,b</sup> | 2.0                       | 843                                  | 26.3 | -             |
| NPP3 <sup>a,b</sup> | 0.7                       | 936                                  | 19.2 | -             |
| rPP1                | 14.0                      | 217                                  | 5.4  | 2.1           |
| rPP2                | 1.5                       | 317                                  | 3.7  | 4.2           |
| rPP3                | 12.0                      | 195                                  | 3.2  | 5.3           |

<sup>a</sup>Some samples contain fractions with ultra large molecular mass (UHMW)

<sup>b</sup>Samples containing nucleating agents

Molecular weight and polydispersity (*Pd*) of samples containing UHMW fraction cannot be measured by size exclusion chromatography (SEC), thus these values were estimated from rheological experiments. The measurements were carried out using an Anton Paar UDS 200 oscillatory rheometer at 200 °C with plate-plate geometry in accordance with ISO 6271-10. Frequency sweeps were carried out between 0.02 and 600 Hz to determine storage and loss moduli (*G'*, *G''*). Viscosity curves were calculated by assuming the validity of the Cox-Merz relation. Molecular weight was deduced from extrapolated zero shear viscosity ( $\eta_0$ ) with the help of the correlation [19]

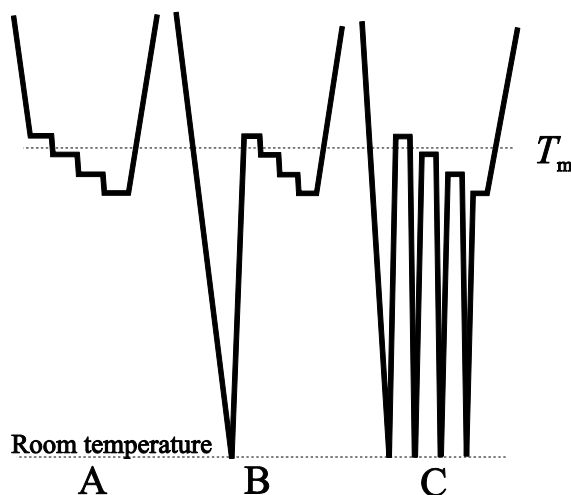
$$M_w = 32.38\eta_0^{0.2344} \quad (3)$$

while the polydispersity index (*Pd*) was calculated from the cross-over modulus (*G<sub>c</sub>*) [20]

$$Pd = \frac{10^5}{G_c} \quad (2)$$

The melting and crystallization characteristics of the samples were determined using a Perkin Elmer DSC-7 apparatus calibrated with Indium and Lead reference materials. Sample mass was between 3-5 mg and the experiments were carried out under continuous Nitrogen flow (20 ml min<sup>-1</sup>). Hermetically sealed aluminum pans were used as sample holders. All samples were heated up to 220 °C and held there for 5 min in order to erase thermal and mechanical prehistory and then they were cooled to room temperature at 10 °C min<sup>-1</sup> cooling rate. Subsequently, the samples were reheated again to 220 °C at 10 °C min<sup>-1</sup> heating rate. The peak temperature of crystallization and melting (*T<sub>cp</sub>* and *T<sub>mp</sub>* respectively) and the end temperature of melting (*T<sub>m</sub>*) were read from the DSC traces. In addition, the enthalpy of crystallization and fusion ( $\Delta H_c$  and  $\Delta H_m$ ) were calculated as well.

Chain regularity was determined using different thermal fractionation methods. The thermal and mechanical prehistory of the samples was erased at 220 °C for 5 min before all stepwise heat treatments. The three different thermal programs used for thermal fractionation are presented in Figure 1.



**Figure 1** Temperature programs applied for thermal fractionation

Method A is the conventional SIST or SC technique, which was proposed by Garoff and his coworkers [12]. The cooling rate was 80 °C min<sup>-1</sup> between the crystallization steps. In Method B an additional cooling step is included before stepwise treatment in order to generate self-nuclei in the sample. Slower cooling and heating rates (10 °C min<sup>-1</sup>) were applied in Method B during cooling to room temperature and reheating, but the cooling rate between the crystallization steps was 80 °C min<sup>-1</sup> in order to provide similar crystallization conditions as in Method A. Method B represents a transition between SC and SSA techniques. Method C contains a cooling run before each crystallization step, in order to reproduce self-nuclei after each isothermal step. Technique C is actually an SSA program. The rates of cooling to room temperature and heating to the crystallization temperature were 10 °C min<sup>-1</sup> in Method C. After stepwise crystallization the samples were heated immediately from the last isothermal step at 10 °C min<sup>-1</sup> in all techniques and the melting peak was recorded.

Two measurement sequences were performed in order to study the effect of thermal program in details. First, the temperature increment ( $T_i$ ) between the isothermal crystallization steps was set at 10 °C, which results in eight steps from 170 to 100 °C and the time of isothermal steps ( $t_s$ ) was varied (15, 60, 90, 120, 150 and 180 min).  $I_{av}$  was evaluated and the shortest  $t_s$  was selected as reliable step time, which did not influence the value of  $I_{av}$ . Secondly,  $t_s$  was set to the reliable value and  $T_i$  was decreased from 10 to 7 and 5 °C in order to increase the resolution of the measurements. Smaller  $T_i$  resulted in more crystallization steps in order to cover the same temperature window mentioned above, which may lead to significantly longer measurement time.

The polymorphic composition was studied by wide angle X-ray scattering (WAXS) using a Philips PW 1830/PW type equipment with CuK $\alpha$  radiation at 40 kV and 35 mA. The WAXS patterns were recorded between 10 and 30 2 $\theta$  at 2°min<sup>-1</sup> of scanning rate.

## Results and discussion

### *Melting and crystallization characteristics of the studied samples*

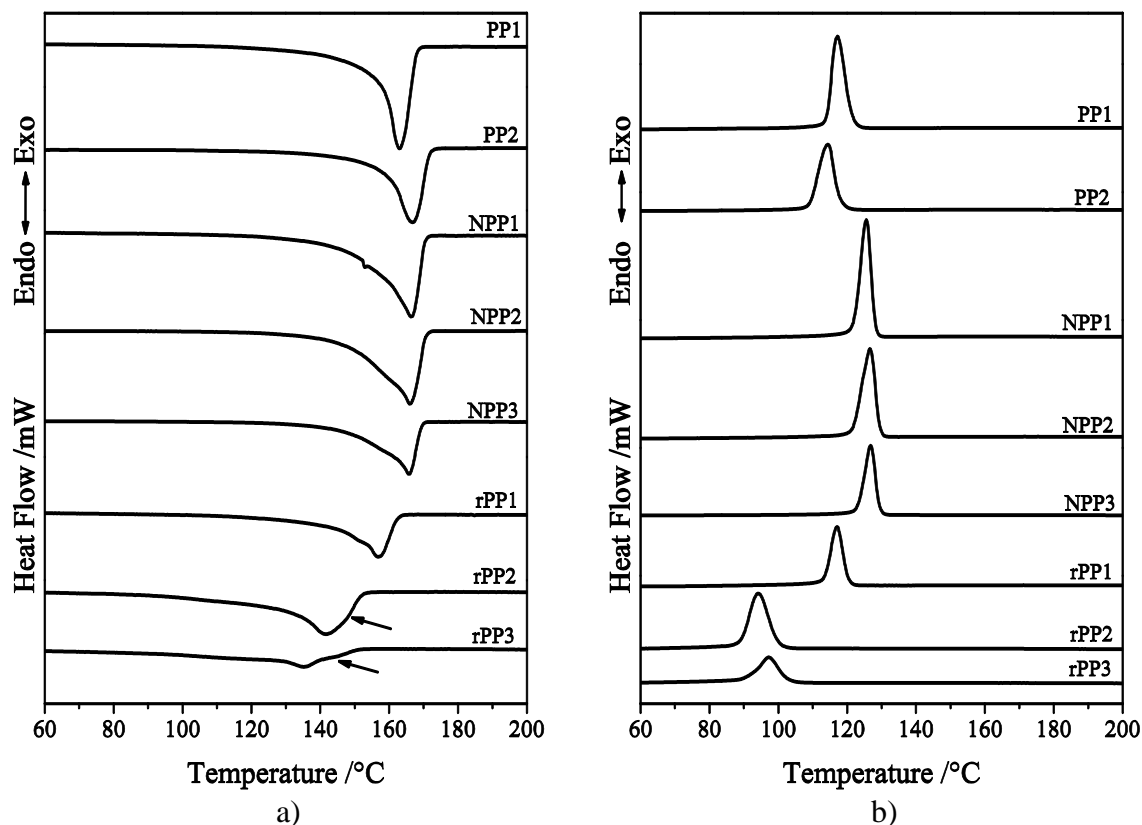
Melting and crystallization characteristics derived from standard DSC experiments are presented in Figure 2 and Table 2. The results are in agreement with our expectations that homopolymer grades showing a higher melting temperature, around 165 °C, and a larger crystallinity compared to similar characteristics of random copolymers. The disturbing effect of co-monomer in rPP grades usually results in smaller crystallinity and more imperfect lamellar structure, which is accompanied by lower melting temperature (145 °C) [13, 21, 22].

We have to emphasize that random copolymers have less regular chain structure, which leads to more pronounced crystal perfection during melting and consequently multiple melting peaks (marked by arrow in Figure 2a) is recorded. In addition, random copolymers have larger inclination for crystallization in  $\gamma$ -form, which might influence the crystallization process during thermal fractionation. Thus the polymorphic composition of random copolymers was investigated by WAXS technique. The WAXS patterns are presented in Figure 3. Three pronounced diffraction peaks can be observed in Figure 3 at 14, 16,5 and 18,3 ° refer to the  $\alpha(110)$ ,  $\alpha(040)$  and  $\alpha(130)$  respectively [22-24]. No pronounced peak at 20 ° indicating the presence of  $\gamma$ -phase can be observed, thus both the melting curves and WAXS measurements prove that all samples crystallize in the traditional  $\alpha$ -modification and neither polymorphic transition nor melting memory effect need to be considered during the experiments [25].

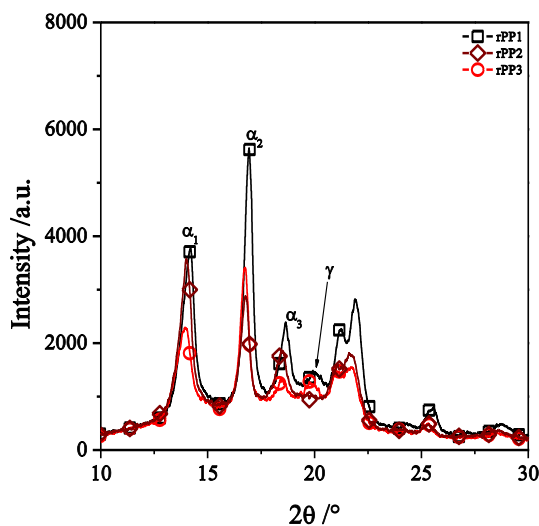
It is clear that the crystallization peak temperatures ( $T_{cp}$ ) of the homopolymers are quite different, because the three samples with high  $T_{cp}$  (above 120 °C) contain nucleating agents. The calorimetric data indicate that the samples represent most of the frequently used polypropylene grades, thus we may suppose that the fractionating technique proposed in this work can be applied universally.

**Table 2** *Melting and crystallization characteristics of the studied samples determined during standard DSC measurements ( $v_c = v_h = 10 \text{ }^\circ\text{Cmin}^{-1}$ )*

| <b>Polymer</b> | $T_{cp}$ /°C | $\Delta H_c$ /J g <sup>-1</sup> | $T_{mp}$ /°C | $T_m$ /°C | $\Delta H_m$ /J g <sup>-1</sup> |
|----------------|--------------|---------------------------------|--------------|-----------|---------------------------------|
| PP1            | 117.1        | 102.9                           | 162.8        | 167.9     | 104.2                           |
| PP2            | 114.5        | 98.1                            | 166.7        | 171.7     | 102.7                           |
| NPP1           | 125.6        | 108.7                           | 166.4        | 170.4     | 112.0                           |
| NPP2           | 126.6        | 108.9                           | 166.0        | 170.6     | 115.0                           |
| NPP3           | 126.8        | 110.0                           | 165.7        | 169.4     | 109.9                           |
| rPP1           | 117.0        | 88.0                            | 156.9        | 162.3     | 87.7                            |
| rPP2           | 94.1         | 69.5                            | 141.7        | 152.0     | 72.2                            |
| rPP3           | 97.3         | 62.7                            | 135.2        | 145.3     | 61.9                            |



**Figure 2** Melting (a) and crystallization (b) traces of the studied samples recorded during standard DSC runs ( $v_c = v_h = 10 \text{ }^\circ\text{Cmin}^{-1}$ )

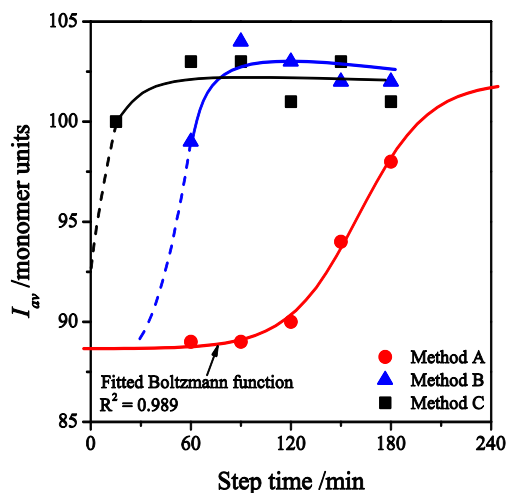


**Figure 3** WAXS patterns of random copolymers studied

### Thermal fractionation of NPP1

In order to demonstrate the difference among the three fractionation techniques the NPP1 sample (nucleated commercial grade) was selected and measured by Methods A, B and C. The  $t_s$  was changed in wide range in order to decide which method is the most

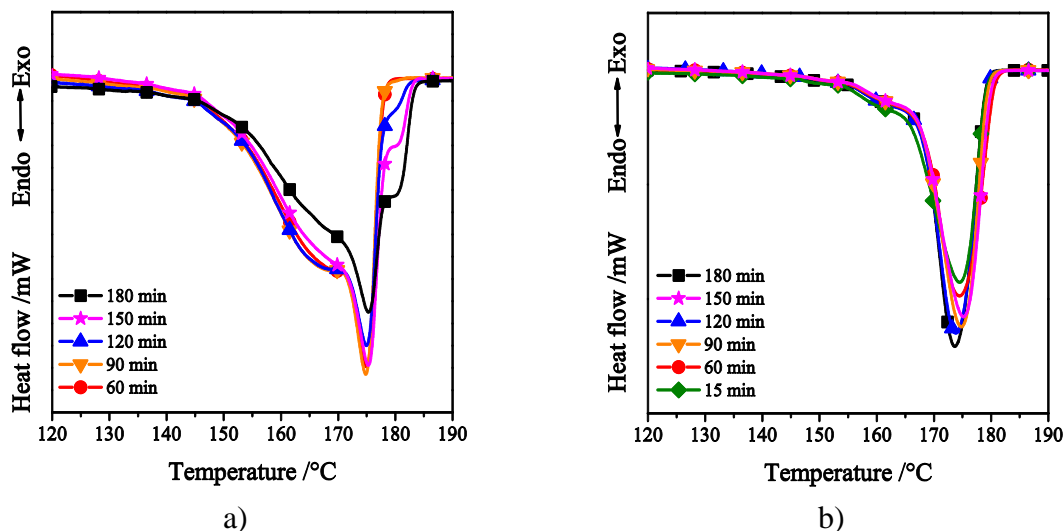
reliable one. That method was selected as reliable one, in which the evaluated  $I_{av}$  remains constant in the widest  $t_s$  range.  $I_{av}$  is plotted against step time in Figure 4. The results prove clearly, that method A is very sensitive to step time. Calculated  $I_{av}$  decreases considerably with decreasing  $t_s$ . The fitted Boltzmann curve indicates that at least 240 min step time were needed in order to achieve similar  $I_{av}$  as with Method B and C. However, 240 min step time could lead to degradation and such long measurement has no practical relevance at all. Method B and C result in constant  $I_{av}$  in a relatively wide  $t_s$  range, but estimated  $I_{av}$  starts to decrease below 90 and 60 min in the case of method B and C, respectively.



**Figure 4** The effect of step time on the average sequence length data evaluated from the sequence length distribution functions

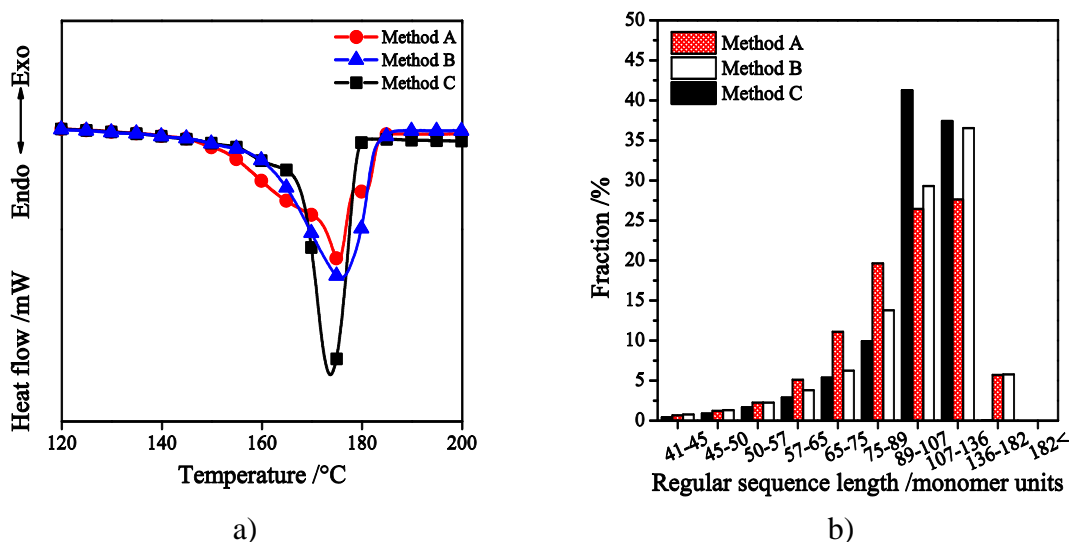
The changes in  $I_{av}$  are resulted by very small differences in the melting profiles, which are presented in Figure 5 at different step times using method A and C. The change of the melting profile is more pronounced, when method A was used, because this Method is the most sensitive to shortening the step time. Changes in the melting traces of Method C are small, but not negligible at all. The fractions crystallizing at lower temperatures increase slightly, and those forming at higher temperature decrease proportionally. The melting curves presented in Figure 5 are weighted with sample mass in order to make them comparable. Changes in the melting profiles can be observed clearly on the intensity of the large melting peak at 175°C.





**Figure 5** Melting profiles of fractionated NPP1 according to method A (a) and C (b) using different step times ( $T_i = 10\text{ }^\circ\text{C}$ )

The melting traces recorded at the longest  $t_s$  and the calculated distribution functions of regular sequence length are shown in Figure 6 to demonstrate the effect of the three fractionation methods on them. The presented curves prove clearly that the method of fractionation influences the melting profile significantly, despite the fact that the same isothermal steps were applied and theoretically all methods should provide the same – as perfect as possible – crystalline structure. These results emphasize the importance of this study, because different melting profiles yield different chain regularities. The SC method results in the most perfectly developed lamellas, so Method A should be selected if the goal is the estimation of the longest regular sequence.



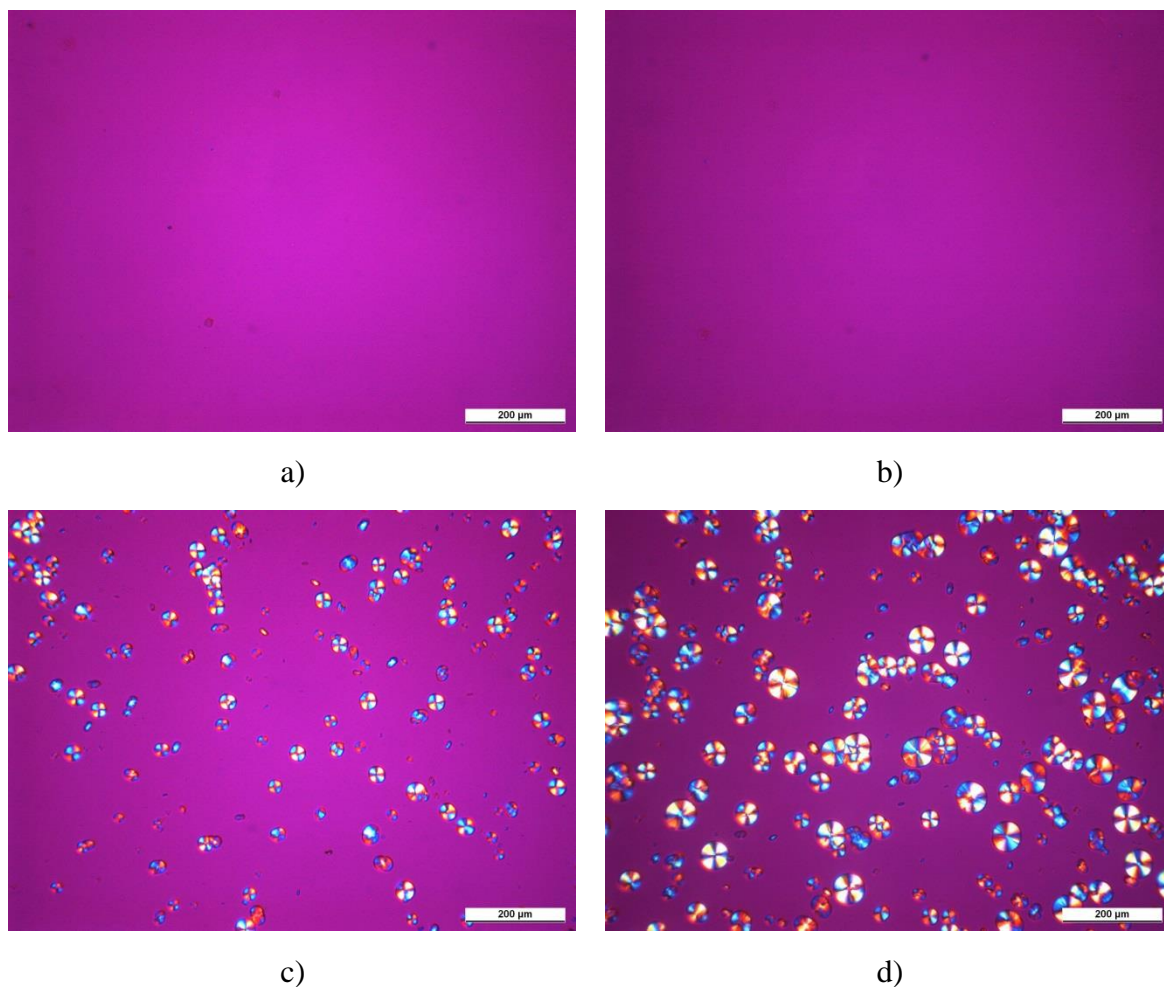
**Figure 6** Melting profile of NPP1 (a) recorded with the different thermal fractionation methods using 180 min step time and the obtained regular sequence length distribution function (b)

However, at high temperature crystallization is very slow during the steps due to the small degree of supercooling. Consequently, the crystalline fraction formed in steps at high temperature is smaller than the possible amount and thus the  $I_{av}$  calculated is relatively small. The successive self-nucleation and annealing (SSA) method however generates primary crystallites during cooling, which accelerate the overall rate of crystallization and consequently larger amount of crystalline phase forms in each isothermal step even at high temperature. That means that the SSA methods results in sharper and less separated melting curves (Figure 5), because in this case the majority of the sample crystallizes within one isothermal step. We can conclude that the most frequent regular sequence length is between 89 and 136 monomer units by all three methods, but the most and the less perfect regions are different resulting in dissimilar  $I_{av}$  values. Accordingly, Method A, B and C result in average chain regularities of 98, 102 and 101, respectively. The value of all constants used during the calculation is given in Table 3.

Crystallization during thermal fractionation was followed by PLM. Although sample dimensions and experimental conditions are different in PLM and in DSC measurements, PLM provides important additional information about the selected thermal program used in the fractionation experiments. The proper temperature range of the isothermal steps can be checked easily with this technique. If crystallization occurs during the first step at the highest temperature, the selected temperature window is too narrow and should be extended. The formation of spherulites is presented in Figure 7 for Method A. The results indicate clearly, that crystalline phase does not form during the first two steps, at 170 and 160 °C (Figure 7a and b) because of thermodynamic restrictions and slow rate. Slow growth of spherulites can be observed only at larger supercooling in the third step, at 150 °C. At this temperature  $\alpha$ -spherulites form with negative birefringence in good agreement with literature data [26]. PLM study proves that the temperature program of Method A is proper and we may assume that the crystalline fraction formed at higher temperature is the perfect achievable structure indeed.

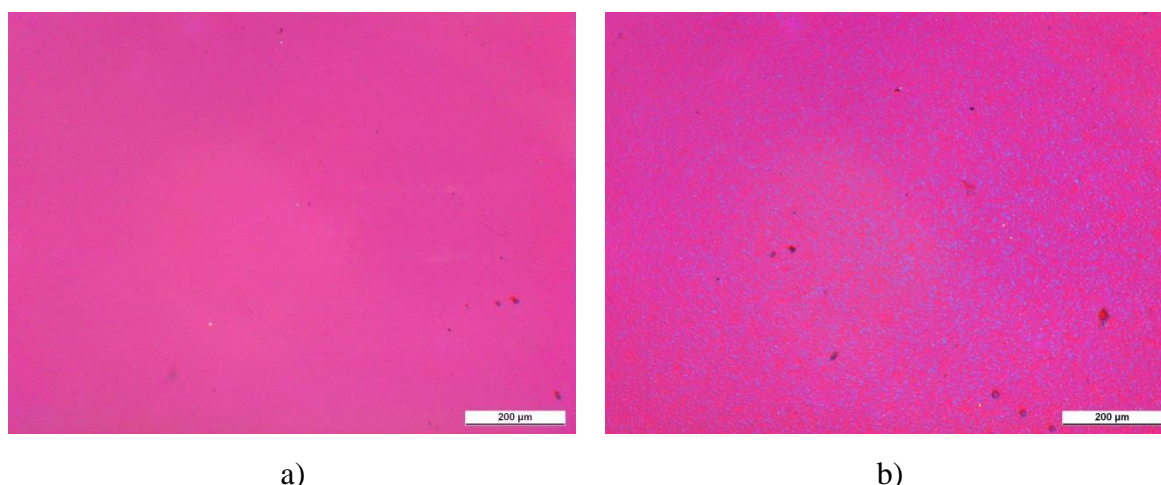
**Table 3** *The values of the constants in Equation 1.*

| Constant       | Value /dimension          | Literature |
|----------------|---------------------------|------------|
| $T_m^0$        | 481 K                     | [22, 27]   |
| $\sigma_e$     | 0.122 J m <sup>-2</sup>   | [27]       |
| $\rho_c$       | 936 kg m <sup>-3</sup>    | [28]       |
| $\Delta H_m^0$ | 146000 J kg <sup>-1</sup> | [22, 27]   |



**Figure 7** Spherulite growth in NPP1 during the isothermal steps of method A; 170 °C, 180 min (a); 160 °C, 180 min (b); 150 °C, 90 min (c); 150 °C, 180 min (d)

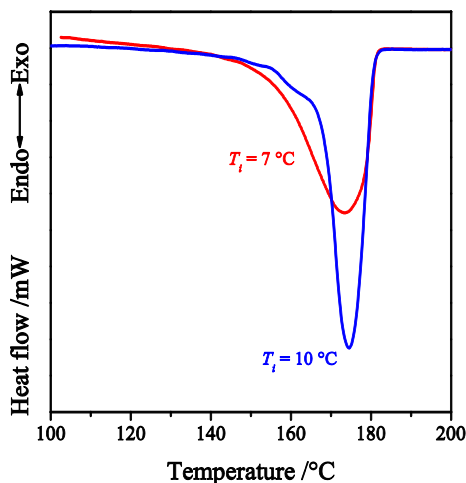
The effect of self-seeding is shown in Figure 8 on samples crystallized according to Method B. Similarly to Method A no crystalline fraction develops at 170 °C, but small microspherulitic structure forms at 160 °C. Growth rate is quite slow at this temperature, thus spherulites can be detected only after 150 min at 160 °C. Well-developed spherulites formed in Method A and significantly different micro-spherulitic structure developed in the procedures of Method B and C. These observations confirm that self-seeding occurs, since nucleus density is considerably larger in the self-seeded sample.



**Figure 8** Crystallization in NPP1 during the isothermal steps of Method B; (a) 170 °C, 180 min; (b) 160 °C, 180 min

#### Resolution of thermal fractionation

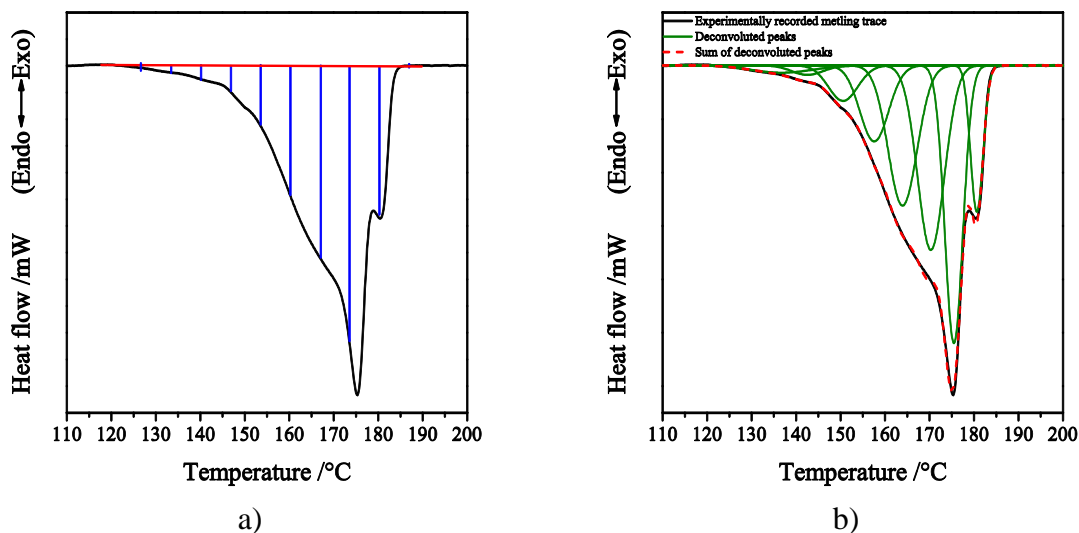
The resolution of thermal fractionation (number of separated fractions) can be varied by the size of the isothermal steps ( $T_i$ ). Enhanced resolution requires more isothermal steps and results in significantly longer experimental procedure. The melting traces recorded after the fractionation of the NPP1 polymer using different  $T_i$  values (10 and 7 °C respectively) are presented in Figure 9. The results indicate clearly, that smaller  $T_i$  is not accompanied by more separated melting peaks (better resolution) in the case of NPP1. Probably, strong nucleating effect and a tendency for crystal perfection might hinder better resolution. This example demonstrates well that small  $T_i$  does not necessarily lead to good resolution. Smaller  $T_i$  might be advantageous in the study of very small structural differences like short chain branching or catalyst performance in non-nucleated “neat” polymer grades. Chang et al. [16] used  $T_i = 5$  °C to study the performance of a catalyst system in non-nucleated PP. Shanks et al. [6] used  $T_i = 4$  °C to investigate co-monomer distribution in low density polyethylene (LDPE).



**Figure 9** Melting profiles of NPP1 after fractionation with Method C ( $t_a = 60$  min) using different  $T_i$  values ( $v_h = 10$  °Cmin<sup>-1</sup>)

Effect of the evaluation technique

Two methods are published in the literature for the evaluation of melting traces recorded after thermal fractionation. According to the simpler approach, the melting profile is partitioned using vertical lines, while the second one is the deconvolution of the melting peak. The two evaluation techniques are demonstrated in Figure 10 for the NPP1 material and their evaluation protocol is discussed below.



**Figure 10** Dividing into sections (a) and deconvolution (b) of a melting peak recorded after thermal fractionation with Method A using 180 min step time (NPP1) ( $v_h = 10$  °Cmin<sup>-1</sup>)

The possible number of fractions must be defined first to partition the melting curve into sections. It was demonstrated during the pioneering works [1, 5], that the number of fractions formed during stepwise crystallization equals the number of steps plus one. Therefore, nine sections should be defined in the present methods (Figure 10a). If the melting peaks of the sections are not separated clearly, like in our case, the melting peak (126.7-187 °C) can be divided into nine similar ranges. Accordingly, the width of each section is 6.7 °C. The temperatures of the vertical separator lines and the calculated sequence lengths are given in Table 4. The advantage of this evaluation technique is that it is easy and can be done for any materials. The lamella thickness ranges are calculated using Equation 1 and the sequence length values are obtained using Equation 2.

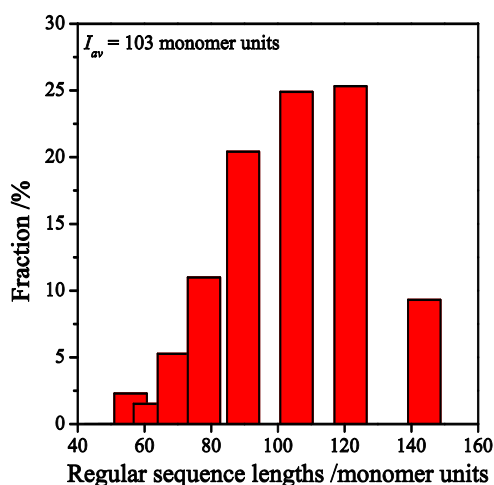
**Table 4** Calculation the average chain regularity of NPP1 by dividing the melting peak into sections

| Temperature limit<br>/°C                  | Lamella thickness<br>ranges<br>/nm | Sequence length<br>/monomer units | Fraction<br>/% |
|---|------------------------------------|-----------------------------------|----------------|
| 126.7                                     | 9-10                               | 41-45                             | 0.67           |
| 133.4                                     | 10-11                              | 45-50                             | 1.24           |
| 140.1                                     | 11-12                              | 50-57                             | 2.33           |
| 146.8                                     | 12-14                              | 57-65                             | 5.23           |
| 153.5                                     | 14-16                              | 65-75                             | 11.17          |
| 160.2                                     | 16-19                              | 75-89                             | 19.78          |
| 166.9                                     | 19-23                              | 89-107                            | 26.4           |
| 173.6                                     | 23-29                              | 107-136                           | 27.67          |
| 180.3                                     | 29-39                              | 136-182                           | 5.31           |
| <b><math>I_{av}</math> /monomer units</b> |                                    |                                   | <b>97</b>      |

In the case of the deconvolution, the peak temperatures of each fraction should be defined first. If the crystalline fractions separate well, their peak temperatures can be estimated easily. In case of non-separated melting peaks the peak temperatures are the center of the nine sections estimated above. Microcal Origin 8.5 was used for the deconvolution procedure. The peaks representing the crystalline fractions must be integrated separately, and the weight of each peak can be defined as the ratio of the area under the specific peak and the sum of all peak areas.

Both techniques can be used for evaluation however, peak deconvolution is a mathematical fitting procedure, which is somewhat more time consuming than the other one. The peak fitting method might be very informative if the goal is the detailed study of small differences in chain structure on similar materials, like short chain branching for example. If the goal is the comparison of different polymers the partitioning of the melting peak is more advantageous, despite the fact that sometimes the vertical lines do not agree

accurately with the boundaries of suspected partial peaks (see in Figure 10a). The distribution function of regular sequence lengths can also be derived from the areas of the fitted peak (Figure 11).  $I_{av}$  values calculated from the different separation techniques presented in Figure 10a and 10b are 97 and 103 respectively, although both values were derived from the same melting curve. This clearly proves that  $I_{av}$  values are comparable only if they are obtained by the same evaluation technique. Consequently, researchers must select the technique to be used in their study. The peak fitting procedure results in little larger  $I_{av}$ , because peaks with relatively large area near  $T_{mp}$  influence strongly the final value. The results discussed above prove clearly that chain regularity value estimated by thermal fractionation techniques is not an absolute value and depends both on the thermal program as well as on the evaluation method. An experimental protocol is suggested and used below for the comparison of the  $I_{av}$  values of eight different polypropylenes.

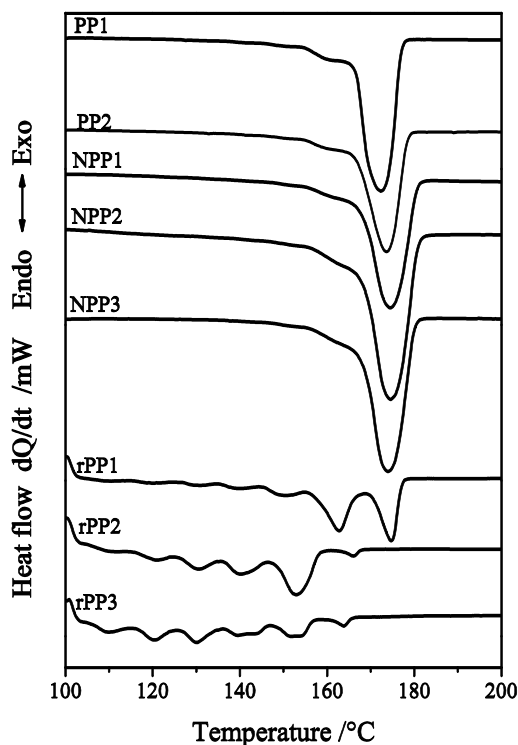


**Figure 11** Distribution of regular sequence lengths estimated from the area of fitted peaks presented in Figure 10b (NPP1,  $t_s = 180$  min, Method A)

#### Correlation of properties with estimated chain regularity

$I_{av}$  characterizes the chain regularity of a polymer, thus its reliable estimation is important from the scientific and the practical point of view. Based on the results discussed above, Method C is selected for fractionation. This method provides the fastest experimental procedure without influencing the value of  $I_{av}$ . Based on the results plotted in Figure 4  $t_a$  was set to 60 min, since shorter step times might bias the  $I_{av}$  values. 10 °C was selected as  $T_i$ , because unknown materials might behave like NPP1, for which increased resolution (decreased  $T_i$ ) does not provide more information, but results in much longer experimental procedure. The melting traces recorded after thermal fractionation are plotted in Figure 12. The curves clearly demonstrate the differences among homopolymers and random copolymers. The homopolymers have more regular structure and higher melting temperature, which allows a more significant crystal perfection during heating leading to

overlapping and less separated fractions.



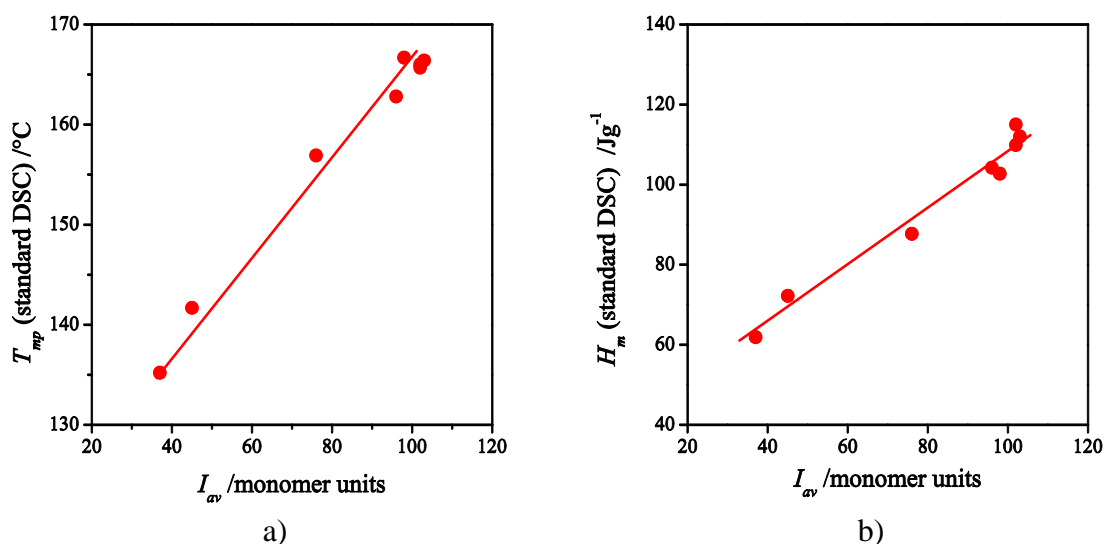
**Figure 12** Melting curves recorded after thermal fractionation according to method C ( $t_a = 60$  min;  $T_i = 10$  °C;  $v_h = 10$  °Cmin<sup>-1</sup>)

In order to facilitate the comparison of the different polymers, partitioning technique was selected and all the materials were evaluated according to the same protocol. The  $I_{av}$  values obtained are listed in Table 5. They cover a wide range from 37 to 103, which clearly shows the large differences in the chain regularity of the polymers studied. Since the ability of polymers to crystallize depends strongly on chain regularity, estimated  $I_{av}$  values should correlate with their crystallization and melting characteristics. The values of  $I_{av}$  is plotted against  $\Delta H_m$  and  $T_{mp}$  obtained in standard DSC experiments in Figure 13 and the strong correlation indicates clearly that  $I_{av}$  reflects molecular structure reliably.

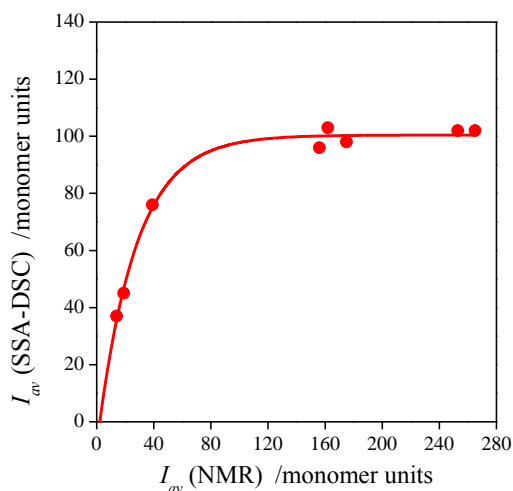


**Table 5**  $I_{av}$  values estimated according to method C ( $t_a = 60$  min;  $T_i = 10$  °C)

| Polymer | $I_{av}$ /monomer units |
|---------|-------------------------|
| PP1     | 96                      |
| PP2     | 98                      |
| NPP1    | 103                     |
| NPP2    | 102                     |
| NPP3    | 102                     |
| rPP1    | 76                      |
| rPP2    | 45                      |
| rPP3    | 37                      |



**Figure 13** The correlation of  $I_{av}$  with the melting temperature (a) and the enthalpy of fusion (b) of the studied PP grades



**Figure 14**  $I_{av}$  values determined by SSA-DSC and TREF-NMR

More interesting is the comparison of  $I_{av}$  values determined by SSA-DSC and TREF-NMR (Figure 14).  $I_{av}$  values of random copolymers estimated by NMR are significantly smaller compared to those obtained by SSA-DSC, and contrary to that  $I_{av}$  obtained by NMR is much larger for NPP2 and NPP3. The larger chain regularity might not be surprising, because the NMR experiments are made in dilute solution, thus the measurements are not affected by any kinetic effect of the polymer chain. Despite that, the crystallization during SSA-DSC is influenced by the presence of nucleating agents and kinetics especially in the samples of NPP2 and NPP3, which contain both UHMW fraction and nucleating agent. The presence of UHMW fraction hinders the crystallization [29] at high temperature resulting in apparently smaller chain regularity in these samples. Moreover, we have to emphasize that the evaluation of NMR results is much more complicated than that of SSA-DSC traces. In addition, NMR differentiates both kind of chain defect and the presence of ethylene influences the results in co-polymers making the evaluation of the NMR results even more complicated.

## Conclusions

Various thermal fractionation methods are often used for the determination of the chain regularity of polypropylenes without taking into account that the estimated value depends strongly on the selected temperature program and on the evaluation technique used. In this comparative study we proved that the fastest temperature program is the successive self-nucleation (SSA-DSC, method C in the present work) widely referred to in the literature. However, isothermal steps must be long enough (at least 60 min) in order to achieve reliable average chain regularity data. At shorter times, the obtained results might be useful for the comparison of different polymers, but the calculation of average chain regularity should be avoided. The experimental protocol proposed in this work (SSA Method A) is relatively fast (approximately 12 hours) compared to a conventional 18-24 hours long SIST method (method A in the present work). Moreover, the proposed fractionation method contains relatively large temperature increments between the steps, thus it covers a wide temperature range, which allows the comparative study of significantly different polymers (random and homopolymers) using the same experimental technique. The resolution of fractionation should be increased only if the goal of the research is the detailed investigation of small differences in molecular structure, like short chain branching in polyethylene for example. We clearly showed that the chain regularity value obtained characterizes the molecular structure reliably and correlates strongly with the crystallization behavior of PP. As a consequence, a carefully designed and evaluated thermal fractionation experiment is an important tool for the polymer research and development crystalline polymers.

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