

# Effects of Mineral Additives on the $\beta$ -Crystalline Form of Isotactic Polypropylene

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**ABSTRACT:** Nineteen kinds of minerals, alone and in bicomponent mixtures with LaC (a mixed ternary complex of trivalent lanthanum stearate and stearin), were added to isotactic polypropylene (iPP). The influences of the minerals on the crystallographic forms of iPP were investigated. A wide-angle X-ray diffraction examination demonstrated that no mineral or LaC acting alone could induce the occurrence of the hexagonal  $\beta$ -form, whereas the bicomponent mixtures could when the mineral was a calcium compound or contained calcium compounds, whether the calcium compounds had a hexagonal crystallographic form or not. We surmise that the actual  $\beta$ -iPP substrate in such a system might be some binuclear complexes of calcium and rare earth elements with some specific ligands. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1742–1748, 2002

**Key words:** additives; crystal structures; isotactic poly(propylene)

## INTRODUCTION

Isotactic polypropylene (iPP) is known to exhibit at least three different crystalline forms: the monoclinic  $\alpha$ -form, the hexagonal  $\beta$ -form, and the triclinic  $\gamma$ -form. The  $\alpha$ -form is the most stable and common one and is the principal modification existing in almost all commercial polypropylene (PP). The  $\beta$ -form is thermodynamically metastable and difficult to obtain under normal processing conditions. A higher proportion of the  $\beta$ -form can be achieved only by melt crystallization with the aid of certain heterogeneous nucleating agents,<sup>1–10</sup> by directional crystallization in certain temperature gradients,<sup>11</sup> or from melts subject to shear.<sup>12</sup> Among these protocols, the addition of so-called  $\beta$ -form nucleating agents is an effective and practical method of obtaining or in-

creasing the  $\beta$ -form in PP. The considerable current interest in  $\beta$ -iPP nucleating agents arises from the fact that, as a result of its metastability and different spherulite architecture, the  $\beta$ -phase has some unique characteristics, such as a lower melting temperature and improved mechanical properties (especially the impact strength) in comparison with the more common  $\alpha$ -phase. The study of the chemical and structural relationships between the nucleating agents and  $\beta$ -iPP (i.e., the chemical and structural requirements these nucleating agents must meet) is an important topic in both research and industry. Although several  $\beta$ -form nucleating agents have been proposed and patented,<sup>1–10</sup> there still remains the problem of the relationship between the molecular characteristics of the nucleating agent and the formation of the  $\beta$ -form.

A large number of compounds can be used as nucleating agents of  $\alpha$ -iPP, and the nucleating ability of many kinds of these nucleating agents (i.e., substrates, from the viewpoint of epitaxial

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crystallization of polymers onto various substrates), including alkali halides, ionic or partially ionic crystals, numerous organic compounds, and mineral additives, toward polymers has been extensively investigated in the past. Also, a number of selection rules to determine the correlation between nucleating activity and molecular or crystallographic parameters of nucleating agents have been established, although many controversies still exist.<sup>13–15</sup> In contrast, just a few small molecular compounds can act as  $\beta$ -crystalline nucleating agents. Until now, only two classes of compounds have been used for the most part. The first class is a minority of aromatic ring compounds, such as  $\gamma$ -quinacridone (permanent red dye E3B; C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>),<sup>1</sup> triphenodithiazine (TRDT; C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>),<sup>2,3</sup> and *N,N'*-dicyclohexylterephthalamide (DCTH; C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>).<sup>8–10</sup> The second class includes certain bicomponent mixtures consisting of group II A metal compounds (the first component) and specific dicarboxylic acids or derivants (the second component), such as a mixture of calcium stearate and pimelic acid.<sup>4–7</sup> The chemical and structural features of the first class of  $\beta$ -nucleating agents have been investigated on occasion. Garbarczyk and Pauksza<sup>2,3</sup> examined some aromatic ring compounds and proposed that  $\beta$ -modification of iPP occurred only when the molecular structure was quasiplanar and that it might also be related to the existence of S ... S, S ... O, or S ... C axes. Wittmaan, Lotz, and other researchers<sup>16–18</sup> studied the epitaxial crystallization of iPP on E3B and DCTH and raised some structural requirements that efficient  $\beta$ -iPP nucleating agents must meet. For the second class of  $\beta$ -iPP nucleating agents, however, almost no similar studies have been carried out. This may be due to the complexity of the systems. First, it is difficult to determine what the substantially real nucleating agent is in the system. Shi et al.<sup>5</sup> once presumed that the crystallographic form of II A metal salts (the first component) might be connected with the occurrence of the  $\beta$ -form. Unfortunately, no thorough investigation of the molecular and structural features of II A metal salts has been documented. To our knowledge, this topic has not been systemically discussed and remains far from being fully understood.

We recently found that a mixture of a lanthanum(III) complex and some mineral additives could induce  $\beta$ -crystalline iPP and act as the second class of  $\beta$ -nucleating agents. In this work, these bicomponent additives were added to iPP,

and the effects of 19 kinds of mineral additives on the crystalline structure of iPP were investigated with wide-angle X-ray diffraction (WAXD) measurements. The aim was to obtain certain useful information about the relationship between the occurrence of  $\beta$ -iPP and the chemical or structure features of the mineral additives, especially the chemical requirements that the minerals must meet. Moreover, the minerals were selected because mineral modification is one of the most common methods of modifying the properties of polymeric materials and PP composites containing the  $\beta$ -form have higher impact resistance than  $\alpha$ -iPP composites.

## EXPERIMENTAL

### Materials

The iPP homopolymer used in this work was F401, a product of Guangzhou Petrochemical Factory (Guangzhou, China); it had a melting point of 172°C and a density of 0.91 g/cm<sup>3</sup>. The mixed lanthanum(III) complex (LaC) was prepared by a method described in an earlier report.<sup>19</sup> Nineteen kinds of mineral additives used in this work were purchased from Guangdong Chemical Materials and Reagents Corporation (Guangzhou, China), and a description of them is given in Table I.

### Sample Preparation and Characterization

The crystal system and space group of each mineral were determined by X-ray powder diffraction analysis, which was performed with a Rigaku D/max-1200 diffractometer. The results are listed in Table I.

Ten percent of the bicomponent additive of each mineral and LaC (100/2.5 w/w) was mixed with iPP on a two-roll mill at 170°C for 12 min. The mixture was subsequently molded into 1-mm-thick sheets at 190°C under a pressure of 15 MPa. The sheets of PP composites containing 10% of each mineral alone were prepared in the absence of LaC and used as controls. Also, a pure PP sample was prepared with an identical mixing and molding schedule. All the minerals were dried in a vacuum oven at 120°C for 10 h before the X-ray power diffraction examination and mixing process.

The crystal form of PP composites or pure PP was determined by WAXD analysis. The specimens for WAXD were cut from 1-mm-thick

**Table I Minerals and Their Characteristics**

Mineral	Specification	Crystal System	Space Group
CaCO <sub>3</sub>	400-mesh commercial filler	Hexagonal	Pbnm
CaCl <sub>2</sub>	Chemically pure reagent	Orthorhombic	Pnmm
CaSO <sub>4</sub>	Chemically pure reagent	Hexagonal	P6 <sub>2,4</sub> 22
Ca(OH) <sub>2</sub>	Chemically pure reagent	Hexagonal	P3m1
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	Chemically pure reagent	Monoclinic	C2/c
Ca(NO <sub>3</sub> ) <sub>2</sub>	Chemically pure reagent	Cubic	Pa3
MgCO <sub>3</sub>	Chemically pure reagent	Hexagonal	R3c
Mg(NO <sub>3</sub> ) <sub>2</sub>	Chemically pure reagent	Cubic	Pa3
Mg(OH) <sub>2</sub>	1000-mesh commercial filler	Hexagonal	P3m1
MgSO <sub>4</sub>	Chemically pure reagent	Orthorhombic	Pbnm
MgCl <sub>2</sub>	Chemically pure reagent	Hexagonal	R3m
BaSO <sub>4</sub>	400-mesh commercial filler	Orthorhombic	Pbnm
Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Chemically pure reagent	Hexagonal	R3m
BaCl <sub>2</sub>	Chemically pure reagent	Orthorhombic	Pnam
BaCO <sub>3</sub>	Chemically pure reagent	Orthorhombic	Pnam
Ba(OH) <sub>2</sub>	Chemically pure reagent	Cubic	Pa3
Mica	400-mesh commercial filler	Monoclinic	Am
Talc	800-mesh commercial filler	Monoclinic	A2/a
Wollastonite	800-mesh commercial filler	Anorthic	—

sheets, and WAXD profiles were recorded on a Rigaku D/max-1200 diffractometer in a reflection mode with Ni-filtered Cu K $\alpha$  radiation (40 kV, 30 mA).

The crystallization behavior was studied with a PerkinElmer DSC-7 differential scanning calorimeter. Specimens were heated to 200°C, kept there for 10 min, and cooled at 10°C/min; crystallization was then carried out.

Figure 1(a) shows the WAXD pattern of pure PP. Within the given range of scattering angles, there are five local maxima at  $2\theta$  values of approximately 14.0, 16.8, 18.6, 21.2, and 21.8°, corresponding to the (110), (040), (130), and overlapping (131) and (111) reflections, respectively; this is characteristic of monoclinic  $\alpha$ -form PP. This indicates that only  $\alpha$ -form crystals were present in the pure iPP sample. Figure 1(b) shows the WAXD pattern of PP/CaCO<sub>3</sub>, and we can see that the crystal form of iPP in this composite is still monoclinic ( $\alpha$ ). All other PP composites filled with any of the minerals adopted in this work had WAXD patterns similar to Figure 1(b). As shown in Figure 1(c), obvious differences exist between PP-associated diffraction peaks of PP/CaCO<sub>3</sub>/LaC and those in Figure 1(a,b). In addition to the features associated with  $\alpha$ -form PP, an additional peak is clearly seen at a  $2\theta$  value of approximately 16.0°. These changes clearly indicate the presence of the hexagonal  $\beta$ -form of PP in the composites.<sup>11</sup>

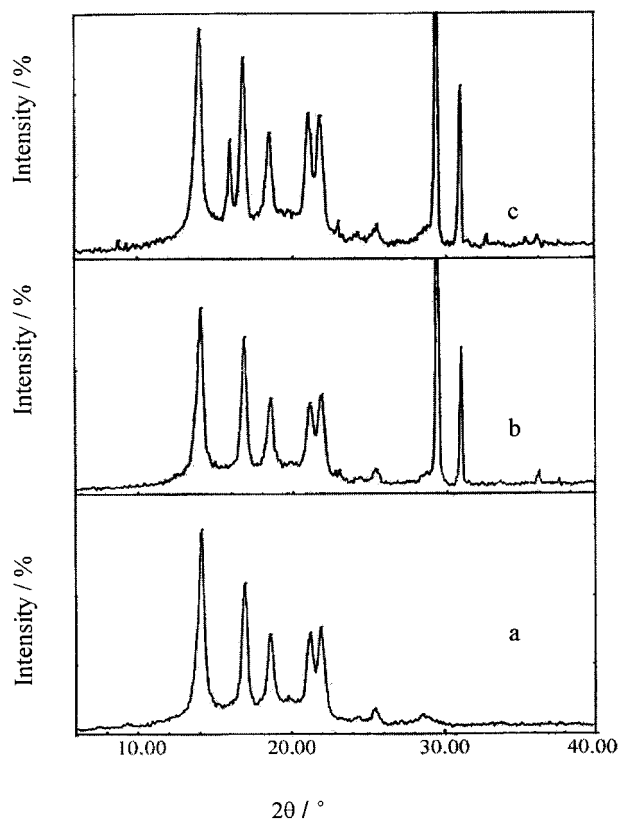
The relative amount of the  $\beta$ -form,  $k$ , is determined with the Turner-Jones equation:<sup>11</sup>

$$k = H(300)/[H(300) + H(110) + H(040) + H(130)] \quad (1)$$

where  $H(300)$  is the height of the characteristic  $\beta$ -form peak (300).  $H(110)$ ,  $H(040)$ , and  $H(130)$  are those of the three strong equatorial  $\alpha$ -form peaks, (110), (040), and (130), respectively.

There are two types of diffraction patterns in iPP composites filled with bicomponent additives of various minerals and LaC. Some patterns are similar to Figure 1(b), whereas others are similar to Figure 1(c). The numerical values of the diffraction angle ( $2\theta$ ), the distances between the parallel planes in the crystallites ( $d$ ), and the relative intensities ( $I/I_0$ ) of diffraction faces (110), (300), (040), and (130) (corresponding to  $2\theta$  values of approximately 14.0, 16.0, 16.8, and 18.6°), as well as the  $k$  values of various composites, are summarized in Table II.

We can see from Table II that no mineral adopted in this work could induce  $\beta$ -iPP and that all the  $k$  values of PP composites filled with a mineral alone were equal to zero. Although McGenity et al.<sup>20</sup> reported that a low level of the  $\beta$ -form could be found in an iPP/CaCO<sub>3</sub> system, like most other previous results obtained with



**Figure 1** WAXD patterns of (a) pure PP, (b) a PP/CaCO<sub>3</sub> composite, and (c) a PP/CaCO<sub>3</sub>/LaC composite.

iPP/mineral composites,<sup>21,22</sup> no  $\beta$ -form was found in our investigation.

In iPP composites filled with a bicomponent additive consisting of various minerals (the first component) and LaC (the second component), three kinds of II A metal compounds, including six calcium compounds, five magnesium compounds, and five barium compounds acting as the first compound, were investigated. As shown in Table II, not all the II A metal compounds could induce the  $\beta$ -form of iPP. In fact, the  $\beta$ -form occurred only in the systems in which the minerals were calcium compounds. None of the magnesium or barium compounds adopted were able to induce the  $\beta$ -form.

Structurally, it is noteworthy that, among all the kinds of calcium compounds we investigated, a hexagonal crystallographic form was not an indispensable factor for the appearance of the  $\beta$ -form. This may be confirmed by the fact that the  $\beta$ -form occurred in all the PP systems filled with these calcium compounds and LaC mixtures, whether the calcium compounds were hexagonal [CaCO<sub>3</sub>, CaSO<sub>4</sub>, and Ca(OH)<sub>2</sub>], orthorhombic (CaCl<sub>2</sub>), mono-

tonic [Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>], or cubic [Ca(NO<sub>3</sub>)<sub>3</sub>]. Furthermore, the relative amount of the  $\beta$ -form observed in these systems ranged from 13.7 to 24.3%, and no substantial difference existed. However, when the first component was a magnesium compound or a barium compound, no matter what crystallographic form it had, no  $\beta$ -form occurred. This suggests that the presence of calcium compounds in the systems is a prerequisite for the induction of  $\beta$ -iPP. However, their crystallographic form need not necessarily be hexagonal.

These phenomena are not consistent with Zhang and Shi's hypothesis,<sup>5</sup> that the hexagonal  $\beta$ -iPPs related to the first compound were II A group metal compounds (not only calcium compounds) with similar hexagonal crystallographic forms.

Six kinds of negative ions (CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>) were examined, and all their calcium compounds, combined with LaC, were found capable of inducing the  $\beta$ -form. No close relationship between the  $\beta$ -form and the type of negative ion was found. Similarly, the crystalline space group of minerals seems to have no determinate matching relationship with whether the  $\beta$ -form can be induced or not.

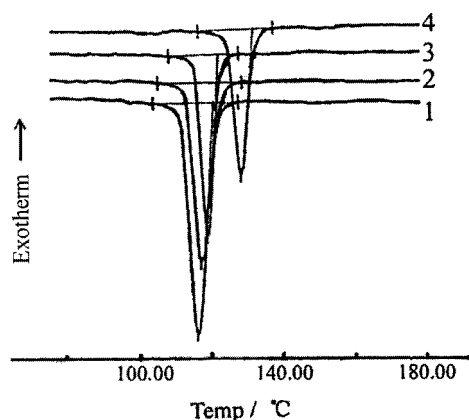
Determined by X-ray powder diffraction analysis, the chemical formulae for the mica and talc used in this work were KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub> and Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>, respectively. No calcium ion was present in these two minerals, and no  $\beta$ -form occurred in iPP composites filled with them. According to data available in the literature, all except CaCO<sub>3</sub> had the ability to induce  $\beta$ -iPP,<sup>20</sup> and wollastonite also induced various levels of the  $\beta$ -form.<sup>23</sup> We found that the  $k$  values of PP/wollastonite (90/10) and PP/wollastonite/LaC (90/10/0.25) were 0 and 15.8%, respectively. Because the chemical formula of wollastonite is CaSiO<sub>3</sub>, there was calcium present. The presence of the  $\beta$ -form in PP/wollastonite/LaC might further confirm that our conclusions are reasonable.

The LaC used in this work was a mixed ternary complex of trivalent lanthanum stearate and stearin. However, neither lanthanum stearate/calcium carbonate nor calcium stearate nor stearin/calcium carbonate nor LaC alone could induce the  $\beta$ -form. Figure 2 shows the differential scanning calorimetry (DSC) traces of pure PP, PP/LaC (100/2.5), PP/CaCO<sub>3</sub> (70/30), and PP/CaCO<sub>3</sub>/LaC (70/30/2.5) during the crystallization process. The crystallization temperature of PP/CaCO<sub>3</sub>/LaC was 129.6°C, which was much higher than that of other systems (112.1, 116.6, and 119.1°C for pure

**Table II WAXD Data ( $2\theta$ ,  $d$ , and  $I/I_0$ ) and Contributions of the  $\beta$ -form ( $k$ ) in iPP Composites Containing Various Additives**

Additive	$2\theta$	$d$	$I/I_0$	$k$	Additive	$2\theta$	$d$	$I/I_0$	$k$
CaCO <sub>3</sub>	14.2	6.254	100	0	CaCO <sub>3</sub> /LaC	14.1	6.272	100	0.185
	16.9	5.240	85			16.0	5.532	51	
	18.6	4.760	52			16.9	5.246	80	
CaCl <sub>2</sub>	14.1	6.232	100	0	CaCl <sub>2</sub> /LaC	14.1	6.272	100	0.133
	16.9	5.234	66			16.0	5.523	33	
	18.6	4.770	48			16.9	5.246	70	
CaSO <sub>4</sub>	14.2	6.236	100	0	CaSO <sub>4</sub> /LaC	14.1	6.272	100	0.157
	16.9	5.227	65			16.0	5.525	38	
	18.6	4.760	48			16.9	5.246	77	
Ca(OH) <sub>2</sub>	14.3	6.176	100	0	Ca(OH) <sub>2</sub> /LaC	14.1	6.272	100	0.243
	17.1	5.179	28			16.1	5.518	57	
	18.8	4.715	54			16.9	5.240	84	
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	14.1	6.225	100	0	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> /LaC	14.1	6.272	100	0.176
	16.9	5.234	78			16.0	5.531	43	
	18.6	4.760	55			16.9	5.240	82	
Ca(NO <sub>3</sub> ) <sub>2</sub>	14.2	6.246	100	0	Ca(NO <sub>3</sub> ) <sub>2</sub> /LaC	14.1	6.272	100	0.163
	16.9	5.292	68			16.0	5.523	37	
	18.6	4.763	57			16.9	5.246	57	
MgCO <sub>3</sub>	13.9	6.393	100	0	MgCO <sub>3</sub> /LaC	14.0	6.272	100	0
	16.8	5.308	51			16.9	5.235	47	
	18.5	4.822	37			18.6	4.770	43	
Mg(NO <sub>3</sub> ) <sub>2</sub>	14.1	6.268	100	0	Mg(NO <sub>3</sub> ) <sub>2</sub> /LaC	14.1	6.276	100	0
	16.9	5.230	68			17.0	5.210	62	
	18.7	4.729	55			18.7	4.749	50	
Mg(OH) <sub>2</sub>	14.0	6.331	10	0	Mg(OH) <sub>2</sub> /LaC	14.1	6.286	8	0
	16.8	5.280	14			16.9	5.250	8	
	18.5	4.799	100			18.6	4.773	100	
MgSO <sub>4</sub>	14.0	6.340	100	0	MgSO <sub>4</sub> /LaC	14.2	6.228	100	0
	16.9	5.238	83			17.0	5.203	77	
	18.6	4.765	65			18.7	4.750	59	
MgCl <sub>2</sub>	14.0	6.334	100	0	MgCl <sub>2</sub> /LaC	14.1	6.286	100	0
	16.8	5.282	65			16.9	5.246	50	
	18.6	4.786	43			18.6	4.775	36	
BaSO <sub>4</sub>	14.1	6.286	71	0	BaSO <sub>4</sub> /LaC	14.1	6.286	92	0
	16.8	5.281	100			16.9	5.250	100	
	18.5	4.799	59			18.6	4.773	62	
Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	14.1	6.280	82	0	Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> /LaC	14.1	6.286	73	0
	16.8	5.259	100			16.9	5.252	100	
	18.6	4.762	76			18.7	4.748	68	
BaCl <sub>2</sub>	14.2	6.230	100	0	BaCl <sub>2</sub> /LaC	14.2	6.246	100	0
	16.9	5.252	39			16.9	5.234	32	
	18.6	4.778	57			18.6	4.749	51	
BaCO <sub>3</sub>	14.0	6.332	100	0	BaCO <sub>3</sub> /LaC	14.1	6.278	100	0
	16.8	5.282	79			16.9	5.247	77	
	18.5	4.770	51			18.6	4.756	53	
Ba(OH) <sub>2</sub>	14.3	6.176	100	0	Ba(OH) <sub>2</sub> /LaC	14.2	6.236	100	0
	16.9	5.234	68			16.9	5.252	60	
	18.7	4.863	46			18.7	4.872	43	
Mica	14.1	6.286	58	0	Mica/LaC	14.1	6.286	98	0
	16.9	5.250	100			16.9	5.249	100	
	18.6	4.773	47			18.6	4.773	68	
Talc	14.1	6.286	9	0	Talc/LaC	14.1	6.286	11	0
	16.9	5.250	100			16.9	5.250	100	
	18.9	4.698	47			18.9	4.698	61	
Wollastonite	14.2	6.217	54	0	Wollastonite/LaC	14.2	6.202	45	0.158
	16.9	5.231	100			16.1	5.495	34	
	18.7	4.738	40			17.0	5.214	100	
						18.7	4.753	36	





**Figure 2** DSC traces of crystallization: (1) pure PP, (2) 100/2.5 PP/LaC, (3) 70/30 PP/CaCO<sub>3</sub>, and (4) 70/30/2.5 PP/CaCO<sub>3</sub>/LaC.

PP, PP/LaC, and PP/CaCO<sub>3</sub>, respectively). This means that the nucleating efficiency of CaCO<sub>3</sub>/LaC was much higher than that of CaCO<sub>3</sub> or LaC and that a synergistic reaction was taking place between CaCO<sub>3</sub> and LaC. In other words, it suggests that perhaps complexes of CaCO<sub>3</sub> and LaC were formed.

Some researchers found the  $\beta$ -form in the PP/CaCO<sub>3</sub> system, and others did not; we think that this may be due to the different sources of PP matrices adopted by various researchers. Certain impurities present in some PPs might have played the role that LaC had in this study. The impurities could have constituted a bicomponent or polycomponent additive with CaCO<sub>3</sub> as the CaCO<sub>3</sub>/LaC mixture and, therefore, could have induced the formation of the  $\beta$ -form in PP, whereas in other PPs without similar impurities, no  $\beta$ -form was consequently induced. Perhaps the impurities came mainly from the residual catalyst used during the polymerization of PP. This hypothesis is based on the fact that most polymerization catalysts are complexes of transition metals, and the transition-metal elements, like the rare earth elements (in this work, lanthanum), have very strong complexation and various coordination numbers with organic ligands.

The bicomponent nucleating agent consisting of calcium compounds and LaC had  $\beta$ -form nucleating activity, whereas its component alone did not. This reveals that perhaps a new substance, which played the role of an actual  $\beta$ -iPP nucleating agent ( $\beta$ -crystalline substrate) in the system, had been formed from a calcium compound and LaC or even from impurities in iPP. The first class

of  $\beta$ -form nucleating agents of aromatic ring compounds, such as E3B, TRDT, and DCTH, has a definite chemical formula, a clearly established crystalline structure, and a large crystal in the substrate (several micrometers squared, a size suitable for observation with electron and atomic force microscopy), and the study of PP crystallization in the presence of those agents is feasible.<sup>16</sup> With respect to the bicomponent nucleating agents, at this stage of our research it is impossible to determine a close relationship between the molecular and crystal features of minerals and the crystallographic form of iPP because it is not clear what the actual  $\beta$ -crystalline substrate is. If the substrate could be determined clearly, the epitaxial crystallization of  $\beta$ -iPP could be investigated with techniques developed by Lotz et al.<sup>16</sup> This should be helpful in establishing the requirements that the chemical and structural features of  $\beta$ -iPP nucleating agents must meet.

We surmise that the true  $\beta$ -iPP substrate in our systems might be some binuclear complexes of calcium and rare earth elements with some ligands (in a PP/calcium stearate/pimelic acid system<sup>6</sup> or perhaps binuclear complexes of calcium and transition elements with some ligands, which possibly include at least pimelic acid). Certain exploratory research has been carried out in this direction, and the problem is worth further investigation.

## CONCLUSIONS

Various minerals alone and bicomponent mixtures consisting of both these minerals (the first component) and an identical second component of LaC (a mixed ternary complex of trivalent lanthanum stearate and stearin) were added to iPP. The influences of the minerals on the crystallographic forms of iPP were investigated with WAXD measurements. Neither the minerals nor LaC on their own could induce the occurrence of the hexagonal  $\beta$ -form. In contrast, the bicomponent mixtures of calcium compounds and LaC could induce  $\beta$ -iPP. The presence of calcium compounds in the mixture was a prerequisite for the induction of  $\beta$ -iPP. However, their crystallographic forms did not need to be hexagonal. Also, the occurrence of  $\beta$ -iPP had no close relationship with the type of negative ion or the crystalline space group of the minerals.

Our results suggest that certain complexes of calcium and LaC formed in the composite. We

hypothesize that the true  $\beta$ -iPP substrates in the systems might be some binuclear complexes of calcium and rare earth elements with some specific ligands.

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