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# NUCLEATION OF THE β-MODIFICATION OF ISOTACTIC POLYPROPYLENE

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## Abstract

The effects of the organic pigments C.I.P. RED 177 and C.I.P. Yellow 83 as nucleating agents on the crystallization of polypropylene were studied by DSC. The anthraquinone pigment exerted a significant effect, resulting in structural modifications with lower melting point, and particularly the β-modification. The DSC curves exhibit four transition regions, with the following temperature intervals: I. 415–417 K, II. 423–425 K, III. 430–432 K and IV. 438–439 K. For evaluation of the β-nucleation effect of pigments, the ratio $(\Delta H_1+\Delta H_2)/(\Delta H_3+\Delta H_4)$ was suggested.

**Keywords:** crystallization, DSC analysis, β-modification, nucleation, polypropylene

## Introduction

During the crystallization of polypropylene from a melt, mainly its stable α-crystalline modification with a melting point of approximately 438 K (165°C) is formed. By variation of the polymer cooling rate and through the influence of nucleation agents, one can obtain structural modifications with a lower melting point, mostly the β-modification, with a transition temperature of about 425 K (152°C) [1–10]. The melting temperature also affects the size of the crystallites and the perfection of the crystalline structure for a given structural modification [5]. Recent work has been oriented mainly towards elucidation of the mechanism of the β→α transition [5, 9, 11] and the selective effect of nucleation agents [8, 10, 12–14].

As concerns the nucleation effect of solid particles (fillers and pigments) during polypropylene crystallization, both the crystalline structure of the particle surface and the physical interactions on the particle – polymer interface play important roles [8, 10, 15]. These interactions are interesting from both theoretical and practical points of view in a three-component system composed of polypropylene-pigment-dispersing agent (dispersant), particularly in terms of the influence of the last two components on the formation of crystalline modifications of polypropylene.

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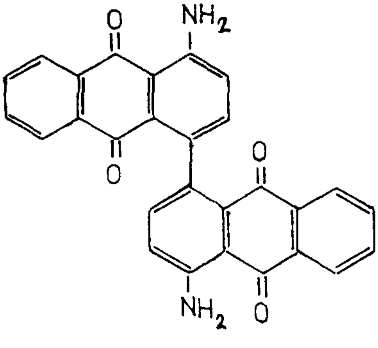
In the present work, we have investigated the influence of pigments and dispersants on the nucleation of polypropylene by means of DSC.

## Experimental

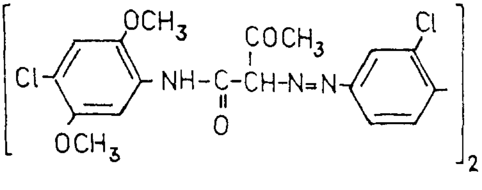
### *Materials used*

Polymers
Polypropylene PP TI 902 (Slovnaft, a.s.), melt flow index=27 g/10 min
Polypropylene HPF (Slovnaft, a.s.) powdered polymer for the preparation of pigment concentrates, melt flow index=6 g/10 min

Pigments
C.I.Pigment Red 177, anthraquinone pigment (VCHZ Pardubice, CZ), $\rho_{20^\circ C}=1368$ kg m$^{-3}$



C.I.Pigment Yellow 83, bis-azo pigment (Sandoz), $\rho_{20^\circ C}=1355$ kg m$^{-3}$



Dispersants
MGS (monoester of glycerine and stearic acid); surface tension at 30°C: 25 mN m$^{-1}$
NSPO (ester of polypropylene glycol and stearic acid); $M=1000$, surface tension at 30°C: 30 mN m$^{-1}$
N310 (copolymer of ethylene oxide and propylene oxide); $M=1000$, surface tension at 30°C: 35 mN m$^{-1}$

## Preparation of pigment concentrates and polypropylene fibres

The coloured concentrate (as nucleation component) was prepared by a classical procedure in the following two stages: 1. homogenization of the powdered polymer and pigment with the dispersant in a quick agitator at ambient temperature; 2. melting the mixture in a two-threaded equipment (ϕ 28 mm; Werner-Pfleiderer), at a temperature following from the experimental conditions (Table 1).

**Table 1** Conditions of the pigment Red 177 concentrate preparation

| No.<br>Cooling rate, K min$^{-1}$ | | Dispersant | $C_{\mathrm{disp}}$ / % | $C_{\mathrm{pigment}}$ / % | $T$ / °C |
|---|---|---|---|---|---|
| 10 | 80 | | | | |
| 1 | 17 | NSPO | 4 | 15 | 90 |
| 2 | 18 | NSPO | 8 | 15 | 90 |
| 3 | 19 | N310 | 4 | 15 | 90 |
| 4 | 20 | N310 | 8 | 15 | 90 |
| 5 | 21 | NSPO | 4 | 25 | 90 |
| 6 | 22 | NSPO | 8 | 25 | 90 |
| 7 | 23 | N310 | 4 | 25 | 90 |
| 8 | 24 | N310 | 8 | 25 | 90 |
| 9 | 25 | NSPO | 4 | 15 | 190 |
| 10 | 26 | NSPO | 8 | 15 | 190 |
| 11 | 27 | N310 | 4 | 15 | 190 |
| 12 | 28 | N310 | 8 | 15 | 190 |
| 13 | 29 | NSPO | 4 | 25 | 190 |
| 14 | 30 | NSPO | 8 | 25 | 190 |
| 15 | 31 | N310 | 4 | 25 | 190 |
| 16 | 32 | N310 | 8 | 25 | 190 |

For the pigment Yellow 83, MGS dispersant was used instead of NSPO. The dispersant concentration was 6 or 10% and the homogenization temperature was 145 or 215°C, respectively.

The samples of polypropylene fibres (PP TI 902) coloured by pigment concentrates (RED 177 and Yellow 83) were prepared by means of a model pilot plant with an extruder (ϕ 30 mm) at 230°C. The pigment content was constant, at 1.0 wt%.

## Method of measurement

Thermal properties of fibre samples were measured with a DSC II apparatus (Perkin-Elmer), using the following procedure: The original fibre sample was

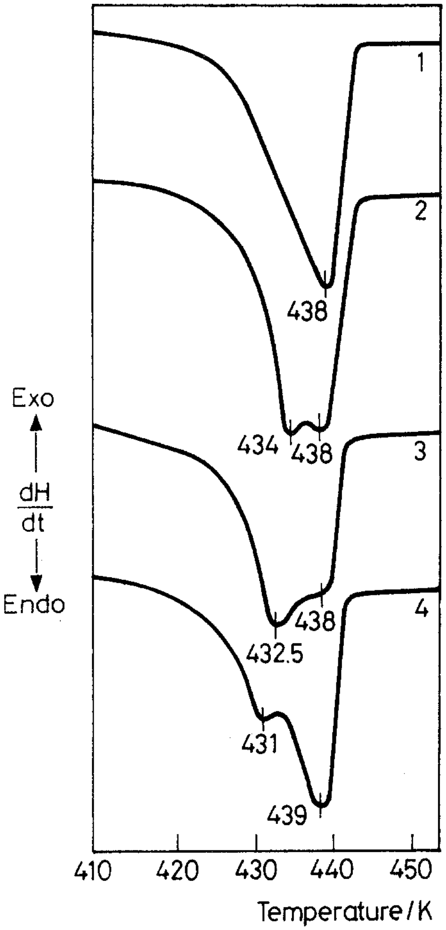


**Fig. 1** DSC analysis of polypropylene TI 902 (fiber). 1. original sample, first heating. Second heating after crystallization, cooling rate 2. 5 K min$^{-1}$; 3. 10 K min$^{-1}$; 4. 80 K min$^{-1}$

heated at a rate of 5 K min$^{-1}$ up to 493 K. Thus, a melting temperature $T_m$ was obtained. The sample was then cooled at a rate of 10 or 80 K min$^{-1}$ and the crystallization temperature $T_c$ was determined. After 353 K was reached, the sample was heated in a second cycle, again at a rate of 5 K min$^{-1}$, while DSC curves were obtained with maxima $T_i$ corresponding to the melting point and melting enthalpy $\Delta H_i$ of crystalline modifications formed during the controlled cooling process (10 and 80 K min$^{-1}$). In the measurements, a nitrogen atmosphere was used.

## Evaluation of the experiment

In the investigation of the influence of individual factors on the crystallization process, a method of factorial two-level experiments was used. For this purpose, a full factorial two-level experimental design was chosen. In accordance with the theory of factorial experiments, the effects of the individual factors were estimated and their statistical significance was tested by the method of analysis of scatter [16].

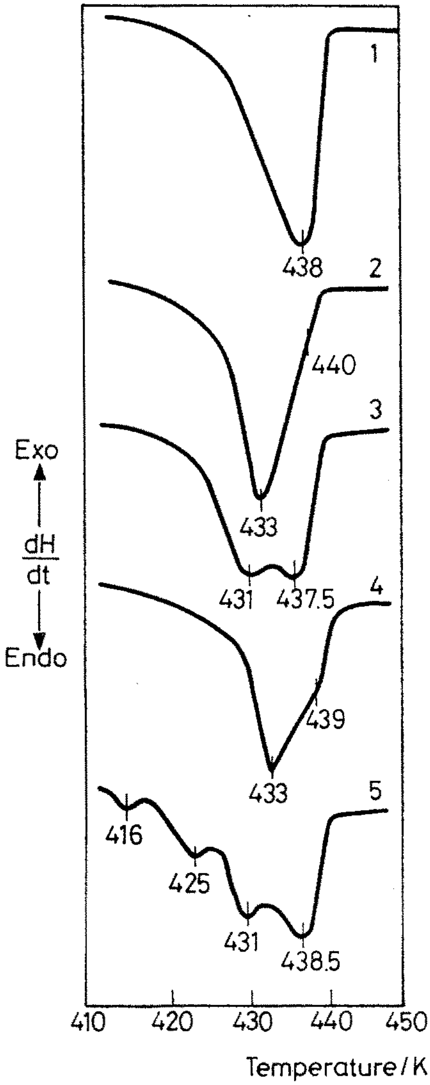


**Fig. 2** DSC analysis of polypropylene TI 902 (fiber) with 1 wt% of pigment Yellow 83: cooling rate 10 K min$^{-1}$ (2,4), 80 K min$^{-1}$ (3,5). Pigmentation of polypropylene by concentrates: 1. 25% pigment, 6% N310, $T_{\mathrm{homog}}$=145°C, first heating; 2., 3. sample 1., second heating; 4. 25% pigment, 6% N310, $T_{\mathrm{homog}}$=215°C, 5. sample 4., second heating

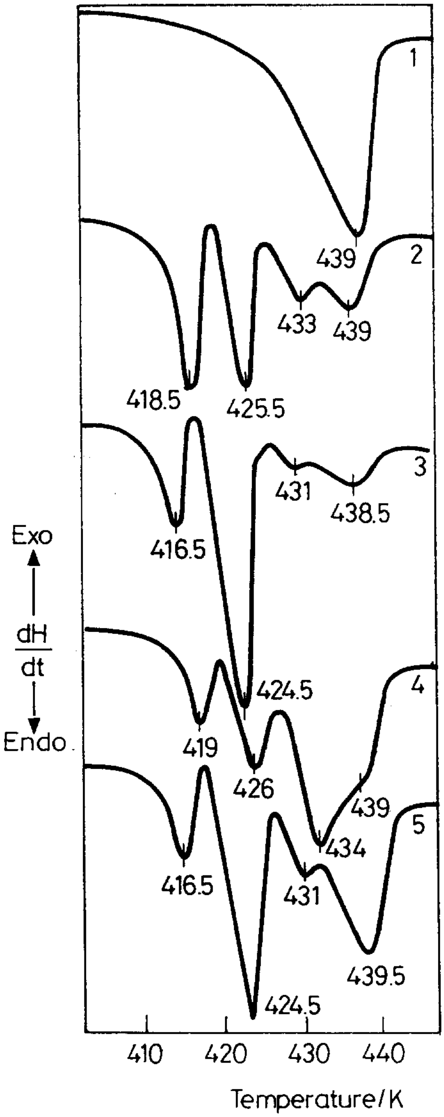


**Fig. 3** DSC analysis of polypropylene TI 902 (fiber) with 1 wt% of pigment Yellow 83 cooling rate: 10 K $\text{min}^{-1}$ (2, 4), 80 K $\text{min}^{-1}$ (3, 5). Pigmentation of polypropylene by concentrates: 1. 25% pigment, 6% MGS, $T_{\text{homog}}$ = 145°C, first heating; 2., 3. sample 1., second heating; 4. 25% pigment, 6% MGS, $T_{\text{homog}}$=215°C, 5. sample 4., second heating

## Results and discussion

Typical curves for pure polypropylene and for polypropylene containing pigment and dispersant are given in Figs 1–5. The melting points $T_m$ of the original samples (first heating) in all cases range from 438 to 440 K and the curve exhibits one maximum. After crystallization of the sample in a calorimeter, depending on the conditions, the type of pigment and dispersant and their contents, one obtains thermal curves exhibiting two maxima, as in the case of pure polypropylene (Fig. 1) or for some samples containing the pigment Yellow 83 (Fig. 2). Similar curves have been reported relatively frequently by numerous authors [5, 7]. Thermal curves of polypropylene containing the pigment Red 177 (in all cases) or Yellow 83 (only under certain conditions) exhibit

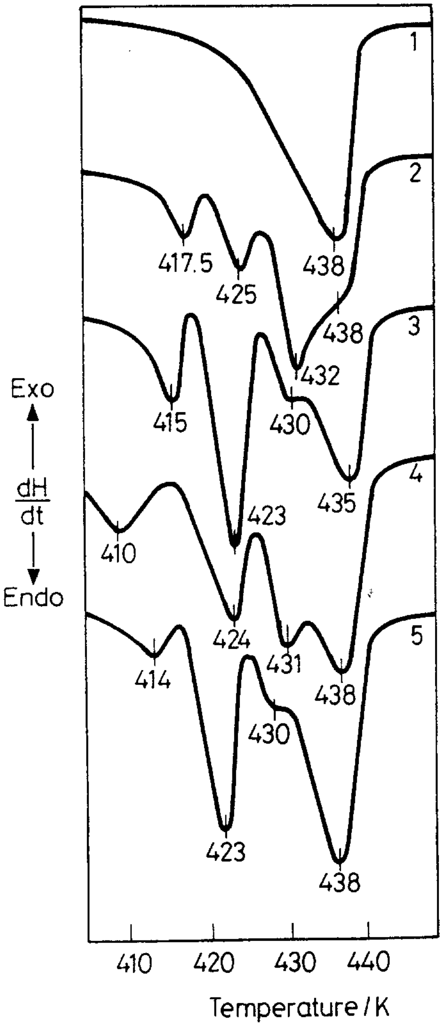


**Fig. 4** DSC analysis of polypropylene TI 902 (fiber) with 1 wt% of pigment Red 177, cooling rate: 10 K min$^{-1}$ (2,4), 80 K min$^{-1}$ (3,5). Pigmentation of polypropylene by concentrates: 1. 15% pigment, 8% N310, $T_{homog}$=90°C; 2., 3. sample 1., second heating; 4. 25% pigment, 8% NSPO, $T_{homog}$=190°C; 5. sample 4., second heating

marked maxima with melting points of from 408 to 440 K. Figures 2–5 and Table 2 indicate four transition regions, with the following characteristic temperature intervals: I. 415–417 K, II. 423–425 K, III. 430–432 K and IV. 438–439 K.

The formation of structural modifications with lower melting point under the given experimental conditions is proportional to the cooling rate (Figs 2–5). At a higher cooling rate, the probability of formation of these modifications is higher, which is in accordance with the literature [5].

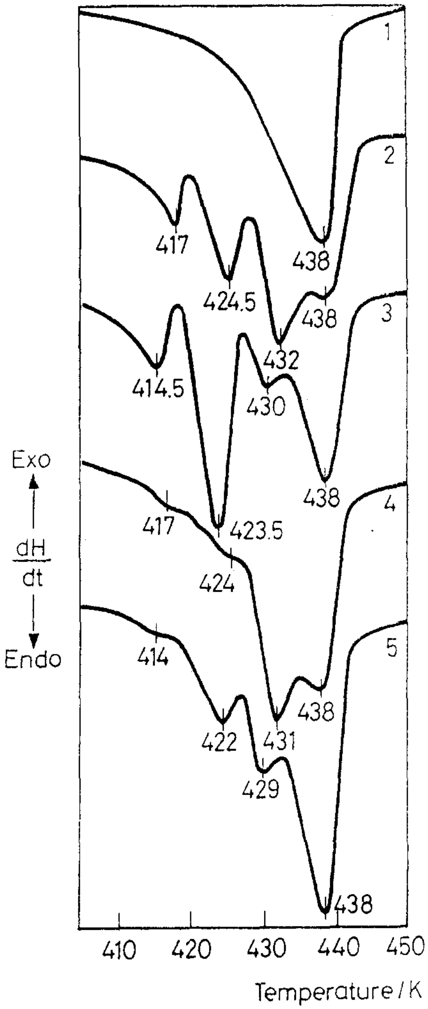


**Fig. 5** DSC analysis of polypropylene TI 902 (fiber) with 1 wt% of pigment Red 177, cooling rate: 10 K min$^{-1}$ (2,4), 80 K min$^{-1}$ (3,5). Pigmentation of polypropylene by concentrates: 1. 15% pigment, 4% N310, $T_{\mathrm{homog}}$=190°C; 2., 3. sample 1., second heating; 4. 25% pigment, 4% NSPO, $T_{\mathrm{homog}}$=90°C; 5. sample 4., second heating

**Table 2** Experimental conditions for pigment Red 177

| Denotation | Factor | Unit | –1 | +1 |
|---|---|---|---|---|
| A | Concentration of dispersing agent | wt % | 4 | 8 |
| B | Type of dispersing agent | $\gamma$ [mNm$^{-1}$] | 30 | 35 |
| C | Concentration of pigment | wt % | 15 | 25 |
| D | Temperature of mixing | °C | 90 | 190 |
| E | Rate of cooling | K min$^{-1}$ | 10 | 80 |

**Table 3** Characteristic of melting and crystallization temperatures of polypropylene containing pigments Red 177 and Yellow 83 (1.0 wt%) for the cooling rate 80 K min$^{-1}$

| No. | P. Red 177, K | | | | | | P. Yellow 83, K | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_m$ | $T_c$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $T_m$ | $T_c$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ |
| PP | 439 | 389 | – | – | – | – | 439 | 389 | – | – | – | – |
| 1 | 438 | 387 | 418 | 425 | 433 | 439 | 439 | 389 | – | – | 430 | 437 |
| 2 | 438 | 386 | 417 | 425 | 432 | 437 | 440 | 390 | – | – | 433 | 440 |
| 3 | 437 | 385 | 417 | 424 | 432 | 438 | 439 | 388 | – | – | 433 | 438 |
| 4 | 438 | 387 | 417 | 425 | 432 | 439 | 440 | 389 | 415 | 425 | 431 | 438 |
| 5 | 438 | 384 | 417 | 424 | 432 | 439 | 439 | 389 | 416 | 424 | 431 | 439 |
| 6 | 438 | 385 | 417 | 423 | 430 | 439 | 439 | 391 | – | – | 432 | 439 |
| 7 | 437 | 385 | 416 | 423 | 431 | 437 | 439 | 391 | – | – | 431 | 438 |
| 8 | 437 | 384 | 416 | 424 | 431 | 438 | 439 | 389 | 415 | 424 | 431 | 438 |
| 9 | 438 | 385 | 418 | 425 | 433 | 439 | 439 | 390 | – | – | 431 | 438 |
| 10 | 438 | 386 | 416 | 424 | 431 | 438 | 441 | 389 | – | – | 431 | 438 |
| 11 | 438 | 385 | 417 | 424 | 432 | 438 | 440 | 385 | 416 | 424 | 431 | 439 |
| 12 | 437 | 386 | 417 | 424 | 432 | 438 | 439 | 387 | – | – | 431 | 436 |
| 13 | 438 | 385 | 416 | 424 | 431 | 439 | 439 | 388 | – | 424 | 431 | 438 |
| 14 | 438 | 384 | 416 | 424 | 431 | 438 | 440 | 388 | 416 | 425 | 431 | 440 |
| 15 | 437 | 386 | 416 | 423 | 431 | 438 | 439 | 389 | 416 | 425 | 431 | 438 |
| 16 | 438 | 384 | 416 | 423 | 430 | 438 | 439 | 390 | – | – | 431 | 440 |

A comparison of the curves from the second heating cycle with those for the original samples (oriented polymer) reveals that the formation of modifications with lower melting point is suppressed by the orientation of the macromolecules in the sample preparation. Also, in the case of the significant selective influence of the pigment Red 177, the original curve does not exhibit individual maxima at lower temperatures, though the beginning of the endothermic process already appears at 413 K (Figs 4 and 5). This could be evidence of the presence of less ideal structural modifications in the original oriented sample, which should be quantified.

Table 3 reveals a generally higher nucleation effect of the pigment Yellow 83 in comparison with Red 177, manifested by a higher temperature $T_m$, a substantially higher crystallization temperature $T_c$ and a partially higher temperature $T_4$. In contrast, Red 177 has a higher selective influence on the formation of the β-structural modification and other less ideal polypropylene structures, which is not the case for Yellow 83, whose selective effect often does not appear at all under the given experimental conditions.

The transition region 438–440 K (IV) represents the presence of a stable α-modification, while the transition at 423–425 K (II) is characteristic of the β-modification. The $\alpha_2$-modification with a melting point of 442 K, formed by recrystallization of the β-modification [5], was not observed in our experiment. Transitions with melting points ranging from 430 to 432 K can be ascribed to either α- or β-modifications. Oriented polypropylene samples with one maximum and melting points 431–434 K can be obtained, for instance, at higher cooling rates at orientation or by using one of the pigments with a nucleation effect [17].

Additionally, it follows from Figs 2–5 and Tables 4 and 5 that the influence of nucleation additives on the formation of structural modifications depends strongly on the type and concentration of the dispersant and on the conditions of preparation of the nucleation additive (pigment concentrate). A higher selective influence of the pigment Red 177 on the formation of modifications with lower melting point is demonstrated by dispersant with a higher dispersing effect, i.e. MGS and NSPO for the pigments Yellow 83 and Red 177, respectively.

From analyses of the results in Tables 4 and 5, where enthalpies of individual transitions are given for the pigment Red 177 for cooling rates of 10 and 80 K $\mathrm{min}^{-1}$, it follows that the selectivity of β-nucleation is generally higher for a lower (15%) pigment concentration and for a higher temperature of homogenization (463 K), when NSPO is used as dispersant in the preparation of a concentrate. These conditions of preparation ensure a better contact of the polymer with the surface of the solid particles (manifested significantly especially for samples 25 and 26), due to the diphilic character of the NSPO molecule, its possible orientation on the interface and a good compatibility with polypropylene. The more polar dispersant N310 (a copolymer of ethylene oxide and propylene oxide) is less compatible with polypropylene and has a less selective effect and the selectivity of formation of the β-modification does not appear at all for the pigment Yellow 83 (Fig. 2, Table 3).

Moreover, Figs 2–5 and Tables 4 and 5 show that the structural modifications are relatively stable and no apparent recrystallization occurs. Despite the fact that the expression of enthalpies in a multistage melting process is very

**Table 4** Enthalpies of structural modifications of polypropylene containing pigment Red 177 according to Table 1, cooling rate 10 K min$^{-1}$

| No. | $\Delta H_1$ / | $\Delta H_2$ / | $\Delta H_3$ / | $\Delta H_4$ / | $Z_1$ | $Z_2$ | $\sum\Delta H_i$ / | Code for |
|---|---|---|---|---|---|---|---|---|
| | J g$^{-1}$ | | | | | | J g$^{-1}$ | factor plan |
| 1 | 25.8 | 30.0 | 30.0 | 25.7 | 3.34 | 1.00 | 111.5 | (1) |
| 2 | 14.2 | 22.1 | 43.2 | 32.7 | 2.43 | 0.48 | 112.2 | a |
| 3 | 7.3 | 12.1 | 34.2 | 24.7 | 2.17 | 0.33 | 78.3 | b |
| 4 | 14,2 | 19.5 | 32.7 | 24.7 | 2.69 | 0.59 | 91.1 | ab |
| 5 | 16.8 | 29.0 | 43.2 | 37.9 | 2.35 | 0.56 | 126.9 | c |
| 6 | 22.1 | 39.5 | 24.7 | 26.9 | 3.21 | 1.19 | 113.2 | ac |
| 7 | 14.7 | 24.2 | 28.9 | 24.7 | 2.74 | 0.73 | 92.5 | bc |
| 8 | 11.5 | 19.5 | 31.1 | 30.0 | 2.07 | 0.51 | 92.1 | abc |
| 9 | 29.5 | 39.0 | 33.2 | 30.0 | 3.39 | 1.08 | 131.7 | d |
| 10 | 19.5 | 29.0 | 34.2 | 27.4 | 3.02 | 0.79 | 110.1 | ad |
| 11 | 14.2 | 24.2 | 34.8 | 29.0 | 2.52 | 0.60 | 102.2 | bd |
| 12 | 17.4 | 24.7 | 24.7 | 22.1 | 3.02 | 0.90 | 88.9 | abd |
| 13 | 26.3 | 43.7 | 16.3 | 23.2 | 3.72 | 1.77 | 109.5 | cd |
| 14 | 14.2 | 27.9 | 30.0 | 33.7 | 2.14 | 0.66 | 105.8 | acd |
| 15 | 11.5 | 19.5 | 29.5 | 25.8 | 2.34 | 0.56 | 86.3 | bcd |
| 16 | 10.5 | 16.8 | 21.0 | 21.0 | 2.30 | 0.65 | 69.3 | abcd |

complex, the good agreement of $\Sigma\Delta H_i$ in Tables 4 and 5 for the same samples at often very different values of $\Delta H_1$–$\Delta H_4$ indirectly offers the possibility of unambiguous assignment of these enthalpies to definite structural modifications. The tendency towards the formation of less stable structures is seen from the ratio $Z_1=(\Delta H_1+\Delta H_2+\Delta H_3)/\Delta H_4$ or $Z_2=(\Delta H_1+\Delta H_2)/(\Delta H_3+\Delta H_4)$ in Tables 4 and 5. Higher numerical values correspond to a higher selective efficiency of the nucleation agent.

If the ratio $Z_1=(\Delta H_1+\Delta H_2+\Delta H_3)/\Delta H_4$ or $Z_2=(\Delta H_1+\Delta H_2)/(\Delta H_3+\Delta H_4)$ is taken as a measure of the selectivity of formation of structural modifications with lower melting point for the pigment Red 177, an increased selectivity for the cooling rate of 80 K min$^{-1}$ follows (Fig. 6). The values of $Z_2$ are higher in the whole range of $Z_1$ for the cooling rate of 80 K min$^{-1}$.

The linearity of the dependence $Z_2=f(Z_1)$ (Fig. 6) supports the approach that, during a multistage process of melting of structural modifications, evident recrystallization does not occur between modifications (I+II) and (III+IV). The slope of this plot corresponds with the cooling rates of the sample before the second heating in the DSC analysis. We can conclude that, at constant cooling, the ratio of structural modifications expressed by means of $Z_1$ and $Z_2$ is constant, despite different absolute values of $\Delta H_i$.

**Table 5** Enthalpies of structural modifications of polypropylene containing pigment Red 177 according to Table 1, cooling rate 80 K min$^{-1}$

| No. | $\Delta H_1$ | $\Delta H_2$ | $\Delta H_3$ | $\Delta H_4$ | $Z_1$ | $Z_2$ | $\sum \Delta H_i$ | Code for |
|---|---|---|---|---|---|---|---|---|
| | J g$^{-1}$ | | | | | | J g$^{-1}$ | factor plan |
| 17 | 20.5 | 50.1 | 13.1 | 24.7 | 3.39 | 1.87 | 108.4 | de |
| 18 | 19.5 | 56.4 | 14.2 | 29.0 | 3.11 | 1.76 | 119.1 | ae |
| 19 | 6.3 | 14.2 | 24.2 | 32.7 | 1.37 | 0.36 | 77.4 | be |
| 20 | 15.2 | 35.3 | 15.2 | 27.4 | 2.40 | 1.19 | 93.1 | abe |
| 21 | 13.1 | 31.1 | 31.6 | 48.5 | 1.56 | 0.55 | 124.3 | ce |
| 22 | 16.8 | 56.4 | 14.2 | 24.7 | 3.54 | 1.88 | 112.1 | ace |
| 23 | 8.9 | 16.8 | 24.7 | 33.2 | 1.52 | 0.44 | 83.4 | bce |
| 24 | 7.9 | 16.8 | 26.3 | 37.9 | 1.36 | 0.38 | 88.9 | abce |
| 25 | 27.4 | 74.9 | 8.9 | 24.7 | 4.50 | 3.04 | 135.1 | de |
| 26 | 20.0 | 60.1 | 7.3 | 26.3 | 3.32 | 2.38 | 113.7 | ade |
| 27 | 13.1 | 37.9 | 18.4 | 34.2 | 2.03 | 0.97 | 103.6 | bde |
| 28 | 15.2 | 43.5 | 10.5 | 21.0 | 3.30 | 1.87 | 90.2 | abde |
| 29 | 16.3 | 48.5 | 9.4 | 25.3 | 2.93 | 1.87 | 99.5 | cde |
| 30 | 11.5 | 34.2 | 17.9 | 39.0 | 1.62 | 0.81 | 102.6 | acde |
| 31 | 8.9 | 20.5 | 21.6 | 30.0 | 1.70 | 0.57 | 81.0 | bcde |
| 32 | 8.4 | 16.8 | 14.2 | 24.7 | 1.60 | 0.65 | 64.1 | abcde |

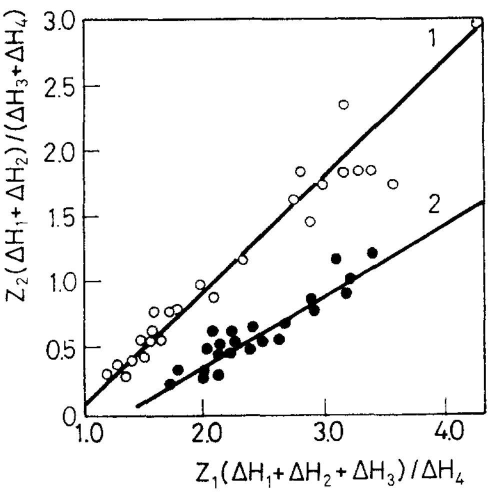


**Fig. 6** The plot of enthalpies of various structures of polypropylene with 1 wt% of pigment Red 177 $(\Delta H_1+\Delta H_2)/(\Delta H_3+\Delta H_4)$ *vs.* $(\Delta H_1+\Delta H_2+\Delta H_3)/\Delta H_4$ at a cooling rate of 80 K min$^{-1}$ (1) and 10 K min$^{-1}$ (2)

On the basis of the above-mentioned analyses of the experimental results for the pigment Red 177, it was inevitable to use the method of factorial two-level experiments to evaluate the influence of the individual factors on the crystallization process. We evaluated the ratios of enthalpies $Z_1$ and $Z_2$. The conditions for the individual experiments and the values of the output quantities are listed in Tables 4 and 5. The letter in the trial code is a factor at the level +1, while other factors are at the level –1. The code (1) means a trial involving all factors investigated at the level –1.

Values of $Z_1$ and $Z_2$ were treated by the method of scattering analysis with decomposition into components with one level of freedom. With regard to the great volume of experimental work, the whole experiment was not repeated. Since the probability of significance of higher interactions is very small, the share of variation corresponding to interactions of fourth and higher orders was considered to be independent of the change in factors and it was employed as an estimation of the residual scatter. To facilitate a survey, interactions of fourth and higher orders are not given in Tables 6 and 7.

**Table 6** Scattering analysis for the ratio of enthalpies $Z_1$

| Factor | Value of the effect | Scatter | F Criterium | F criteria, crit. value | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 95% | 90% | 80% | 75% | 70% |
| | | | | 5.99 | 3.77 | 2.07 | 1.62 | 1.29 |
| A | –0.0275 | 0.0061 | 0.02 | | | | | |
| B | –0.7775 | 4.8361 | 19.59 | + | + | + | + | + |
| C | –0.5813 | 2.7038 | 10.95 | + | + | + | + | + |
| D | 0.2625 | 0.5512 | 2.23 | | | ? | + | + |
| E | –0.2625 | 0.5513 | 2.23 | | | ? | + | + |
| AB | 0.3213 | 0.8256 | 3.34 | | ? | + | + | + |
| AC | 0.1000 | 0.0800 | 0.32 | | | | | |
| AD | –0.3238 | 0.8385 | 3.4 | | ? | + | + | + |
| AE | 0.1838 | 0.2701 | 1.09 | | | | | ? |
| BC | 0.0975 | 0.0760 | 0.31 | | | | | |
| BD | 0.0487 | 0.0190 | 0.08 | | ? | + | + | + |
| BE | –0.3088 | 0.7626 | 3.09 | | | ? | + | + |
| CD | –0.2625 | 0.5512 | 2.23 | | | | | |
| CE | –0.3675 | 1.0804 | 4.38 | | + | + | + | + |
| DE | 0.0812 | 0.0528 | 0.21 | | | | | |
| Residual | | 0.2469 | | | | | | |

Notation: + the factor has a significant influence with the given percentage of probability, ? the significance of the influence of the factor is questionable

**Table** 7 Scattering analysis for the ratio of enthalpies $Z_2$

| Factor | Value of the effect | Scatter | F Criterium | F criteria, crit. value | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 95% | 90% | 80% | 75% | 70% |
| | | | | 5.99 | 3.77 | 2.07 | 1.62 | 1.29 |
| A | 0.0244 | 0.0048 | 0.04 | | | | | |
| B | –0.6494 | 3.3735 | 26.55 | + | + | + | + | + |
| C | –0.3394 | 0.9214 | 7.25 | + | + | + | + | + |
| D | 0.3344 | 0.8945 | 7.04 | + | + | + | + | + |
| E | 0.5119 | 2.0961 | 16.50 | + | + | + | + | + |
| AB | 0.2481 | 0.4925 | 3.88 | | ? | + | + | + |
| AC | –0.0644 | 0.0332 | 0.26 | | | | | |
| AD | –0.2431 | 0.4729 | 3.72 | | ? | + | + | + |
| AE | 0.1319 | 0.1391 | 1.09 | | | | | |
| BC | 0.0494 | 0.0195 | 0.15 | | | | | |
| BD | –0.0544 | 0.0237 | 0.19 | | | | | |
| BE | –0.3169 | 0.8033 | 6.32 | ? | + | + | + | + |
| CD | –0.1719 | 0.2363 | 1.86 | | | | ? | + |
| CE | –0.4469 | 1.5976 | 12.57 | + | + | + | + | + |
| DE | 0.1319 | 0.1391 | 1.09 | | | | | |
| Residual | | 0.1271 | | | | | | |

Notation: + the factor has a significant influence with the given percentage of probability, ? the significance of the influence of the factor is questionable

It follows from the results in Tables 6 and 7 that changes in the crystallization character are better described by the ratio $Z_2$ than by the ratio $Z_1$. However, in both cases, the most significant influence is that of factor *B*, i.e. the polarity and/or type of the dispersant. Due to the negative value of the effect, it is obvious that the change in the dispersant from an ester of stearic acid and polypropylene oxide (–1) to a copolymer of ethylene oxide and propylene oxide (+1) decreases the share of crystalline structures I and II or of I, II and III. In contrast, a significant increase in the ratio of structures I and II with respect to structures III and IV can be attained by an increase in the rate of sample cooling. In the case of $Z_2$, this factor (cooling rate) seems to be the second most significant as concerns the influence on the resulting share of the structures discussed. In comparison with factors *B* and *E*, factors *C* and *D* (concentration of pigment and concentration of polymer) have a 1/2–1/3 share in the control of the proportional share of the individual structures. The actions of factors *C* and *D* are approximately the same, but in opposite directions (factor *C* decreases the share of structures I and II, while factor *D* increases this share).

As regards the interaction influences, interaction *CE* is more significant in the case of the ratio $Z_2$; other interactions are insignificant, or significant but with a lower percentage of probability.

A comparison of the significance of the influence of factor *E* (cooling rate) on $Z_1$ and $Z_2$ reveals that, whereas the cooling rate greatly influences the ratio $Z_2$, which increases with increase in rate, the ratio $Z_1$ is not significantly affected by this factor, even at the level of 80% probability.

On this basis, structural modifications I and II are presumed to have a similar character and to correspond to the β-modification of polypropylene. Similar structures III and IV can be ascribed to the α-modification, while, depending on the experimental conditions, structures I and II are formed to the detriment of structures III and IV.

From this point of view, the ratio $Z_2$ seems to be more suitable for an assessment of the nucleation selectivity than the ratio $Z_1$.

## References

1 A. Turner-Jones, J. M. Aizlewood and D. R. Becket, Makromol. Chem., 75 (1964) 134.
2 W. Ullmann and J. H. Wendorf, Progress Colloid. Polymer Sci., 66 (1979) 25.
3 K. H. Moos and C. Tilger, Angew. Makromol. Chem., 94 (1981) 213.
4 Guan-yi Shi, Bin Huang and Jung-yun Zhang, Makromol. Chem. Rapid Commun., 5 (1984) 573.
5 J. Varga, β-Modifikaciya polypropylena i dvuchkomponentnye sistemy na ego osnove. In: Proc. of the Conference: 'Modification of Polymers', CHTF STU, Bratislava-Smolenice, 1987, p. 164.
6 J. Menczel and J. Varga, J. Thermal Anal., 28 (1985) 161.
7 A. Celi et al., European Polymer J., 29 (1993) 1037.
8 J. J. Lin et al., J. Appl. Polymer Sci., 47 (1993) 2111.
9 B. Fillon et al., J. Polym. Sci., Part B, Polymer Phys., 31, 3 (1993) 1407.
10 D. D. Filho and C. M. F. Oliveira, Makromolekulare Chemie – Macromolecular Chemistry and Physics, 194 (1993) 279, 285.
11 J. Varga and J. Karger-Kocsis, Polymer Bulletin, 30 (1993) 105.
12 G. B. A. Lim and D. R. Lloyd, Polymer Engn. Sci., 33 (1993) 522.
13 C. Y. Kim, Y. C. Kim and S. C. Kim, Polymer Engn. Sci., 33 (1993) 1445.
14 J. O. Iroh and J. P. Berry, Polymer, 34 (1993) 4747.
15 D. T. Quillin, D. F. Caufield and J. A. Kontsky, J. Appl. Polym. Sci., 50 (1993) 1187.
16 D. C. Montgomery, Design and Analysis of Experiments, J. Willey & Son, New York 1991, p. 649.
17 K. Marcinčin, A. Marcinčin and E. Pašková, Proc. of the Conference: 'Modified Polymers', 7. IUPAC Conference, Bratislava, Slovak Republic, 1988, p. 47.