

# Effects of Substituted Aromatic Heterocyclic Phosphate Salts on Properties, Crystallization, and Melting Behaviors of Isotactic Polypropylene

Yue-fei Zhang, Zhong Xin

UNILAB Research Center of Chemical Reaction Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Received 25 June 2005; accepted 14 September 2005

DOI 10.1002/app.23209

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Nucleation effects of 2,2'-methylene-bis(4,6-di-*tert*-butylphenyl) phosphate metal salts as a nucleating agent for isotactic polypropylene (iPP) were investigated with differential scanning calorimeter and polarized optical microscope, and their effects on mechanical, optical, and heat resistance properties of iPP were also studied. The results showed that monovalent metal salts of substituted aromatic heterocyclic phosphate such as sodium salt, lithium salt, and potassium salt had a good performance. With 0.2 wt % of sodium salt, lithium salt, or potassium salt incorporated into iPP, the crystallization peak temperature of iPP could be increased by 13.5, 13.6, and 15.0°C, respectively; the mass fraction of crystallinity of iPP could be increased by about 5%; and crystallization rate was en-

hanced increasingly. Meanwhile the tensile strength and flexural modulus of iPP could be increased by about 10 and 30%, respectively, and the clarity and heat distortion temperature of iPP could also be improved significantly. But bivalent and trivalent metal salts of substituted aromatic heterocyclic phosphate had little effect on properties of iPP. Meanwhile the morphology study showed that the addition of monovalent sodium salt could decrease the spherulite size of iPP significantly. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4868–4874, 2006

**Key words:** nucleation effect; isotactic polypropylene; heterocyclic aromatic heterocyclic phosphate salts; crystallization behavior; morphology

## INTRODUCTION

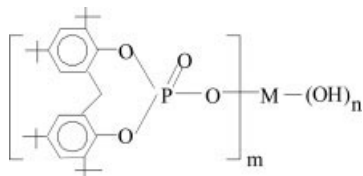
In the processing of polypropylene (PP), nucleating agents are usually used as additives to improve mechanical properties and increase crystallization rates. There are many articles concerning nucleated PP.<sup>1–6</sup> Most developments of nucleating agents are conducted empirically. It is believed that effective nucleating agents for PP are crystalline and include carbon plus hydrogen groups (such as CH<sub>3</sub>, CH<sub>2</sub>, and CH, which are compatible with PP) and polar groups or aromatic ring structures (incompatible with PP).<sup>3</sup> Sodium salt of 2,2'-methylene-bis(4, 6-di-*tert*-butylphenyl) phosphate shows good nucleation effects when used as a nucleating agent for modification of PP, and it can improve the mechanical properties and crystallization rate of PP significantly.<sup>4</sup> Meanwhile study shows that sodium salt of organic phosphoric acid has better nucleation effects than organic phosphoric acid esters.<sup>5</sup> Although some articles focused on PP nucleated with substituted aromatic heterocyclic phosphate salts, most of them focused on sodium salt. Gui et al.<sup>4</sup> studied the effects of concentration of sodium 2,2-

methylene-bis(4, 6-di-*tert*-butylphenyl) phosphate on crystallization behaviors and mechanical properties of isotactic polypropylene (iPP). Zhang et al.<sup>5,6</sup> studied the nucleation efficiency of organic phosphates in PP and the crystallization kinetics of nucleated iPP. Yoshimoto et al.<sup>7</sup> utilized epitaxial crystallization to explain the nucleation effect of sodium 2,2'-methylene-bis(4,6-di-*tert*-butylphenyl) phosphate on iPP. Whether other metals salts of substituted aromatic heterocyclic phosphate are effective as sodium salt or not is intangible. In this study, a series of metal salts of substituted aromatic heterocyclic phosphate were synthesized. Our objective is to investigate the effects of different metal salts of substituted aromatic heterocyclic phosphate on crystallization, morphology, mechanical properties, and optical properties of PP. We also expect to get some rules for substituted aromatic heterocyclic phosphate salts as a nucleating agent acting on PP, which will provide some foundation for molecule design of nucleating agents for PP.

## EXPERIMENTAL

An iPP pellets with a MFR of 2.5 g/10 min (supplied by Yangzi Petrochemical, China) was used in this work. The nucleating agents prepared according to

Correspondence to: Z. Xin (xzh@ecust.edu.cn).



	NA11	NA03	NA19	NA20	NA12	NA30	NA13
M	Na	Li	K	Ca	Mg	Zn	Al
<i>m</i>	1	1	1	2	2	2	2
<i>n</i>	0	0	0	0	0	0	1

**Scheme 1** Structure of nucleating agents in this study.

literature<sup>8</sup> were metal salts of substituted aromatic heterocyclic phosphate, and their structures are shown in Scheme 1.

The iPP pellets and a nucleating agent (0.2 wt %) were mixed in a high-speed mixer for 5 min. Then the mixture was extruded by an SJSH-30 twin-screw extruder through a strand die and pelletized. The pellets were molded into standard test specimens by a CJ-80E injection-molding machine.

The nucleation effect of different metal salts of substituted aromatic heterocyclic phosphate was examined using a Perkin–Elmer Diamond DSC (differential scanning calorimeter) (Perkin–Elmer Company, USA). The samples of about 3 mg were heated from 50 to 200°C at a heating rate of 20°C/min and maintained at 200°C for 5 min to erase their thermal history. Then the samples were cooled to 50°C at a cooling rate of 20°C/min. On completion of the crystallization, a heating scan at 20°C/min was then run from 50 to 200°C to obtain the final sample enthalpy of fusion.

The morphology studies of iPP and nucleated iPP were performed with the aid of an Olympus BX51 (Japan) polarized optical microscope attached with a DP70 digital camera, and a THMS 600 hot-stage. The thin-film samples were sandwiched between microscope slides, melted at 210°C for 5 min to erase any trace of crystal, and then rapidly cooled to a predetermined crystallization temperature. The samples were kept isothermally until the crystallization process was completed, and meanwhile, photographs were automatically taken.

The mechanical and optical properties were measured according to ASTM test methods, such as D-638 for the tensile strength and D-790 for the flexural modulus, using a universal testing machine. The Izod impact strength was tested on the basis of D-256 and the haze value was tested on the basis of D-1003. The heat distortion temperature was tested according to ISO 75–2(1993) using a HDT 3 VICAT test instrument (Ceast Company, Italy).

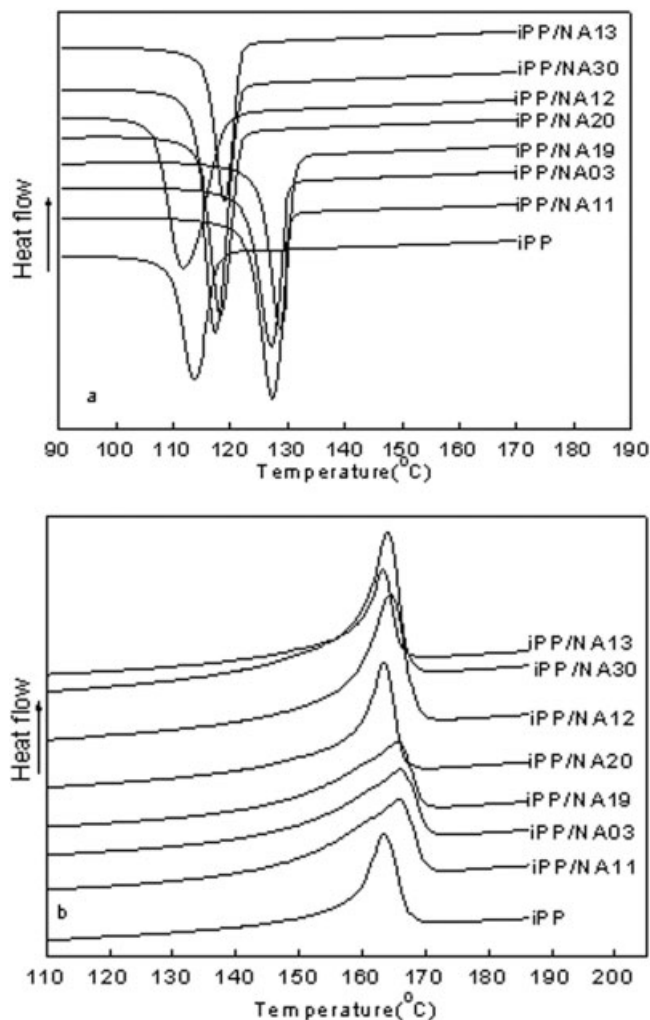
## RESULTS AND DISCUSSION

### Effect of substituted aromatic heterocyclic phosphate salts on crystallization and melting behaviors of iPP and nucleated iPP

Four parameters are often used to evaluate the crystallization rate of polymers<sup>9</sup>: (1) crystallization peak temperature of polymers; (2) the crystallization half-time  $t_{1/2}$  of polymers or crystallization rate constant  $K$  in Avrami equation under isothermal crystallization; (3) nuclei density of crystallization or spherulite size after crystallization finished; and (4) surface free energy of crystallization nucleation. It is the simplest method using crystallization peak temperature and sharp degree of crystallization peak to evaluate the crystallization rate of polymers. In general, the higher the crystallization peak temperature and the sharper the crystallization peak, the faster is the crystallization rate. Cooling and heating thermograms of virgin iPP and nucleated iPP performed by DSC dynamic scans at a cooling or heating rate of 20°C/min are shown in Figure 1. The corresponding crystallization and melting peak temperatures determined from Figure 1 are given in Table I. It can be seen from cooling thermograms of iPP [Fig. 1(a)] that the addition of nucleating agents can increase the crystallization peak temperature of iPP, in which monovalent sodium salt (NA11), lithium salt (NA03), and potassium salt (NA19) of substituted aromatic heterocyclic have better effect than bivalent calcium salt (NA20), magnesium salt (NA12), zincum salt (NA30), and trivalent aluminum salt (NA13). When 0.2 wt % of sodium salt, lithium salt, or potassium salt is added into iPP, crystallization peak temperature ( $T_c$ ) of iPP can be increased from 113.8 to 127.3, 127.4, and 128.8°C, respectively. However, other salts of substituted aromatic heterocyclic phosphate increase the crystallization peak temperature of iPP considerably less, which shows that these salts have weak nucleation effects on iPP. It can be also seen from Figure 1(a) that the addition of sodium salt, lithium salt, or potassium salt can make the crystallization peak become sharper and scope of crystallization temperature become narrower, which shows the addition of these salts increases the crystallization rate of iPP significantly.

The heating thermogram [Fig. 1(b)] shows that there is only a single melting peak in the DSC curves of the nucleated iPP. This means that the metal salts of substituted aromatic heterocyclic phosphate used in this study appear to act as nucleating agents for  $\alpha$ -spherulites of iPP. The melting peak temperatures ( $T_m$ ) of iPP are listed in Table I.

It can be seen from Table I that addition of substituted aromatic heterocyclic phosphate metal salts can increase the  $T_m$  and crystallinity ( $X_c$ ) of iPP. With 0.2 wt % sodium salt (NA11), lithium salt (NA03), and potassium salt (NA19) incorporated into iPP, the  $T_m$  of iPP/NA11, iPP/NA03, and iPP/NA19 can be increased by about 3°C, and  $X_c$  can be



**Figure 1** DSC cooling thermograms (a) and melting thermograms (b) for iPP and nucleated iPP at 20°C/min.

increased by about 5%, while the  $T_m$  and  $X_t$  of iPP/NA20, iPP/NA12, iPP/NA30, and iPP/NA13 are increased considerably less. This means the nucleation ability of monovalent metal salts such as NA11, NA03, and NA19 is much stronger than that of bivalent salts NA20, NA12, NA30, and trivalent

salts NA13. The stronger the nucleating ability, the higher the melting temperature and crystallinity are. Because the nucleating agents increase the crystallization temperature, iPP crystallizes at a higher temperature. Thus, the perfection of nucleated iPP increases with the increment of crystallization temperature, which makes the melting temperature and crystallinity rise.

Some articles put forward to several evaluation criteria for nucleation ability. Beck and Ledbetter<sup>11</sup> stated that the supercooling,  $\Delta T$  ( $\Delta T = T_m - T_c$ ), i.e., the difference between the melting peak temperature and the crystallization peak temperature was a function of the overall rate of crystallization. Rybnikar<sup>12,13</sup> utilized the difference between the crystallization peak temperature of the nucleated polymer and that of virgin polymer,  $\Delta T_c$ , as a criterion for evaluating the nucleating effect. If  $\Delta T_c \geq 6.5^\circ\text{C}$ , the nucleating efficiency was high. If  $\Delta T_c = 5\text{--}6.5^\circ\text{C}$ , the efficiency was medium. For a difference of 3–5°C, the nucleating efficiency was low. This evaluation of nucleating ability agreed, on the whole, with the classification according to the spherulite size by microscopy (mean size of spherulites less than 50  $\mu\text{m}$ , high nucleating efficiency; 50–100  $\mu\text{m}$ , medium; and 100–200  $\mu\text{m}$ , low). It can be seen in Table I that  $\Delta T$  of iPP/NA11, iPP/NA03, and iPP/NA19 is 38.6, 38.9, and 37.2°C, respectively, considerably less than that of iPP, 49.7°C, and  $\Delta T_c$  of iPP/NA11, iPP/NA03, and iPP/NA19 is 13.5, 13.6, and 15.0°C, respectively, while other salts have little effect on  $\Delta T$  and  $\Delta T_c$  of iPP, which denotes that monovalent salts NA11, NA03, and NA19 are nucleating agents of high efficiency, and nucleation efficiency of bivalent salts NA20, NA12, NA30, and trivalent salts NA13 is weak.

#### Effect of substituted aromatic heterocyclic phosphate salts on mechanical and optical properties of iPP and nucleated iPP

The effect of substituted aromatic heterocyclic phosphate salts on mechanical and optical properties of iPP and nucleated iPP are compared (Table II).

**TABLE I**  
Crystallization and Melting Parameters of iPP and Nucleated iPP

Index	iPP	iPP/NA11	iPP/NA03	iPP/NA19	iPP/NA20	iPP/NA12	iPP/NA30	iPP/NA13
$T_c$ (°C)	113.8	127.3	127.4	128.8	118.8	114.1	117.9	119.2
$T_{\text{onset}}$ (°C)	117.8	130.3	130.1	131.6	121.8	119.3	121.5	122.1
$T_{\text{end}}$ (°C)	109.7	123.2	122.9	125.1	114.9	107.3	113.9	116.0
$T_m$ (°C)	163.5	165.9	166.3	166.0	163.7	164.7	164.0	163.4
$\Delta T$ (°C)	49.7	38.6	38.9	37.2	44.9	52.6	46.1	44.2
$\Delta T_c$ (°C)	0	13.5	13.6	15.0	5.0	0.3	4.1	5.4
$\Delta H$ (J/g)	101.4	111.6	113.3	110.8	103.0	100.9	103.7	104.7
$X_t$ (%)	48.5	53.4	54.2	53.0	49.3	48.3	49.6	50.1

$$X_t = \Delta H / \Delta H_f \times 100\%^{10} \text{ (here, } \Delta H_f \text{ is 209 J/g for iPP).}$$

TABLE II  
Effect of Nucleating Agents on Mechanical and Optical Properties of iPP

Properties	iPP	iPP/NA11	iPP/NA03	iPP/NA19	iPP/NA20	iPP/NA12	iPP/NA30	iPP/NA13
Tensile strength (MPa)	33.73	37.44 ± 0.17	37.22	36.49	35.66	34.22	33.50	32.84
Tensile modulus (MPa)	983	1111 ± 13	1101	1076	1061	994	963	946
Flexural strength (MPa)	43.79	54.01 ± 0.60	54.68	53.79	45.64	43.69	42.34	41.52
Flexural modulus (MPa)	1261	1631 ± 34	1684	1614	1365	1291	1267	1206
Impact strength (J/m)	35.27	30.55 ± 0.48	32.94	31.47	42.91	31.93	32.05	33.50
Haze value (%)	83.85	48.39 ± 0.93	45.90	51.08	73.68	81.58	84.13	83.58

It can be seen that the addition of monovalent metal salts such as sodium salt (NA11), lithium salt (NA03), and potassium salt (NA19) of substituted aromatic heterocyclic phosphate can improve the mechanical and optical properties of iPP obviously. With 0.2 wt % sodium salt (NA11), lithium salt (NA03), and potassium salt (NA19) of substituted aromatic heterocyclic phosphate incorporated into iPP, tensile strength of iPP can be increased by 11.00, 10.35, and 8.18%, respectively; flexural modulus of iPP can be increased by 29.34, 33.54, and 28.00%; and haze value of iPP can be decreased by 42.29, 45.26, and 39.08%, which indicates that sodium salt (NA11), lithium salt (NA03), and potassium salt (NA19) of substituted aromatic heterocyclic phosphate have good performance in iPP. The addition of NA11, NA03, and NA19 can increase the crystallinity and decreased the spherulite size of iPP, and then the mechanical and optical properties of iPP can be increased. Other nucleating agents such as bivalent calcium salt (NA20), magnesium salt (NA12), zincum salt (NA30), and trivalent aluminum salt (NA13) have little effect on properties of iPP. This is consistent with the result as seen from thermal analysis earlier. In addition, the impact strength of iPP/NA11, iPP/NA03, and iPP/NA19 has slight decline, which may be caused by the increasing of crystallinity degree due to the addition of nucleating agents. Shiho Yoshimoto et al.<sup>7</sup> utilized epitaxial crystallization to explain the nucleation effect of sodium 2,2-methylene-bis(4,6-di-*tert*-butylphenyl) phosphate (expressed as NA-11) on iPP. As the *c* cell dimension of iPP is very close to the *b* cell dimension of sodium 2,2-methylene-bis(4,6-di-*tert*-butylphenyl) phosphate, and further the *a* cell dimension of sodium 2,2-methylene-bis(4,6-di-*tert*-butylphenyl) phosphate is about four times the *a* value of iPP cell, the lattice matching is able to be performed between two crystal lattices, and then the following epitaxial crystallization will take place preferentially:  $[010]_{\text{NA-11}} // [001]_{\text{iPP}}$  and  $[001]_{\text{NA-11}} // [010]_{\text{iPP}}$ . The free energy barrier of nucleation is reduced because of the existing of epitaxial crystallization, and then the rate of nucleation increases. The strong or weak nucleation ability of other metal salts of 2,2-methylene-bis(4,6-di-*tert*-butylphenyl) phos-

phate may result from whether there is crystal lattice matching between the nucleating agent and iPP, which we will study in further work.

#### Effect of substituted aromatic heterocyclic phosphate salts on heat distortion temperature (HDT) of iPP and nucleated iPP

The effect of different metal salts of substituted aromatic heterocyclic phosphate on HDT of iPP is shown in Figure 2.

It can be seen that the addition of monovalent metal salts can significantly increase the heat distortion temperature of iPP. With 0.2 wt % sodium salt (NA11), lithium salt (NA03), and potassium salt (NA19) of substituted aromatic heterocyclic phosphate incorporated into iPP, the heat distortion temperature of iPP can be increased from 75 to over 100°C. However, bivalent metal salts such as calcium salt (NA20), magnesium salt (NA12), zincum salt (NA30), and trivalent aluminum salt (NA13) have little effect on heat distortion temperature of iPP. This also means monovalent metal salts have stronger nucleation ability than bivalent and trivalent metal salts, and the addition of these nucleating agents can increase the crystallinity of iPP and make the crystals become more perfect so that the heat distortion temperature of iPP increases.

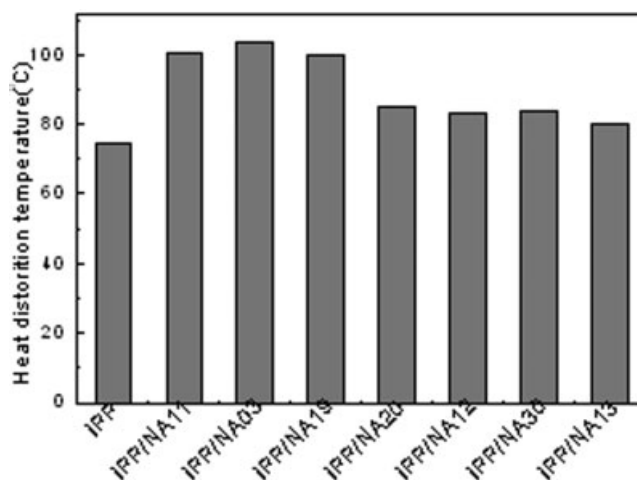
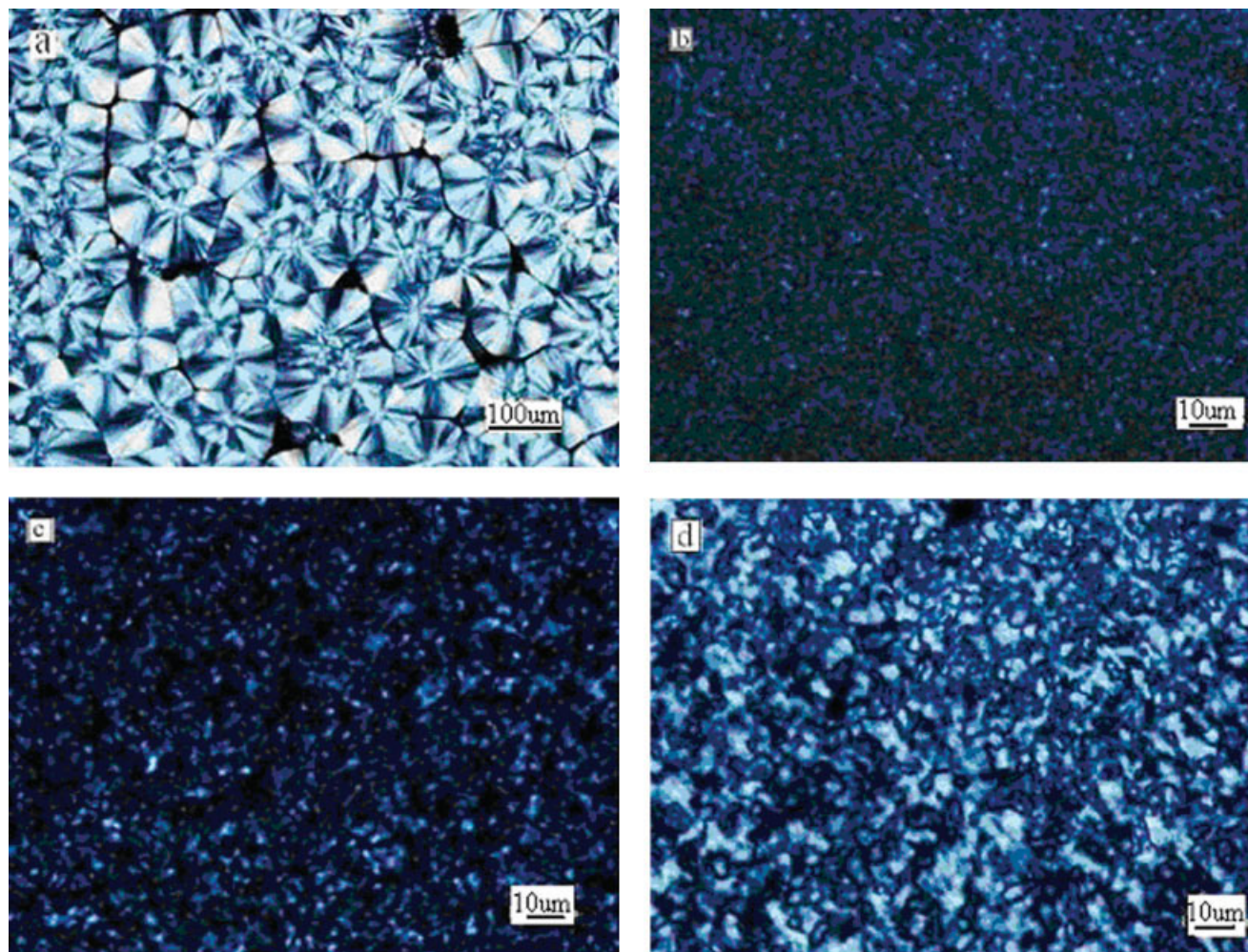


Figure 2 Effect of nucleating agents on HDT of iPP and nucleated iPP.



**Figure 3** Polarized optical micrographs of iPP (a), iPP/NA11 (b), iPP/NA12 (c), and iPP/NA13 (d) under isothermal crystallization at 140°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

#### Effect of substituted aromatic heterocyclic phosphate salts on micromorphology of iPP and nucleated iPP

Polarized optical micrographs of virgin iPP and nucleated iPP crystallized under isothermal conditions (140°C) are shown in Figure 3.

As seen in Figure 3, the addition of NA11, NA12, and NA13 can decrease the spherulite size of iPP remarkably. It is well known that the overall crystallization rate of polymer is determined by both the rate of crystal nucleation and the rate of crystal growth rate. As in virgin iPP nuclei are difficult to form, spherulite growth in it is mainly homogeneous nucleation, followed by nucleation-controlled spherulite growth; the nucleation rate is slow and number of nucleus is very few, and so the spherulite of iPP can become very large before it impinges another spherulite. While in nucleated iPP, a large number of nuclei should be produced because of the existence of nucleating agents, and so the nucleation rate is very fast and the spherulite growth in it is heterogeneous nucle-

ation, followed by diffusion-controlled growth. Because of the existing of a large number of nuclei the spherulite can not grow large enough to overlap, and so the size of spherulites in nucleated iPP should be far smaller than those in virgin iPP.

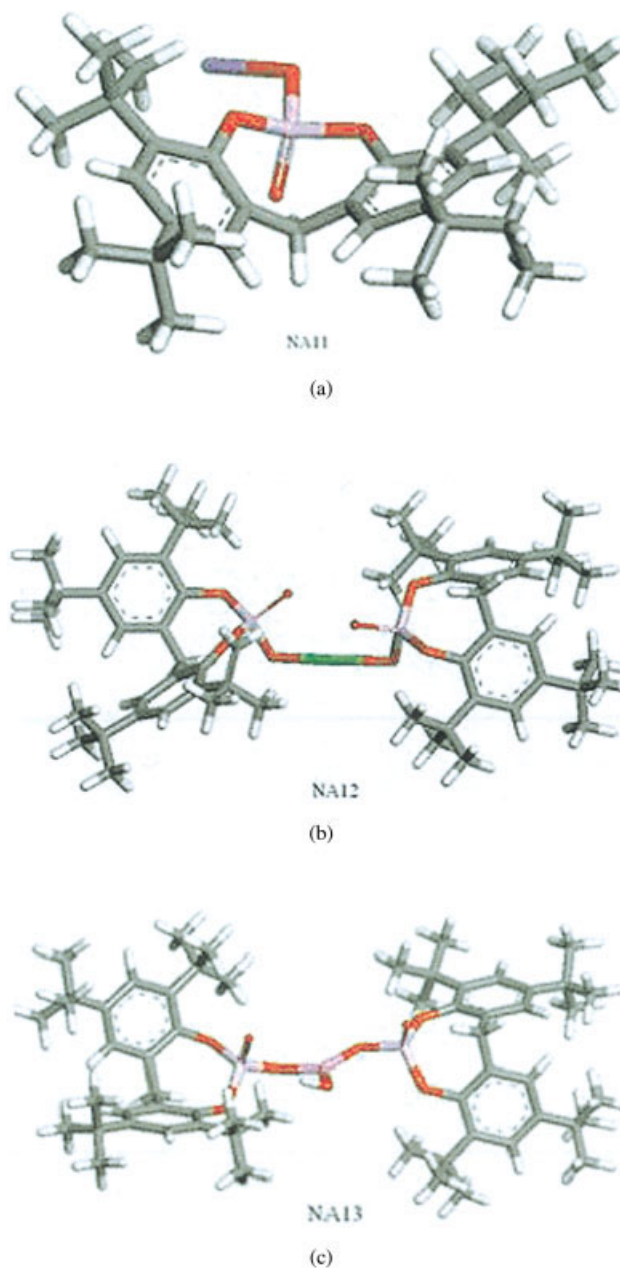
Different metal salts of substituted aromatic heterocyclic phosphate have different effect on morphology of iPP. The spherulite size of iPP/NA11 is much smaller than that of iPP/NA12 and iPP/NA13, especially the spherulite of iPP/NA13 is loose and nonuniform. This means monovalent metal salt NA11 is the most effective in nucleation activity. Wittmann and Lotz<sup>14,15</sup> used epitaxial crystallization between polymer and substrates to explain the nucleation effect of different nucleating agents on polymers. Epitaxial crystallization is the growth of one phase on the surface of a crystal of another phase in one or more strictly defined crystallographic orientation, and it is often defined in terms of purely geometric lattice matching: 10–15% registries between the matching lattice spacing of host and guest crystals are considered as an

upper limit. Nucleation densities are higher when lattice matching is approached, then the spherulite size of iPP can be decreased significantly. It has been found that NA11 has a monoclinic unit cell with parameters  $a = 2.6348$  nm,  $b = 0.608$  nm, and  $c = 3.7172$  nm, and iPP also has a monoclinic unit cell with parameters  $a = 0.665$  nm,  $b = 2.096$  nm, and  $c = 0.65$  nm<sup>7</sup>. There is good lattice matching between crystals of NA11 and that of iPP. As stated before the  $c$  cell dimension of iPP is very close to the  $b$  cell dimension of NA11. Further the cell dimension of NA11 is about four times the a value of iPP cell, and so the lattice matching is able to be performed between two crystal lattices, and then the following epitaxial crystallization will take place preferentially:  $[010]_{\text{NA-11}} // [001]_{\text{iPP}}$  and  $[001]_{\text{NA-11}} // [010]_{\text{iPP}}$ , which will make NA11 have good nucleation ability and can decrease the spherulite size of iPP increasingly.

The molecular configurations of NA11, NA12, and NA13, simulated by means of Accelrys Materials Studio Modeling, are displayed in Figure 4. Twin aromatic rings in NA11 form a v-shaped structure, and there are two such v-shaped structures in NA12 and NA13. Some articles<sup>5,16</sup> put forward that v-shaped structure in nucleating agents is the main reason that nucleating agents have good performance because the v-shaped structure in them can stabilize the PP helix effectively. Although NA12 and NA13 have similar chemical structures as NA11 while the only difference is on metal ion and all of them have v-shaped structures, they have different effect on morphology of iPP. Maybe this is lead by the mismatching of crystal lattice between them and iPP. This denotes that nucleation effect may have close relationship with crystal structure of nucleating agents. The crystal structures of NA12 and NA13 are not reported as yet. Crystal system of NA12 and NA13 may also be monoclinic because of their similar chemical structure as that of NA11, but the lattice parameters of their crystals may have large difference with those of NA11 crystal, which will lead to mismatching of crystal lattice between them and iPP then their nucleation effect are weak. This should be testified in the further work.

### CONCLUSION

Different metal salts of 2,2'-methylene-bis(4,6-di-*tert*-butylphenyl) phosphate are nucleating agents for  $\alpha$ -spherulites of iPP. The monovalent metal salts such as sodium salt, lithium salt, and potassium salt have stronger nucleation ability than bivalent and trivalent metal salts; they can significantly increase the crystallization peak temperature and crystallization rate of iPP. They can also improve the mechanical properties of iPP such as tensile strength and flexural modulus increasingly; meanwhile they can decrease the haze value of iPP so that the clarity of iPP can be improved.



**Figure 4** Molecular configurations of NA11, NA12, and NA13. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Morphological study on iPP and nucleated iPP shows that different metal salts of substituted aromatic heterocyclic phosphate have different effect on spherulite size of iPP, in which sodium salt can decrease the spherulite size of iPP significantly and it is the most effective nucleating agent. The different nucleation effects of different nucleating agents may be lead by the mismatching of crystal lattice between nucleating agents and iPP.

### References

1. Feng, Y.; Jin, X.; Hay, N. *J Appl Polym Sci* 1998, 69, 2089.
2. Zhang, Y.-f.; Xin, Z. *China Plastics* 2000, 16, 10.

3. Fillon, B.; Lotz, B.; Thierry, A.; Wittmann, J. C. *J Polym Sci Part B: Polym Phys* 1993, 31, 1395.
4. Gui, Q.; Xin, Z.; Zhu, W. P.; Dai, G. C. *J Appl Polym Sci* 2003, 88, 297.
5. Zhang, G.-P.; Xin, Z.; Yu, J.-Y.; Xin, Z.; Gui, Q. D.; Wang, S. Y. *J Macromol Sci Part B: Phys* 2003, 42, 467.
6. Zhang, G.; Yu, J.; Xin, Z. *J Macromol Sci Part B: Phys* 2003, B42, 663.
7. Yoshimoto, S.; Ueda, T.; Yamanaka, K.; Kawaguchi, A.; Tobita, E.; Haruna, T. *Polymer* 2001, 42, 9627.
8. Xin, Z. CN1358728, 17 July 2002.
9. Chen, Y.; Xu, M. *Acta Polymerica Sinica* 1998, 6, 671.
10. Phillips, R.; Manson, J. A. E. *J Polym Sci Part B: Polym Phys* 1997, 35, 875.
11. Beck, H. N.; Ledbetter, H. D. *J Appl Polym Sci* 1965, 9, 2131.
12. Rybnikar, F. *J Appl Polym Sci* 1969, 13, 827.
13. Rybnikar, F. *J Appl Polym Sci* 1982, 27, 1479.
14. Wittmann, J. C.; Lotz, B. *J Polym Sci Part B: Polym Phys* 1981, 19, 1837.
15. Wittmann, J. C.; Lotz, B. *Prog Polym Sci* 1990, 15, 909.
16. Smith, T. L.; Masilamani, D.; Bui, L. K.; Khanna, Y. P.; Bray, R. G.; Hammond, W. B.; Curran, S.; Belles, J.; Binder-Castelli, S. *Macromolecules* 1994, 27, 3147.