

Calcium Dicarboxylates Nucleation of β -Polypropylene

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ABSTRACT: Seven dicarboxylates of calcium were synthesized. The effect of dicarboxylate on the formation of β -form polypropylene was investigated by X-ray diffraction. Calcium pimelate, calcium suberate, calcium phthalate, and calcium terephthalate have been found to be an effective β -nucleator. The K_x values of the isotactic propylene samples with 0.5 wt % of the nucleators above are 0.95, 0.96, 0.93, and 0.62, respectively. Calcium succinate, calcium adipate, and calcium sebacate behave invalidly on the nucleating of the β -phase. We conducted an investigation on the affect of particle shape, crystal form, and crystallinity upon the level of the β -form. The

X-ray diffraction of the effective nucleators reveals a common character that their first reflection locate at the d-spacing between 10 to 13 Å, indicating structural similarity of the nucleators with β -polypropylene. The nucleation mechanism is explained by the cooperative effect of the nonpolar and polar part of nucleating agents in the crystallization of polypropylene. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 633–638, 2002

Key words: polypropylene (PP); nucleation; structure crystallization

INTRODUCTION

Isotactic polypropylene (iPP) is known to exhibit three different crystalline forms, namely the monoclinic α , the hexagonal β , and the triclinic γ -form. The β -form is occasionally found in commercial polypropylene, but usually at a very low degree.^{1,2} Nucleating agents were applied to obtain a high level of the β -phase.^{3–9} The Quinacridon Dyestuff Permanent Red E3B was found to be a very efficient β nucleating agent for iPP.³ Shi GY⁴ reported that a composition of pimelic acid with calcium stearate was useful for inducing the β phase. It was reported by Garbarczyk^{5,6} that a series of crystalline substances like 2-mercaptan-benzimidazole, triphenodithiazine, phenothiazin, anthracene, and phenanthrene act as good nucleating agents for iPP. Also, a number of paintings, such as Indigosol Grey/IBL, Indigosol Golden Yellow IGK, and Cibantine Blue 2B have been reported by Huang⁷ to nucleate the β -form in isotactic polypropylene. Although nucleators of β -polypropylene have been investigated relatively thoroughly, little is known about the mechanism of the formation of the β -phase nucleus in the presence of nucleating agents.

The mechanism of heterogeneous nucleation in the crystallization of polyolefines has been discussed in several, sometimes controversial, ways. Garbarczyk¹⁰ assumed that active additives play the role of moderating agents for the $\beta \rightarrow \alpha$ transformation process. In view of geometric lattice matching between nucleating

agents and the outgrowth polymer crystals, Wittmann^{11,12} suggested the nucleating activity may result from an epitaxy of the polymer onto the nonpolar part of the nucleating agents. Research of Shi GY¹³ on bicomponent nucleating agents of β -iPP provided evidence supporting epitaxy mechanism. However, the epitaxy mechanism was rejected by Binsbergen,^{14,15} mainly on two rather symmetrical arguments based on the nonspecificity of the nucleating agents; namely a given nucleating agents can be active towards chemically different polymers, and different members of a homologous series of salts are found to be active towards a given polymer. Binsbergen¹⁵ suggested that the heterogeneous nucleating of polymers takes place at steps of limited length in the surface of the particles, and is enhanced by a high degree of accommodation of polymer molecules in the shallow ditches formed by the hydrocarbon groups of the nucleating agents. Recently, work of Wolfgang et al.¹⁰ revealed that the β phase of isotactic polypropylene is crystallized epitaxially on the γ -quinacridone, the (110) plane being the contact face.

In the present work, we investigated the role of a series of calcium carboxylates, with different chemical structure and crystal form, as nucleating agents for β -polypropylene. The affect of the particle shape, crystalline form, and crystallinity degree on the level of the β -form were studied. A nucleating mechanism was proposed on the base of the structural similarity of effective nucleators with the β -phase of polypropylene.

EXPERIMENTAL

Materials

Isotactic polypropylene with melt flow index of 2.3 g/10 min, provided by Anqing Chemistry Works of

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Anhui Province in China, was used in the experiments. The nucleators, calcium succinate, calcium adipate, calcium pimelate, calcium suberate, calcium sebacate, calcium phthalate, and calcium terephthalate were synthesized by double decomposition. For instance, calcium pimelate was prepared through the reaction between equimolar CaCl_2 and sodium pimelate aqueous solution with stirring. The precipitation was filtered, washed twice with distilled water and ethanol, respectively, and dried in an oven at 100°C . The product obtained was a pale yellow powder.

Sample preparation

The nucleating agent was added to ipp using an internal mixer. The concentration was 0.5 wt % unless mentioned elsewhere. The film for X-ray diffraction was prepared using a sheeting-out roller. The additive-containing sample was sandwiched between two glass slides and heated in an oven. After melting, it was kept at 200°C for 5 min, then cooled down to room temperature.

Analysis of sample

X-ray diffraction

Wide-angle X-ray diffraction experiment was conducted with a Rigaku Geigerflex Model D/max-rA rotating anode X-ray diffractometer. Graphite monochromatic $\text{Cu-K}\alpha$ radiation was employed as a radiation source. The relative content of the β -form in the specimen was measured in terms of the K_x value, which was calculated using the Turner-Jones equation.²

Transmission electron microscope

Transmission Electron Microscope (TEM) photographs were taken on a Hitachi TEM Model H-800. The sample was well dispersed in ethane alcohol by ultrasonic disintegrator, then transferred to a carbon membrane.

Infrared spectrometer

Infrared spectra were collected on a Nicolet MAGNA-IR 750 spectrometer with a KBr pellet containing the nucleating agents.

RESULTS AND DISCUSSION

Characterization and structure of nucleating agents

From the TEM photograph in Figure 1, we can see different particle shapes for the calcium carboxylates. Both calcium pimelate [Fig. 1(a)] and calcium suberate [Fig. 1(b)] look like lumpish aggregates composed of

tiny crystalline grain. Calcium phthalate [Fig. 1(c)] and calcium terephthalate [Fig. 1(d)] are plate lamellae. Calcium adipate [Fig. 1(e)] is a needle.

Figure 2 presents the FTIR spectra of seven calcium carboxylates. With the exception of calcium pimelate, which shows a peak at 1541 cm^{-1} , aliphatic carboxylates show two absorption maxima between $1410\text{--}1440\text{ cm}^{-1}$ and $1560\text{--}1600\text{ cm}^{-1}$, which have been assigned to the antisymmetric (ν_{asym}) and symmetric (ν_{sym}) stretching vibration of the carboxyl group in the metal salts.¹⁷ As reported in the literature,¹⁸ the separation of the two COO^- stretching frequencies is an indication of the nature of coordination. Previous work has suggested¹⁹ three types of coordination: unidentate, bridge, and chelate. If the carboxyl group is present as a unidentate ligand, the separation $\Delta\nu$ between ν_{asym} and ν_{sym} is expected to be higher than 170 cm^{-1} . It can be seen in Table I that the separation ($\Delta\nu$) are about 150 cm^{-1} , indicating that the metal-carboxyl bonding are bidentate structures in calcium carboxylates. On the other hand, the ν_{asym} of the bridge coordination is higher than that of the chelate one, while the ν_{sym} of the former is lower than the latter.¹⁸ Thus, the peaks at around 1570 and $1420\text{--}1440\text{ cm}^{-1}$ were, respectively, ascribed to the antisymmetric and symmetric vibration of the carboxyl group as a bridge ligand. The exceptional peak of calcium pimelate at about 1541 cm^{-1} was assigned to antisymmetric vibration of the carboxyl group with the chelate structure. It has been reported²⁰ that double cyclic intermolecular hydrogen bonds are formed in dicarboxylic acid with odd number methene groups, but the hydrogen bonds are not favored in the acid with even number methene groups. In calcium pimelate, a similar structure, the chelate coordination between calcium metal and carbonyl groups of two molecules, is formed, and accounts for the peak at 1541 cm^{-1} .

X-ray diffraction traces in Figure 3 provide more information on the structure of the salts. The first peak found in the X-ray diffraction pattern is of the character of the metal dicarboxylate, which is due to the reflection of (001) profile reported by Ibidapo.²¹ The 2θ in the region of $5\text{--}11$ degrees corresponds to a periodicity of $7\text{--}16\text{ \AA}$ along the c axis of the molecule. Combined with the result of infrared spectra, it can be concluded that the carboxylates are built up of alternating polar and nonpolar layers. The polar layers contain the carbonyl groups and the nonpolar ones the hydrocarbon groups. From the value of crystallite size in the c direction, which can be roughly evaluated from the half-height width of the (001) reflection peak, the numbers of layers can be estimated. The sizes are all in the range $20\text{--}25\text{ nm}$, giving the number of repeats N between 18 and 23. Calcium pimelate, for example, has a crystalline size in the c direction of 24 nm , and the N of 21.

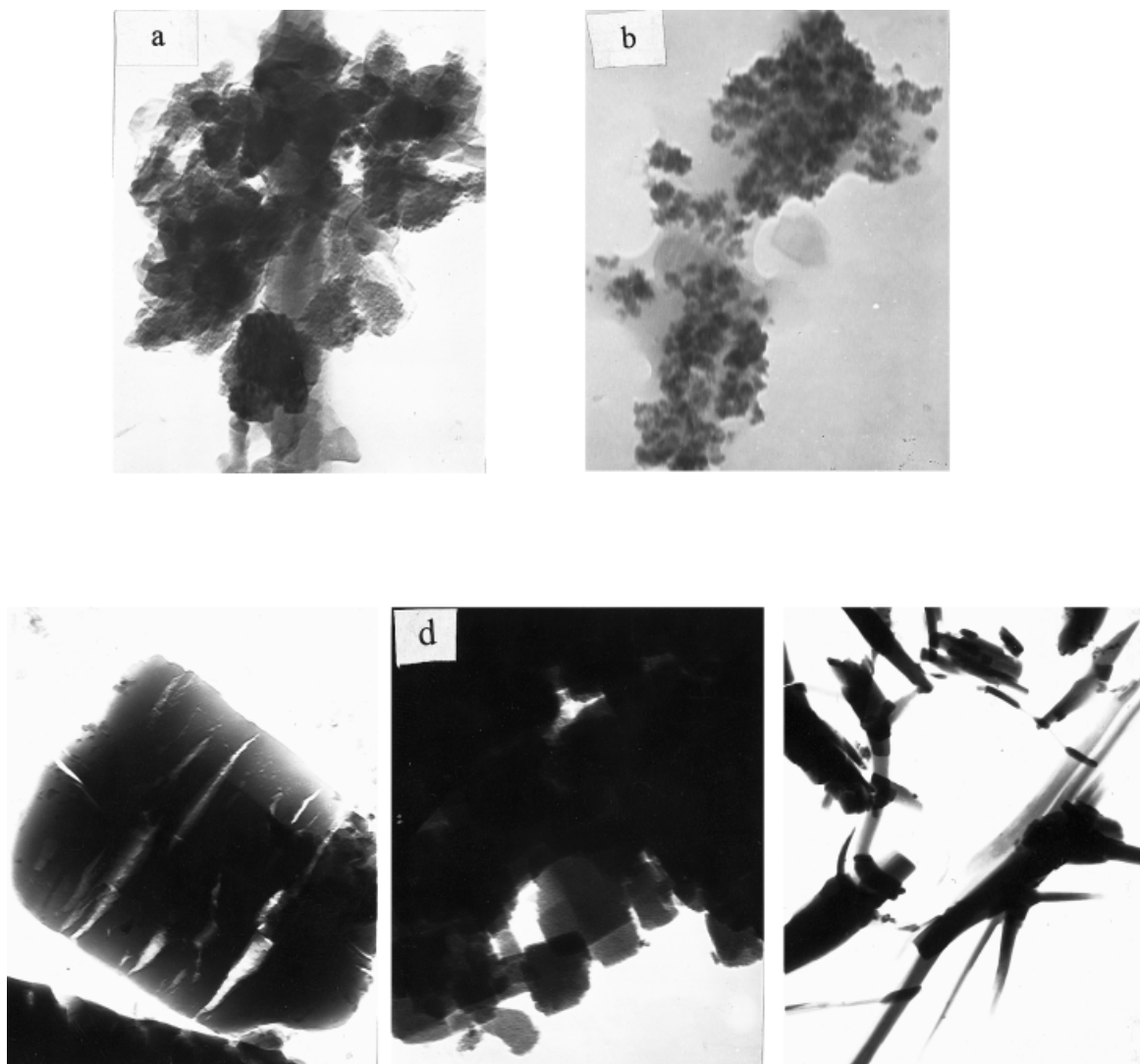


Figure 1 Typical TEM micrography of additives: (a) calcium pimelate, (b) calcium suberate, (c) calcium phthalate, (d) calcium terephthalate, (e) calcium adipate.

Effect of particle shape and particle size on nucleating effectivity

It was reported by Garbarczyk⁵ that the particle shape of the additive is perhaps one of the factors that affect the level of the β -form. As shown in Figures 1 and 4, the additives of plat or lumpish shapes tend to favor the growth of the β -form, while those with the form of needles are less effective. A similar result was observed by Huang.⁷ However, we found that the same nucleating agents with different shapes behave the same as the nucleating effect. For a comparison, calcium pimelate was synthesized in two ways. The sample obtained by the mixing of equimolar calcium hydroxide with pimelic acid is flat, while that prepared by double decomposition is lumpish. The K_x values of the ipp sample containing 0.5 wt % of those two are approximately 0.95. It follows that the particle shape is not the key factor for inducing the β -form in the case.

After being extracted in ethanol for 24 h, a polypropylene membrane containing 1 wt % pimelic acid was washed, dried, and immersed in $\text{Ca}(\text{OH})_2$ aqueous solution for 12 h. The K_x value of the membrane is 0.15. During the extraction, the pimelic acid particles on the surface of the membrane were removed. Only those molecules tangled with polypropylene molecular chains were fixed and remained in the polymer bulk, and reacted chemically with calcium hydroxide in the following process. The aggregates of several calcium pimelate molecules formed in this way, looking like inlay in the polypropylene, act as active sites for nucleating in the crystallization of polypropylene. It indicates that the particle size required for nucleating is at the molecular level, resulting in a high density of "active nucleating sites" in polypropylene even with very low concentration of additives. For instance, polypropylene sample with 0.005 wt % calcium pime-

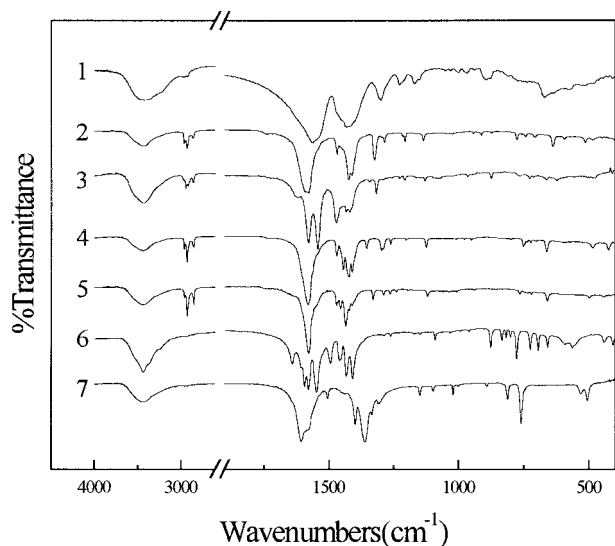


Figure 2 FTIR spectra of the salts: (1) calcium succinate, (2) calcium adipate, (3) calcium pimelate, (4) calcium suberate, (5) calcium sebacate, (6) calcium phthalate, (7) calcium terephthalate.

late, corresponding to a density of 1×10^9 nucleating particles with 25 nm in size per gramme polymer crystallizing substance, possesses a K_x value of 0.92. This explains the high effectivity of calcium pimelate on the growth of β -form polypropylene.

Effect of crystallinity on nucleating effectivity

As claimed by Huang et al.,⁷ the compounds with hexagonal or pseudohexagonal crystallinity might help to form the β -phase. A different result has been reached in our experiment. Calcium pimelate and calcium suberate, belonging to the tetragonal crystal system, possess corresponding K_x values higher than 0.90. Calcium phthalate, in the monoclinic crystallinity, has also proven to be effective nucleating agents. This indicates that the hexagonal or pseudohexagonal crystalline form is not a necessary condition for nucleating agents of β polypropylene. It is different from the conventional explanation of epitaxy. The epitaxy mechanism rests on a structural match of substrate and overgrowth lattice. The compounds that Wittman¹² used in the research of epitaxy of polyethylene,

TABLE I
Infrared Frequencies of Calcium Carboxylates (cm^{-1})

Additive name	$\nu_{\text{asym}}(\text{COO}^-)$	$\nu_{\text{sym}}(\text{COO}^-)$	$\Delta \nu$
Calcium succinate	1562	1421	141
Calcium adipate	1583	1431	152
Calcium pimelate	1579	1419	160
	1541	1432	109
Calcium suberate	1581	1423	158
Calcium sebacate	1578	1421	157

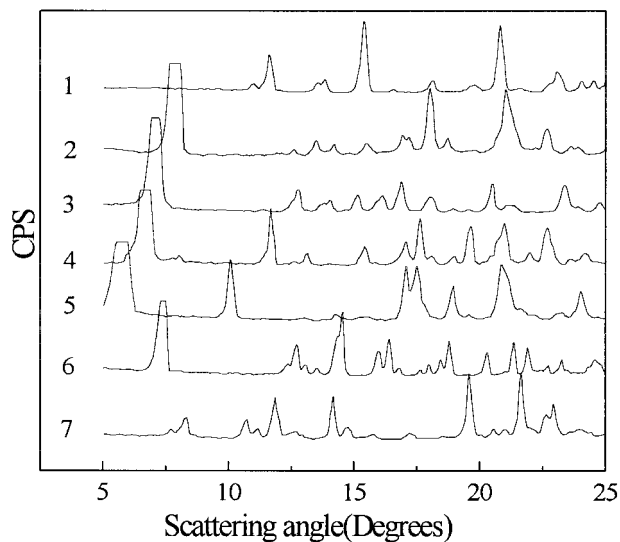


Figure 3 X-ray diffraction diagrams of the salts: (1) calcium succinate, (2) calcium adipate, (3) calcium pimelate, (4) calcium suberate, (5) calcium sebacate, (6) calcium phthalate, (7) calcium terephthalate.

potassium hydrogen phthalate, and aromatic hydrocarbons, belong to the orthorhombic space group, the same as polyethylene. This implies that the epitaxy mechanism is not suitable for nucleating the β -polypropylene in the presence of calcium carboxylates.

The follow experiment gives a better understanding on the relationship of degree of crystallinity and nucleating activity. Calcium pimelate converts to gray powder after melted under 260°C . The X-ray diffrac-

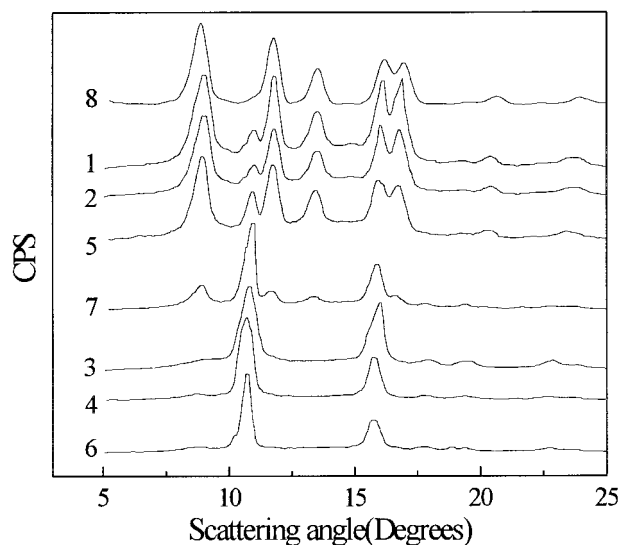


Figure 4 X-ray diffraction diagrams of polypropylene with 0.5 wt % nucleator. The nucleator is: (1) calcium succinate, (2) calcium adipate, (3) calcium pimelate, (4) calcium suberate, (5) calcium sebacate, (6) calcium phthalate, (7) calcium terephthalate, (8) no additive.

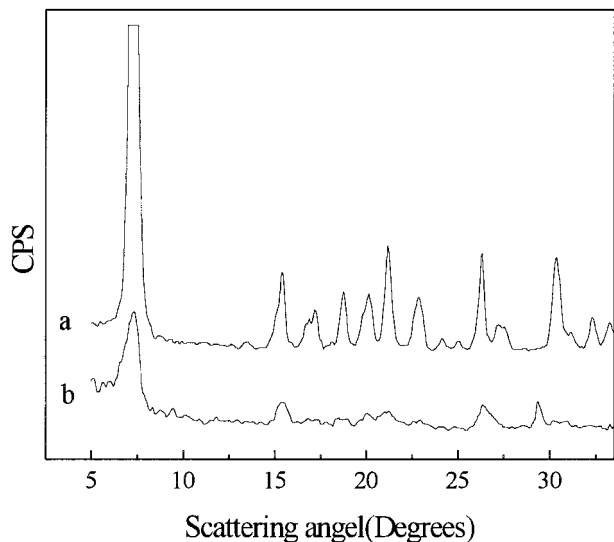


Figure 5 X-ray powder diagrams of calcium pimelate: (a) crystalline form, (b) amorphous form obtained after fusion.

tion in Figure 5 shows the powder possesses a very low degree of crystallinity. In its infrared spectra (Fig. 6), the double absorption peak at 1580 and 1540 cm^{-1} are displaced by a broad band at 1560 cm^{-1} , indicating a change of structure after fusion. The metal-carboxyl bonds undergo interchange reactions and linear dicarboxylate units form a crosslink structure in the molten state. Figure 7 presents X-ray diffraction diagrams of polypropylene with 0.5 wt % calcium pimelate. The K_x value of the polypropylene sample with molten calcium pimelate is 0.93. This suggests that the "active sites" on the surface of calcium pimelate remain active though the crystalline structure has changed after fusion.

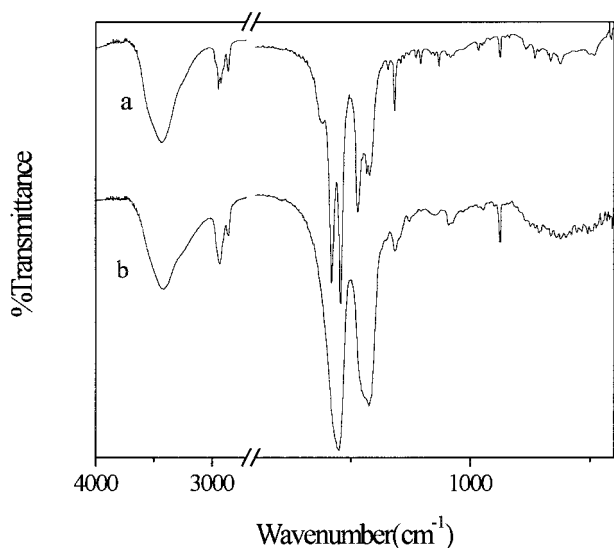


Figure 6 FTIR spectra of calcium pimelate: (a) crystalline form, (b) amorphous form obtained after fusion.

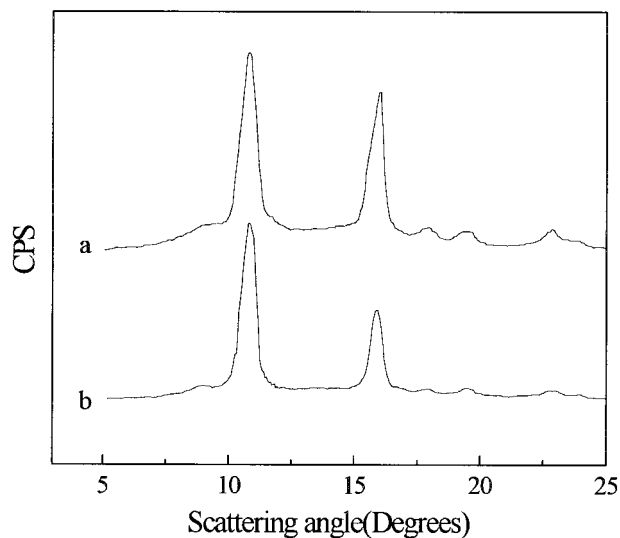


Figure 7 X-ray diffraction diagrams of polypropylene with 0.5 wt % calcium pimelate: (a) crystalline form, (b) amorphous form obtained after fusion.

Mechanism of calcium carboxylates nucleating of β -polypropylene

As discussed above, particle shape, crystalline form, and crystallinity are not the key factors for inducing the β -phase. What is the key factor then? Analysis of the X-ray powder diffraction reveals a common character in the effective β nucleating agents of propylene (Table II). Their spacing of the (001) plane is between $11\text{--}13\text{ \AA}$, which is close to the spacing of helices of the same hand 11 \AA in polypropylene (Fig. 8), using the structural model developed by Dorset.²² It indicates a close relation between the structural similarity of a given nucleating agent with β -polypropylene and its nucleating effectivity.

The mechanism of nucleating is shown by a schematic model of polypropylene molecular segments arranging on the surface of nucleating agent (Fig. 9). The previous study on the structure of the salts has suggested that carboxylates were composed of two parts: a nonpolar layer, containing the aliphatic or aromatic hydrocarbon groups, and a polar layer, containing the carboxyl groups. In the crystallization of

TABLE II
WAXD Data of the Additives and K_x Values of *i*-PP Samples with 0.5 wt% Additives

No.	Additive name	(001) Spacing (\AA)	K_x
1	calcium succinate	6.74	0.07
2	calcium adinate	10.17	0.05
3	calcium pimelate	11.62	0.95
4	calcium suberate	12.96	0.96
5	calcium sebacate	15.49	0.13
6	calcium phthalate	11.18	0.93
7	calcium terephthalate	10.64	0.62

polypropylene, the molecular segments of polypropylene are repelled by the polar part and abstracted to the nonpolar part. The chain is forced to accommodate in the U ditche formed by two parts and aligned perpendicular to the *c* axis of the substrate to form the β nucleus. At the same time, the nonpolar part constrains the translation and rotation of the polymer molecular chains, preventing the $\beta \rightarrow \alpha$ transition, and stabilizes the nucleus. A cooperative effect of the two parts decreases the free energy of forming a critical nucleus.

As to the additives with a (001) face-spacing greater than 13 Å, the polypropylene molecular segments are flexible and easy to translate and rotate. The β nuclei formed on the surface of additives are prone to transfer to the α phase. The additives with a spacing below 10 Å have difficulty accommodating the polypropylene molecular chains. Thus, those two are unable to serve as effective nucleating agents.

CONCLUSION

In this study, additives with different crystallinity and particle shape were found to act as effective β nucleating agents of polypropylene. The particle size required for nucleating of polypropylene is very small at the molecular level, which accounts for the high effectivity of calcium pimelate on the growth of β -form polypropylene. A common character was found in all the active nucleators, namely their (001) spacing is in the range of 11–13 Å. This is explained by the structural similarity of nucleating agents with polypropylene.

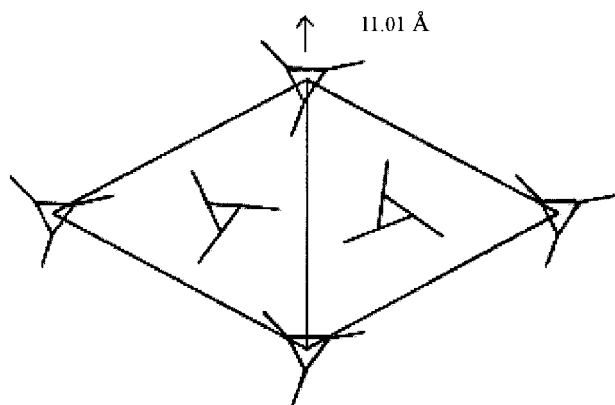


Figure 8 Crystal structure of β polypropylene.

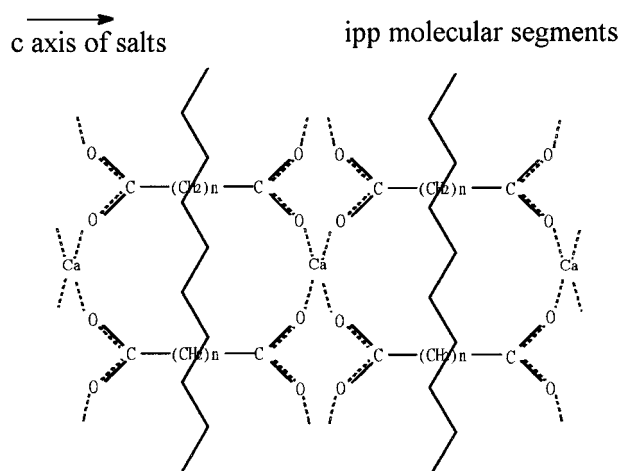


Figure 9 Schematic alignment of polypropylene molecular segments on the surface of calcium carboxylate.

pylene. In the crystallization of polypropylene, the cooperative effect of the nonpolar and polar parts of nucleating agents facilitates the forming of a nucleus.

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