

# Nucleating Activity of the Quinacridone and Phthalocyanine Pigments in Polypropylene Crystallization

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**ABSTRACT:** The nucleating ability of two organic pigments, quinacridone and phthalocyanine, in nonisothermal polypropylene (PP) crystallization was investigated. The investigations were carried out using DSC and polarizing microscopy. The efficiency of pigments in the nucleation process was determined in a simple test comparing the crystallization temperature of the PP-containing pigments with respect to the pure polymer. Both pigments revealed good nucleating activity. In the presence of pigments the increment of the crystallization temperature and the increase

of nucleation rate were observed. The nucleating efficiency of pigments was confirmed in investigations of the obtained structure. The nucleating activity of pigments was explained by their features fulfilling several requirements for good nucleating agents. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3957–3964, 2003

**Key words:** polypropylene (PP); crystallization; nucleation; pigments; differential scanning calorimetry (DSC)

## INTRODUCTION

The coloring of plastics can be achieved easily by adding a small percentage of pigments into the bulk of plastic resin. Through adding of pigments into the polymer melt different products such as moldings, films, and fibers may be obtained.

The application of pigments is a great importance especially for polypropylene (PP) fibers. Because of their good properties, low cost, and light weight, PP fibers have in recent years become increasingly appreciated and have undergone the greatest worldwide growth of all the major synthetic fibers.

However, because of their nonpolar structure PP fibers do not have any affinity for dyestuffs applied by classical dyeing methods. For this reason most PP fibers are colored during spinning with pigments.

During fiber formation pigments added to the polymer melt occur inside the cooled stream and can participate in a process of crystallization that leads to the structural formation of fibers. Pigments present in a crystallized melt can act as nucleating agents, providing a foreign surface and reducing the free energy of formation of a new polymer nucleus. As a result of the nucleating effect, an increase of the crystallization temperature, enhancement of the crystallization rate,

and a decrease in the size of spherulites can be observed.

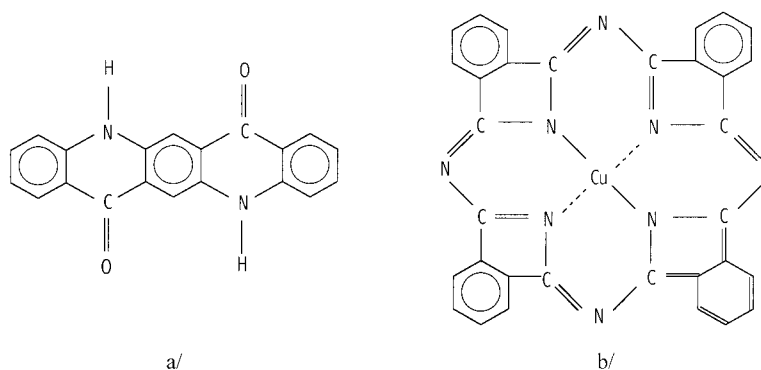
The crystallization of nucleated polypropylene has been the focus of intensive investigation for a number of years. Binsbergen<sup>1</sup> and Beck and Ledbetter,<sup>2</sup> in their investigations of the nucleating ability of many additives, showed that the most active are benzoate derivatives, hydrazones, phosphonic and phosphorous acids and their salts, aluminum salts of aromatic and cycloaliphatic acids, colloidal silver, and gold. Further investigations revealed the good nucleating ability of benzoic acid,<sup>3</sup> sodium benzoate,<sup>4</sup> alkali dehydroabi-  
etate,<sup>5</sup> organic phosphate derivatives,<sup>6</sup> and talc.<sup>7</sup>

Binsbergen reported that good nucleating agents are insoluble in the PP melt or crystallize earlier at higher temperature before the crystallization of PP. Further investigations revealed that sorbitol derivatives,<sup>8,9</sup> substances that dissolve in the polypropylene melt at the melting temperature, also possess a very good nucleating ability.

Most nucleating agents nucleate the monoclinic  $\alpha$ -form of PP, the thermodynamically stable crystalline modification usually obtained under common processing conditions. Several nucleating agents nucleate the more rarely encountered  $\beta$ -form.<sup>10–12</sup>

Among many nucleants for PP some pigments are mentioned. Pigments possess a crystalline structure consisting of tiny molecular crystals. Crystal sizes vary from pigment to pigment. The shape of crystals can be strongly differentiated and can assume cubes, platelets, needles, or bars, as well as a number of irregular shapes.<sup>13</sup> Most pigments are insoluble in the PP melt and exist in a finely dispersed state. In some

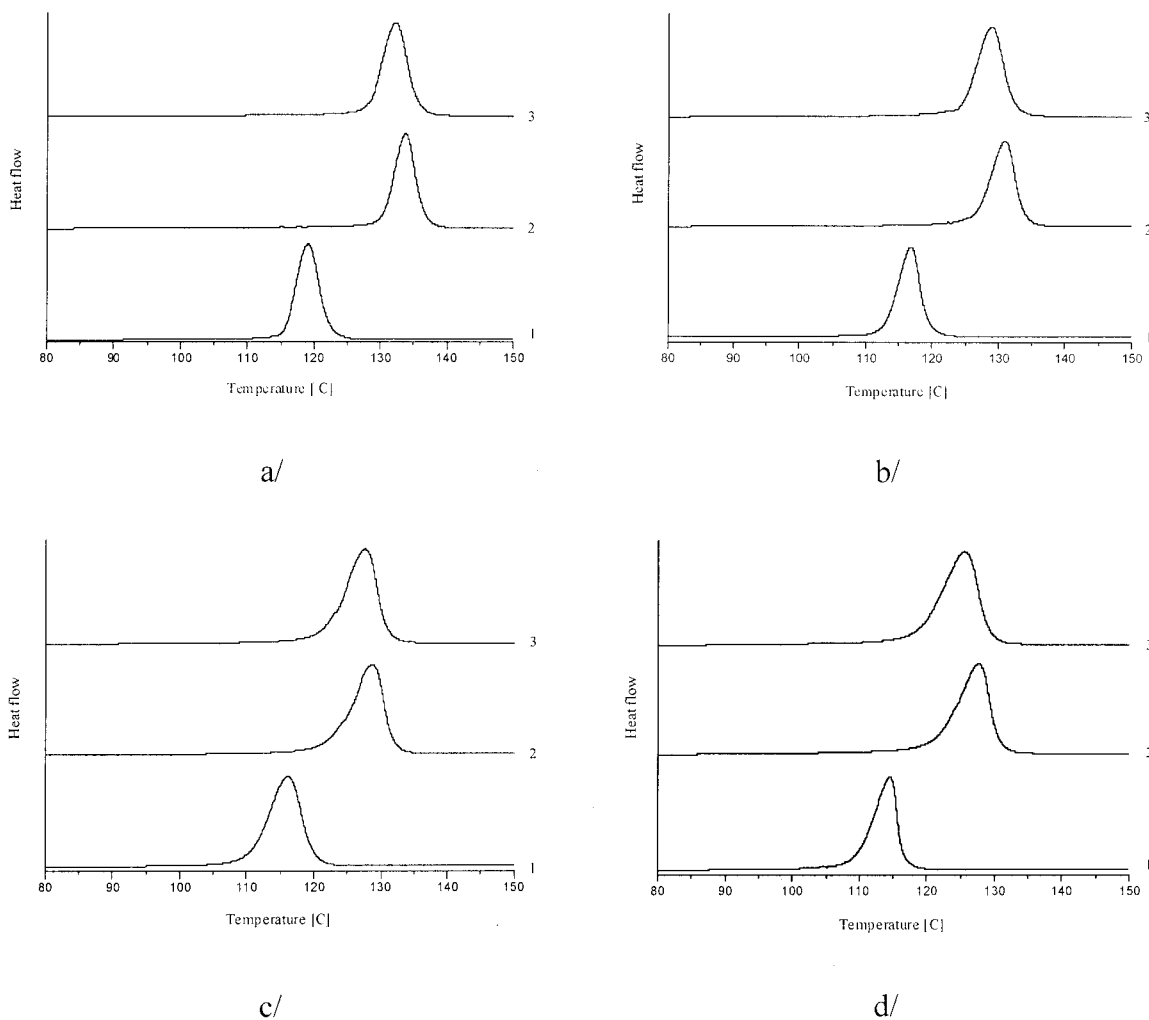
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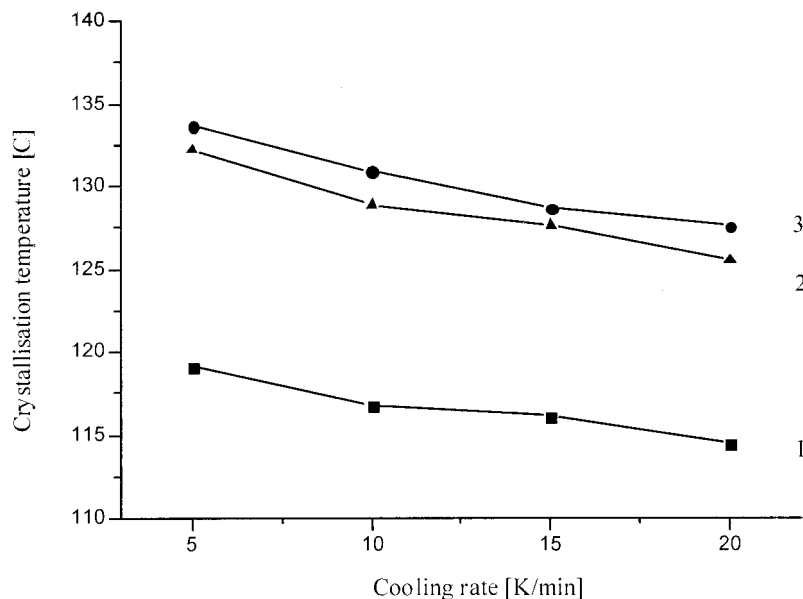
**Figure 1** Chemical structures of: (a) quinacridone; (b) phthalocyanine.

cases chemically identical molecules of pigments can be arranged into different crystal lattice structures. The different polymorphic forms of pigments provide surfaces that can match with the PP chains, thus enabling the epitaxial growth of the PP crystals.

The nucleation ability of pigments in PP crystallization is well known in the case of a quinacridone pigment.<sup>14,15</sup> For many years the  $\gamma$ -form of quinacridone has been known as one of the best nucleants of the  $\beta$ -form of polypropylene. During crystallization in the



**Figure 2** DSC curves for polypropylene cooled at: (a) 5 K/min; (b) 10 K/min; (c) 15 K/min; (d) 20 K/min [(1) iPP; (2) iPP + Q; (3) iPP + Pht].



**Figure 3** Crystallization temperature as a function of the cooling rate: (1) iPP; (2) iPP + Q; (3) iPP + Pht.

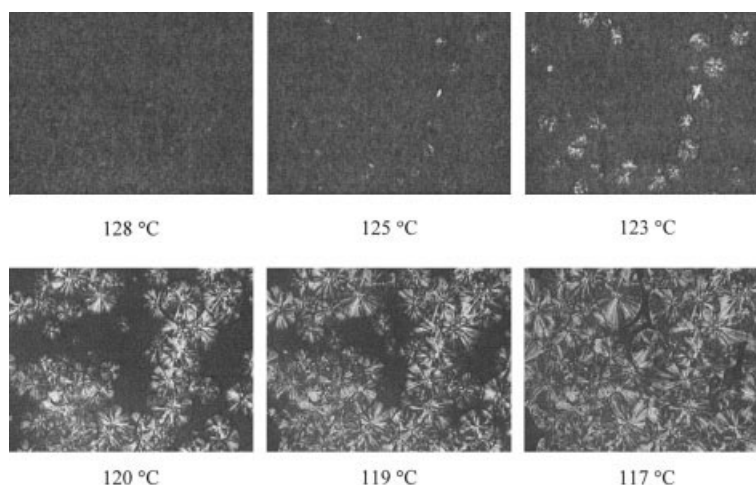
presence of quinacridone pigment a structure containing a high amount of the  $\beta$ -modification was observed. By addition of this pigment, films,<sup>16,17</sup> injection moldings,<sup>18</sup> and fibers<sup>19</sup> with high content of the  $\beta$ -form were obtained. The nucleating efficiency of other pigments is less known.

The nucleating ability of pigments is of great importance in the proper choice of formation parameters of PP fibers.<sup>20,21</sup> This study presents the nucleating efficiency of two organic pigments, quinacridone and phthalocyanine, commonly used for coloration of PP fibers. The nucleating efficiency of both pigments was evaluated during the nonisothermal crystallization of isotactic polypropylene carried out at different cooling rates.

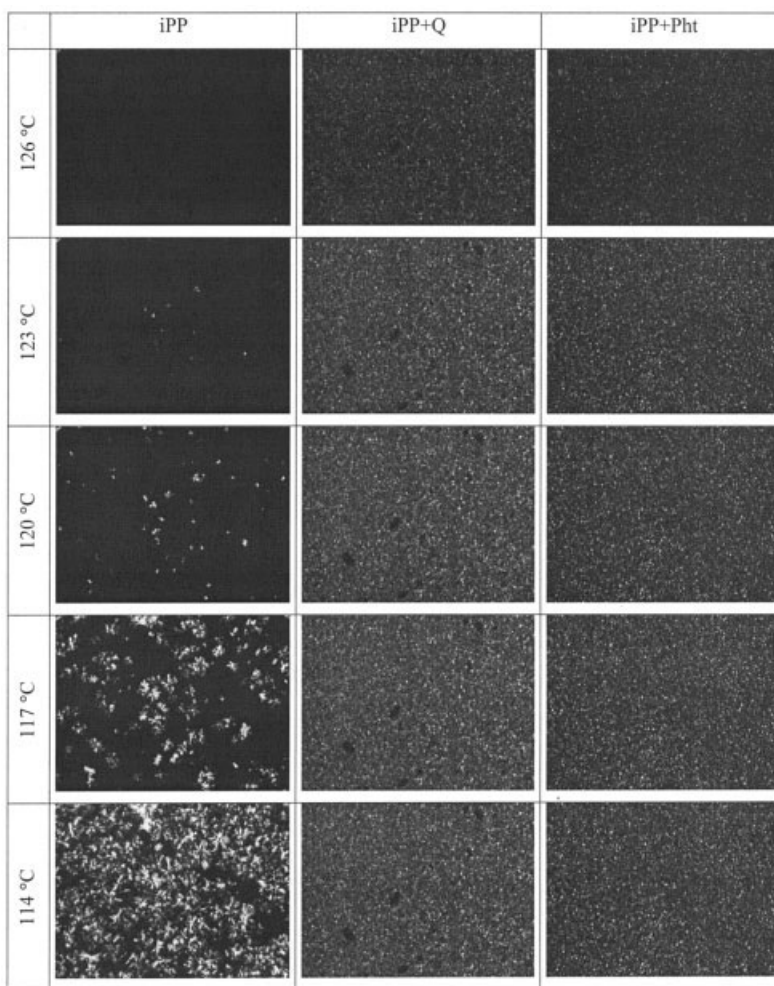
## EXPERIMENTAL

The investigations were performed for two organic pigments: the quinacridone pigment [Pigment Violet 19, C.I. 73900 (Echtrot E3B, Hoechst, Frankfurt/Main, Germany)] and the phthalocyanine pigment [Pigment Blue 15, C.I. 74160 B (Wola Kszysztoporska, Poland)] (Fig. 1). The mechanically grinded pigments were mixed with a polymer granulate in the amount of 0.5% to the polymer mass. The commercial isotactic polypropylene Mosten 52.945 [supplied by Chemopetrol (Litrinov, Czech Republic)] was used.

The polypropylene granulate mixed with the pigment was melted and homogenized in a barrel of the



**Figure 4** Crystallization process in the pure polypropylene at the cooling rate of 5 K/min.



**Figure 5** Nonisothermal crystallization of iPP, iPP + Q, and iPP + Pht at the cooling rate of 15 K/min.

Brabender laboratory screw extruder. The mixed and filtered melt was extruded into the air.

The grinded extrudate was melted at 210°C and then kept at this temperature for 10 min. After annealing, samples were cooled in a nitrogen atmosphere at different cooling rates of 20, 15, 10, and 5 K/min. The investigations were performed by differential scanning calorimetry (DSC) using an analytical system (TA Instruments, New Castle, DE) with a calorimeter (MDSC 2920) equipped with a refrigerated cooling system.

Thermograms were registered in a temperature range from 210 to 20°C. Analysis of the thermograms was carried out using a computer program Universal V2.6D, supplied by TA Instruments.

The structure of the crystallized samples was investigated using an electron scanning microscope (JEOL JSM 5500 LV; Peabody, MA). The observations were carried out for samples sputtered with gold in a JEOL JFC 1200 ionic sputter.

The crystallization process at the same cooling rates was investigated in polarized light. The studies were

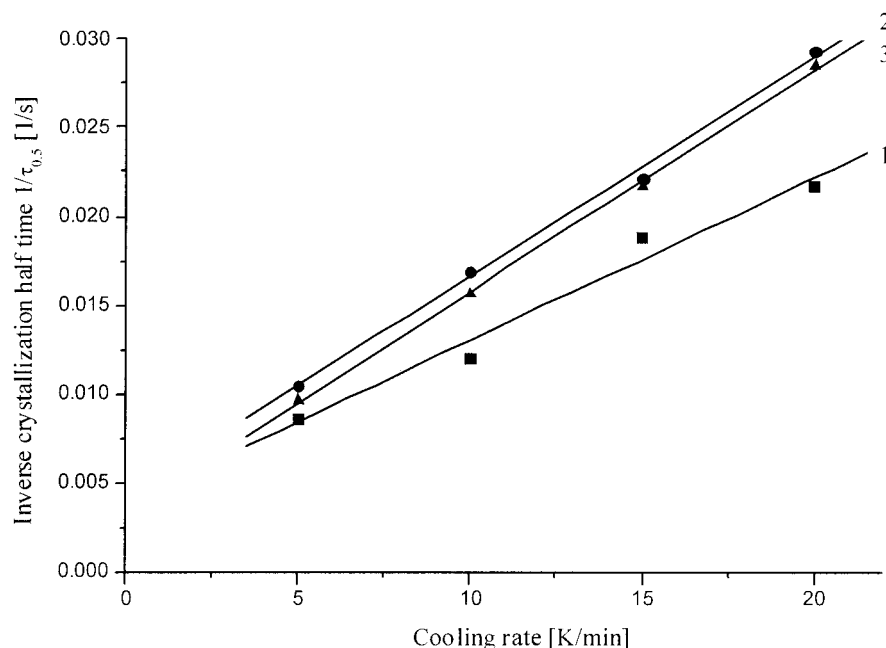
performed using a heated microscope stage Mettler Toledo FP82HT (Mettler, Greifensee, Switzerland) coupled with a control unit Mettler Toledo FP90 mounted on a polarizing microscope (Polam P-113). The course of crystallization was registered by video camera (Panasonic KR-222).

The structure of pigments was determined by the WAXS method using an X-ray diffractometer (HZG-4).

## RESULTS

Figure 2 shows the DSC cooling curves of pure polypropylene (iPP), polypropylene containing the quinacridone pigment (iPP + Q), and the phthalocyanine pigment (iPP + Pht).

In all cases a single exotherm corresponding to the crystallization process was observed. For iPP at the cooling rate of 5 K/min the crystallization starts at 127.2°C. An exothermic peak representing the temperature at maximum crystallization rate occurs at 119.1°C. For iPP + Q and iPP + Pht the peak occurs at



**Figure 6** Inverse crystallization half-time versus cooling rate: (1) iPP; (2) iPP + Q; (3) iPP + Pht.

higher temperatures of 133.7 and 132.2°C, respectively.

The increment in the crystallization temperature  $T_c$  for polypropylene containing the quinacridone compared with that of the pure polypropylene is 14.6 K. In the case of the phthalocyanine pigment the increment in  $T_c$  is slightly lower, at 13.1 K.

With an increase of the cooling rate the activation of nuclei occurs at higher supercoolings. The crystallization starts at a lower temperature and the crystallization peak moves toward lower temperatures. The shifting of the crystallization temperature to lower values at greater cooling rates, observed earlier by several investigators,<sup>22-24</sup> is attributed to kinetic effects. As the cooling rate increases the formation of the nuclei takes place at the lower temperature and a large amount of supercooling occurs before polymer crystallization.

The shifting of the crystallization peak toward lower temperatures is observed in pure polypropylene as well for PP-containing pigments. The slope of the curve of the crystallization temperature versus the cooling rate, independently of pigments, achieves a similar value and the difference in the crystallization temperature between pure PP and PP-containing pigments does not significantly change with a change of the cooling rate (Fig. 3).

The crystallization starts when the melt achieves a temperature equal to the onset temperature of crystallization  $T_o$ . In this moment in the melt the first spherulites appear. Simultaneously, with the growth of those spherulites the new spherulites are formed. The free expansion of spherulites occurs between the onset and

crystallization temperatures. At the peak temperature the impingement of spherulites is observed. The growth of spherulites is stopped and further crystallization leads to a filling of a space between spherulites (Fig. 4).

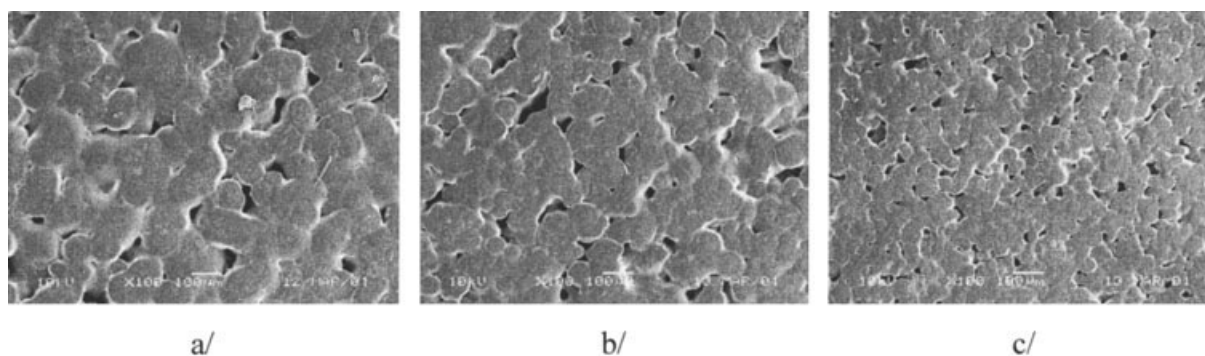
For PP-containing pigments the main part of the crystallization proceeds in the temperature above the  $T_o$  for pure PP. The addition of pigments causes crystallization to start at lower supercooling and proceeds in the range in which the pure PP still does not crystallize. In the temperature in which the crystallization of the pure PP starts the crystallization of PP-containing pigments is practically finished (Fig. 5).

Figure 6 shows a plot of the inverse of the crystallization time  $\tau_{0.5}$  versus the cooling rate.<sup>25</sup> The crystallization rate parameter determined from the slope is  $0.92 \times 10^{-3}$  for iPP,  $1.24 \times 10^{-3}$  for iPP + Q, and  $1.25 \times 10^{-3}$  for iPP + Pht.

The higher slope obtained for PP-containing pigments as well as a smaller difference between the onset and peak temperatures indicate that the crystallization rate is greater in the presence of pigments.

As a result of the crystallization process the spherulitic structure is formed. For pure PP large, round spherulites are obtained (Fig. 7).

The spherulites obtained during crystallization at the lowest cooling rate (5 K/min) possess a diameter in the range 80–100  $\mu\text{m}$ . With increasing of the cooling rate the diameter of spherulites gradually decreases (Table II). At the same time with the increase of the cooling rate the number of spherulites systematically increases.



**Figure 7** Spherulitic structure formed during the nonisothermal crystallization of the pure polypropylene cooled at: (a) 5 K/min; (b) 10 K/min; (c) 20 K/min.

For PP-containing pigments fine spherulites are obtained. The diameter of spherulites formed at the lowest cooling rate (5 K/min) is 3–5  $\mu\text{m}$  and is proportionally smaller compared with the diameter of spherulites formed in the pure PP. The number of spherulites achieves a high value, proportionally higher than that for pure PP.

## DISCUSSION

Pigments added to the crystallizing PP melt cause the crystallization temperature to move toward higher temperature. In the case of quinacridone pigment the increment of the crystallization temperature is 14.5 K for each cooling rate. For phthalocyanine pigment the increment of the crystallization temperature is about 1.5 K lower.

The increase of the crystallization temperature observed for both pigments is very high and comparable with the increase of the crystallization temperature observed for effective nucleating agents.

In the presence of pigments the nucleation rate is greater. As a consequence the overall crystallization

rate increases. The nucleation rate becomes more predominant than the spherulitic growth rate, which consequently leads to the formation of smaller spherulites.

The quinacridone and phthalocyanine pigments meet several requirements for good nucleating agents. Both pigments possess a very high heat stability (Fig. 8). The quinacridone pigment shows a weight reduction only at a temperature near 500°C. Similarly, the phthalocyanine pigment shows a weight reduction at 400°C. The minimal loss of the weight observed for this pigment in lower temperatures is caused by the presence of a small amount of impurities.

The temperature of the thermal degradation for both pigments is much higher than the temperature of the PP melt. Pigments are insoluble in the PP melt and occur in the melt in a crystalline state forming fine dispersed crystals.

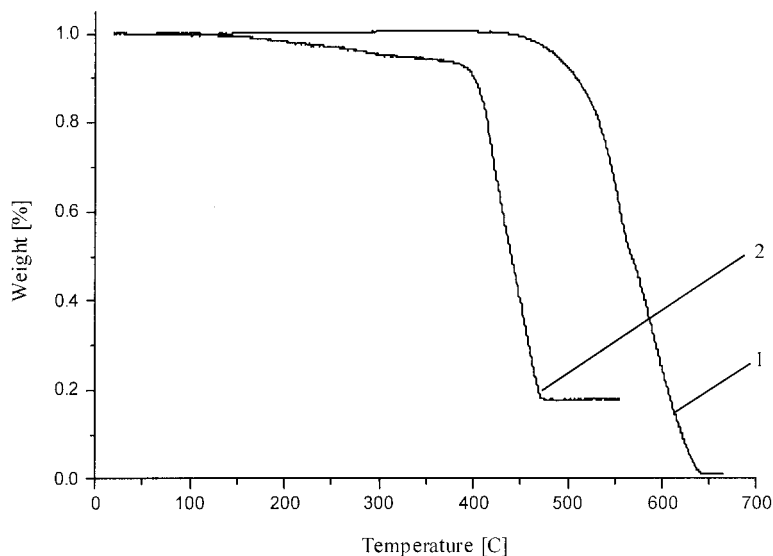
The quinacridone pigment is formed from five-ring polycyclic organic molecules of dimensions  $1.406 \times 0.52 \text{ nm}$ .<sup>26</sup> The molecule is planar with no significant departure of the carbonyl groups from a molecular plane defined by all nonhydrogen atoms. The pigment occurs in the crystalline state. Crystals are formed from molecules arranged in parallel stacks, with the molecule axis tilted to the stack axis. The stacks adopt a herringbone arrangement with individual stacks of molecules rotated with respect to each other. Each molecule is bonded through hydrogen bonds to four adjacent molecules.<sup>27</sup>

**TABLE I**  
Parameters of Crystallization of the Polypropylene Crystallized Nonisothermally at Different Cooling Rates

Sample	$\chi$ (K/min)	$T_0$ (°C)	$T_c$ (°C)	$\tau_{0.5}$ (s)	$H_f$ (J/g)
iPP	5	127.2	119.1	115	111.8
	10	124.4	116.8	83	112.0
	15	122.5	116.1	53	108.7
	20	121.8	114.5	46	105.2
iPP + Q	5	140.6	133.7	95	116.2
	10	137.3	130.9	59	112.9
	15	135.4	128.7	45	111.1
	20	133.9	127.6	34	109.3
iPP + Pht	5	139.2	132.2	103	117.3
	10	136.0	128.9	64	110.4
	15	134.4	127.6	46	110.3
	20	132.4	125.5	35	110.3

**TABLE II**  
Sizes of Spherulites Formed during the Nonisothermal Crystallization of the Polypropylene

Cooling rate (K/min)	Sizes of spherulites ( $\mu\text{m}$ )		
	iPP	iPP + Q	iPP + Pht
5	80–100	3–5	3–5
10	60–80	2–3	2–3
15	40–60	1–2	1–2
20	30–40	1–2	1–2



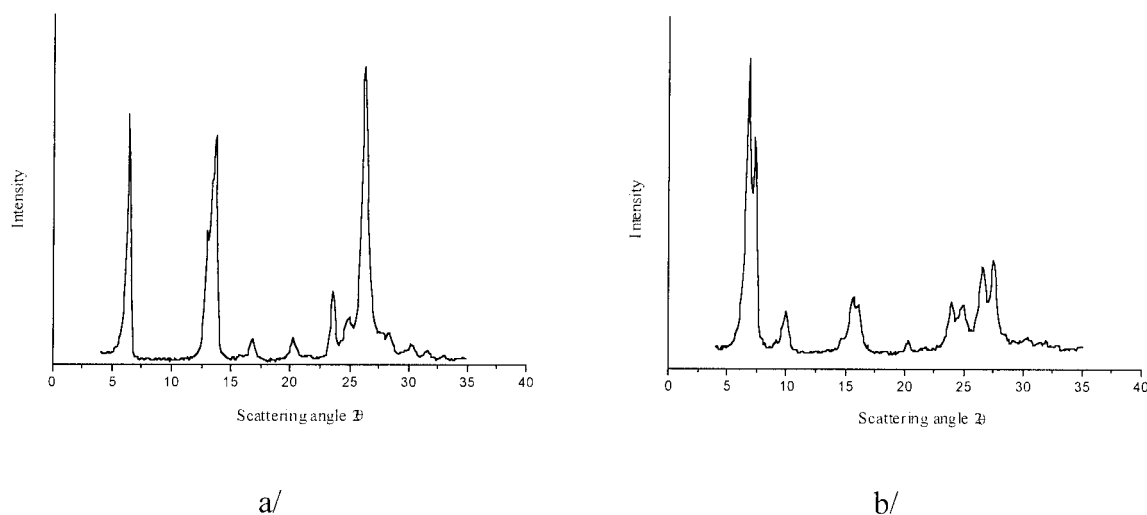
**Figure 8** TG curves for the investigated pigments: (1) quinacridone; (2) phthalocyanine.

The quinacridone can exist in several crystal modifications.<sup>26,28</sup> Most synthetic methods lead to the formation of an unstable  $\alpha$ -form. Subsequent treatments afford the more stable  $\beta$ - and  $\gamma$ -forms, most commonly used as commercial pigments.

The WAXS pattern reveals peaks characteristic for the  $\gamma$ -form of quinacridone [Fig. 9(a)]. The  $\gamma$ -form of quinacridone has a monoclinic unit cell with parameters  $a = 1.378$  nm,  $b = 0.39$  nm,  $c = 1.34$  nm, and  $\beta = 79.5^\circ$ .<sup>29</sup> The rows of the end benzene rings aligned on the surface  $bc$  of the quinacridone crystals generate a structural periodicity with a spacing of  $c/2 = 0.67$  nm. Such grating is matched by the axis repeat distance 0.65 nm of the PP helix. The nearly perfect match between those dimensions enables an epitaxial growth of the PP  $\beta$ -form crystals.<sup>30</sup>

The phthalocyanine pigment contains a tetrabenzo-porphyrane nucleus with a central copper atom. The planar molecule assumes a quadratic shape with a length of 1.3 nm and a thickness of 0.34 nm.<sup>31</sup> The pigment crystallizes, forming crystals consisting of molecules arranged in parallel stacks. Several polymorphic forms of phthalocyanine are known:  $\alpha$ -form,  $\beta$ -form, and three distorted  $\alpha$ -forms. Of these forms, only the  $\alpha$ - and  $\beta$ -forms are of commercial significance.

The pigment used in this study possesses a WAXS pattern characteristic for the  $\alpha$ -form [Fig. 9(b)]. The crystals of the  $\alpha$ -form consist of stacks of tilted molecules in parallel arrangement in adjacent stacks.<sup>13</sup> The edges of molecules form surface parallel ditches on the crystals, which enable the accommodation of straight



**Figure 9** WAXS patterns of the investigated pigments: (a) quinacridone; (b) phthalocyanine.

segments of PP chains. Such accommodation decreases the free energy of forming a critical nucleus.

### CONCLUSIONS

Both the quinacridone and the phthalocyanine pigments belong to the class of efficient nucleating additives for polypropylene. Both pigments added to the nonisothermally crystallized PP melt cause the increase of the crystallization temperature and the increase of the nucleation rate. In the presence of pigments a fine spherulitic structure is formed.

The quinacridone pigment is slightly more effective than the phthalocyanine pigment.

The high nucleating efficiency of pigments results from their features fulfilling several requirements for good nucleating agents. Both pigments possess a very high heat stability, are insoluble in polypropylene melt, and form fine dispersed crystals. On the surface of pigment crystals the nonpolar groups form parallel ditches enabling accommodation of polypropylene chains, thus reducing the free energy of the formation of the critical nucleus.

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