# Heterogeneous Nucleating Agents for Polypropylene Crystallization

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#### Synopsis

A model nucleating agent for polypropylene crystallization is described. A series of compounds consisting mainly of organocarboxylic acid salts is evaluated as heterogeneous nucleating agents for polypropylene crystallization by measuring their effect upon the polymer supercooling. Sodium benzoate and basic aluminum dibenzoate were among the best nucleating agents found. The nucleating abilities of the various compounds are discussed in terms of their structural features.

### **INTRODUCTION**

It has been shown that the presence of a small amount of a deliberately added heterogeneous foreign material in polypropylene may considerably change the polymer's crystallization temperature, its spherulitic size, density, clarity, and its impact and tensile properties.<sup>1,2</sup> However, compounds vary widely in their effectiveness as heterogeneous nucleating agents.<sup>1-7</sup> The present work was undertaken to evaluate a series of compounds as nucleating agents for polypropylene crystallization. It was hoped that some obvious correlation might be found between each compound's nucleating ability and its structural characteristics.

It was considered reasonable to assume that a good nucleating agent should possess at least the five following characteristics. (a) It should be capable of reducing the interfacial surface free energies involved, i.e., it should be wet by polypropylene or adsorb polymer on its surface at and below the polymer melting point. (For recent reviews on nucleation theory see references 8–10.) (b) It should be insoluble in polypropylene at and below the polymer melting point. (c) It should melt above the polymer melting point and preferably without decomposition. (d) It should be nonvolatile, stable, and unreactive towards its environment, i.e., polymer, oxygen, moisture, and miscellaneous polymer additives. (e) Also, if possible, it should possess a crystalline structure similar to that of polypropylene.

Considering property (a), one might expect a good solvent for polypropylene, such as a hydrocarbon, to be an important constituent of the structure of a good nucleating agent for polypropylene crystallization. Property (b), of course, implies that the nucleating agent must present a solid surface to the polymer in the temperature range of importance for crystallization. It also suggests that another constituent of this good nucleating agent would be a group capable of rendering the molecule insoluble in the polymer. Such an "insolubilizing" group might be a highly polar substituent, for example, a carboxylic acid moiety. Preliminary experiments indicated that such a concept of a model nucleating agent might indeed be useful. For example, purely inorganic compounds almost universally were found to be relatively poor nucleating agents. Hydrocarbons were relatively ineffective. However, many organic acids, especially their salts, were in general more effective. Further investigation revealed the correlations between nucleating ability and structure reported in the following sections of this paper.

Polypropylene exhibits a large amount of supercooling that may be easily measured by DTA techniques.<sup>1</sup> The cooling rate of the polymer from the melt and the presence of the heterogeneous nucleating agents can alter the amount of supercooling. The compounds were evaluated as nucleating agents by observing their effect upon the polymer freezing point. The cooling rate and weight per cent of nucleating agent were the same in all compositions. The more effective the nucleating agent, the greater was the observed reduction in polymer supercooling, i.e., the higher the polymer freezing point.

## **EXPERIMENTAL**

The carboxylic acids used and a few of the salts were available commercially. The salts that were not commercially available were prepared (a) by reaction of a slight excess of the aqueous acid with the metal hydroxide or metal carbonate followed by repeated ether extractions to remove excess acid, or (b) more commonly, by titration of aqueous or aqueous ethanol solutions or suspensions with aqueous sodium hydroxide by using a Leeds and Northrup pH meter with glass and calomel electrodes. Aluminum salts were prepared from the acid and triethyl aluminum in hot Decalin or *p*-xylene in a dry nitrogen atmosphere.

Compositions containing the nucleating agents, 0.25 wt.-%, in samples of Dow polypropylene 201 ( $T_p = 106^{\circ}$ C.) were prepared on a Meili mill as described previously.<sup>1</sup> The differential thermal analysis equipment and procedure have been described in a previous paper.<sup>1</sup> The peak freezing temperatures of the polymer-nucleating agent compositions observed upon crystallization are referred to as  $T_p$ .  $T_p$  is reproducible to  $\pm 1^{\circ}$ C. For ease of discussion the compounds are arbitrarily classified as good ( $T_p =$ 125–131°C.), intermediate ( $T_p = 116-124^{\circ}$ C.), or poor ( $T_p = 106-115^{\circ}$ C.) nucleating agents.

### **RESULTS AND DISCUSSION**

### **Inorganic Compounds**

The inorganic compounds examined were poor nucleating agents (Table I). The best were titanium phosphate and finely powdered Pyrex glass.

Compound	<i>T</i> <sub>p</sub> , °C.
Methylsilsesquioxane resin	121
Octadecylsilsesquioxane resin	116
Phenylsilsesquioxane resin*	115
Titanium phosphate	114
Pyrex glass <sup>b</sup>	113
Cab-O-Sil <sup>o</sup>	113
Eutectic alloy <sup>d</sup>	112
Aluminum ammonium sulfate	112
Aluminum sodium sulfate	112
Aluminum potassium sulfate	111
Titanium dioxide (anatase)	111
Aluminum oxide	111
Calcium oxide	110
Magnesium sulfate	110
Sodium sulfate	110
Lithium chloride	109
Bentonite	109
Phenylsilsesquioxane resin <sup>e</sup>	109
Phenylsilsesquioxane resin <sup>f</sup>	108
Silver nitrate	107

 TABLE I

 Representative Inorganic Materials

• Intrinsic viscosity 0.019 dl./g. in toluene at 25°C.

<sup>b</sup> 200–270 mesh.

<sup>o</sup> Concentration 5 wt.-%.

<sup>d</sup> Sn, 49.8 wt.-%; Pb, 32.2 wt.-%; and Cd, 18.0 wt.-%; m.p. = 147°C.

• Only partially soluble in toluene at 25°C.

<sup>f</sup> Intrinsic viscosity 0.031 dl./g. in toluene at 25°C.

Cab-O-Sil silica, even when used at a relatively high concentration, was It has been implied that many inorganic compounds are good poor. nucleating agents.<sup>11</sup> They do nucleate somewhat, but, as will be shown later, by comparison with certain organic salts they are poor. Several low molecular weight organosilsesquioxane resins are included in Table I for comparison. They are representative of a class of substances intermediate in properties between organic and inorganic.<sup>12</sup> The introduction of organic groups, such as methyl, octadecyl, and phenyl, into a silica by hydrolysis of the appropriate organotrichlorosilanes may give compounds of improved nucleating ability. A wide range of nucleating ability was observed with several samples of phenylsilsesquioxane differing in degree of condensation. The differences in nucleating ability observed for these silicone resins illustrate the sensitivity of nucleation to relatively small structural differences in the nucleating agent. Thus modified siliceous materials containing surface alkoxy groups, such as estersils, might also reduce the supercooling of polypropylene.<sup>11</sup> Alkyl quaternary halides also show properties characteristic of both organic and inorganic compounds. However, tetramethyl-, ethyl-, propyl-, and butylammonium chlorides, bromides, and iodides were poor nucleating agents ( $T_p = 109-115^{\circ}$ C.).

## Effect of "Insolubilizing" Group

Most common aliphatic hydrocarbons, benzene, and naphthalene are unsuitable as nucleating agents because of their low melting points. The few high-melting aromatic compounds examined were found in general to be intermediate (anthracene,  $T_p = 119$ °C.) or poor (*p*-terphenyl,  $T_p =$ 115°C., polybenzene,  $T_p = 113$ °C., <sup>13</sup> anthraquinone,  $T_p = 112$ °C., and poly(diphenyl ether),  $T_p = 109$ °C., prepared by method of Kovacic<sup>13</sup>) in nucleating ability. The properties of hydrocarbons can be substantially altered by the addition of a carboxylic acid group to the hydrocarbon species. This group was chosen for study as the "insolubilizing" group because of the commercial availability of a large selection of various organic carboxylic acids and the ease in which their properties may be changed through salt formation.

Though slightly effective, the substituted benzoic acids examined that melt at a higher temperature than polypropylene are poor nucleating agents in general (Table II). Only *p-tert*-butylbenzoic acid showed intermediate nucleating ability. The corresponding sodium salts are much more ef-

		<i>T</i> <sub>p</sub> , °C.			
	Acid	Al salt		Na salt	· · · · · · · · · · · · · · · · · · ·
R	(para)	(para)	para	ortho	meta
н		127	131	131	131
t-C4H9	117	126	131,5	121.5	121
CH₃		120	132	119	118
I	107		130.5	123	123
Br	108	117	130	125	120
Cl	108	121	130	124	122
$C_6H_5$			129		
<i>"</i> 0					
C <sub>6</sub> H <sub>5</sub> C			113	124	
C <sub>2</sub> H <sub>5</sub> O	109	117	128	129	
i-C3H7		118	128		
F	109	126	126	130	128
CH3O	106	121	124	131	116
C <sub>6</sub> H <sub>5</sub> O				121	
$C_2H_5$			123		
OH	108		122	121	116
$\mathbf{CN}$			119.5		
// <sup>0</sup>					
CH₃C				114	
NO <sub>2</sub> \			114	111	111
CO₂Na			112.5	113.5	113
$\rm NH_2$			112	112	112

TABLE II

Effect of Substituent Groups, R, upon  $T_p$  for Substituted Benzoic Acids and Sodium and Aluminum Benzoates

fective. This effect might be due to a combination of the higher solubilities of the free acids in the polymer compared to the salts, a drastic reduction in the acids' melting points when mixed with excess polymer, and a generally more favorable geometry and surface of the salts.

Effect of Metal Cations. Sodium benzoate was the most effective nucleating agent out of 21 metal benzoates examined (Table III). Basic aluminum dibenzoate was the next most effective compound. No obvious correlations appear to exist between nucleating ability and the cation atomic weight, number, and radius or valence. A general tendency for the peak temperatures to converge at approximately 116–117°C. with increasing atomic number is evident.

Effect of Cation of Metal B	Effect of Cation of Metal Benzoates, C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> M, upon $T_p^{a}$	
M	<i>T</i> <sub>p</sub> , °C.	
Li	125	
Na	131	
$\mathbf{M}\mathbf{g}$	117	
Al	127	
К	125	
Ca	116	
Ti	112.5	
$\mathbf{Mn}$	120	
Fe	116	
Со	118.5	
Ni	115	
Cu	118	
Zn	112	
Rb	117	
Sr	114	
Ag	117	
Cd	117	
$\mathbf{Cs}$	117	
Ba	121	
Pb	108	
Bi	117	

TABLE III

\* Arranged in order of increasing atomic number of the metal used.

**Comparison of Sodium and Aluminum Salts.** The nucleating ability of other sodium and aluminum carboxylates were examined (Tables II, IV, and V), since sodium benzoate and basic aluminum dibenzoate were the best of the metal aromatic carboxylates examined. Of the 18 corresponding salts examined, aluminum adipate was the only aluminum salt significantly superior to the corresponding sodium salt. This evidence suggests that the relative effectiveness of the metal benzoates shown in Table III might also be reasonably extrapolated with some confidence to include their corresponding salts of other organocarboxylic acids.

		$T_{p}$	°C.
Acid	No. of C atoms	Na salt	Al salt
	Dibasic Acid	l Salts	
Oxalic	2	115	
Malonic	3	113	
Succinic	4	125	111
Glutaric	5	128	117
Adipic	6	112	124.5
Pimelic	7	110	
Suberic	8	120	
Azelaic	9	111	
Sebacic	10	114	
	Monobasic Ac	eid Salts	
Formic	1	113	
Acetic	2	112	114
Propionic	3	113	
Isobutyric	4	116	
<i>n</i> -Butyric	4	114	
Pivalic	5	126	118
n-Valeric	5	113	
3-Methylbutyric	5	112	
DL-2-methylbutyric	5	109	
4-Methylvaleric	6	118.5	
Caproic	6	118	111
2-Methylvaleric	6	110	
Heptanoic	7	112	
Octanoic	8	113	
Nonanoic	9	110	
Decanoic	10	106	
Undecanoic	11	114.5	
Dodecanoic	12	109.5	
Tridecanoic	13	110	
Myristic	14	110	
Behenic	22	110	
	Alicyclic Aci	d Salts	
Cyclopropanecarboxylic	4	108	
Cyclobutanecarboxylic	5	115	
Cyclopentanecarboxylic	6	115	
Cyclohexanecarboxylic	7	130	
Cycloheptanecarboxylic	8	125	

TABLE IVEffect of Chain and Ring Size upon  $T_p$  for Sodium and Aluminum Salts of Aliphatic<br/>Mono- and Dibasic Acids and Alicyclic Acids

## **Aliphatic Compounds**

The effect of increasing chain size of sodium aliphatic dicarboxylates upon the supercooling of polypropylene is shown in Table IV for sodium oxalate through sodium sebacate. With three exceptions, the salts are generally poor nucleating agents. Sodium suberate has intermediate

	$T_{p}, \ ^{\circ}\mathrm{C}.$	
Acid	Na salt	Al salt
1,2-Cyclohexanedicarboxylic	128	118
Diphenylacetic	125	
2,4,5-Trichlorophenoxyacetic	124	
2,4-Dimethoxybenzoic	122	
cis-4-Cyclohexene-1,2-dicarboxylic	122	123
1,4-Cyclohexanedicarboxylic	121	
Benzophenone-2,4'-dicarboxylic	120	
Homophthalic	120	
Phenylacetic	120	122
Tetraphenylphthalic	120	
Cinnamic	120	
3,5-Dimethylbenzoic	120	
2,5-Dimethylbenzoic	120	
2,5-Dihydroxybenzoic	119	
4-Methyl-4-cyclohexene-1,2-dicarboxylic	118	
Diphenyl-2,2'-dicarboxylic	118	
Phenoxyacetic	118	
α-Phenoxypropionic	118	
2,4,6-Trimethylphenylacetic	118	
Benzenehexacarboxylic	117	
Benzene-1,3,5-tricarboxylic	116	
Phenol	116	
3,4-Dichlorobenzoic	116	
Benzene-1,2,4,5-tetracarboxylic	115	
Triphenylacetic	115	
2,3,5-Triiodobenzoic	115	
Pentafluorobenzoic	114	
Phthalic	113.5	
Diphenyl-4,4'-dicarboxylic	113	
Isophthalic	113	113•
Diphenylmethane-3,3'-dicarboxylic	113	
2,4-Dimethylbenzoic	113	
Terephthalic	112.5	
2-Hydroxy-3,5-diiodobenzoic	112	
<i>p</i> -Methoxyphenylacetic	112	
3,4-Dimethoxyphenylacetic	111	
2,4-Dichlorophenoxyacetic	109	
3-Phenylpropionic	108	

 TABLE V

 Relative Nucleating Ability of

 Sodium and Aluminum Salts of Aromatic Carboxylic Acids

\* Free acid.

nucleating ability, while sodium succinate and sodium glutarate are relatively good. The nucleating abilities of the sodium normal aliphatic monocarboxylates are relatively independent of the chain length of the salt (Table IV). With the exception of sodium caproate, which has intermediate nucleating ability, these salts are relatively poor nucleating agents. Of the isomeric sodium aliphatic monocarboxylates examined, only sodium 4-methylvalerate and sodium isobutyrate were of intermediate nucleating ability, but even these behaviors were not significant within the experimental error when compared to the normal salts. Sodium pivalate was the best of the monobasic salts examined, and its behavior will be discussed later. The nucleating effects of the sodium alicyclic monocarboxylates examined are also shown in Table IV. The maximum nucleating effect appears to be at six ring carbon atoms, sodium cyclohexanecarboxylate being as good a nucleating agent as sodium benzoate within the experimental error. Sodium cycloheptanecarboxylate is as good as aluminum benzoate.

In general, the sodium salts of aliphatic mono- and dibasic acids and alicyclic monocarboxylates are poor nucleating agents. However, within the first two classes, exceptional nucleating ability occurs in the neighborhood of four to six chain carbon atoms, and in the alicyclic series, at six to seven ring carbon atoms. The reason for this behavior is not known, but it possibly reflects an ability of the compound through favorable geometry to form a crystal lattice of optimum surface energy and/or optimum dimensions for nucleation and epitaxial growth of polypropylene.

The presence of unsaturation in the aliphatic chain appears to inhibit nucleation somewhat compared to the saturated analog. For example, sodium succinate  $(T_p = 125^{\circ}\text{C.}) >$  sodium maleate  $(T_p = 115^{\circ}\text{C.}) >$  sodium fumarate  $(T_p = 110^{\circ}\text{C.})$ ; sodium *n*-butyrate  $(T_p = 114^{\circ}\text{C.}) \geq$  sodium 3-butenoate  $(T_p = 113^{\circ}\text{C.})$ ; sodium *n*-caproate  $(T_p = 118^{\circ}\text{C.}) >$  sodium sorbate  $(T_p = 107^{\circ}\text{C.})$ ; and sodium undecanoate  $(T_p = 114.5^{\circ}\text{C.}) >$  sodium undecylenate  $(T_p = 107^{\circ}\text{C.})$ . It is possible that the rigidity introduced into the molecules by the presence of double bonds inhibits the salts from assuming a configuration and surface as favorable for nucleation as when only single bonds are present.

## **Aromatic Compounds**

Effect of Substituent Groups. The data of Tables II and IV-VI show that in general carboxylate salts containing an aromatic group are superior to carboxylate salts containing only aliphatic groups for nucleation of polypropylene crystallization. Sodium benzoate is one of the best nucleating agents examined. The nucleating ability of this salt can be changed substantially by substitution of various groups in the aromatic ring (Table The effect of substituents in general is to impede nucleation com-II). Similarly the presence of more than one ring pared to sodium benzoate. substituent tends to impede nucleation. Thirteen compounds were examined that contained multiple methyl, fluoro, chloro, iodo, hydroxy, and methoxy groups on the aromatic rings of sodium benzoate, phenylacetate, and phenoxyacetate. With one exception, sodium 2,4,5-trichlorophenoxyacetate, the nucleating ability was always poorer than that of the corresponding unsubstituted salt (Table V).

Effect of Orientation of Substituent Groups. The position of ring substituents in substituted sodium benzoates appears to have a pronounced

Acid	<i>T</i> <sub>p</sub> , °C.
2-Naphthoic	127
Naphthalene-1,8-dicarboxylic	126
2-Naphthyloxyacetic	126
2-Naphthylacetic	121
Naphthalene-2,6-dicarboxylic	117
Anthracene-9-carboxylic	117
Naphthalene-2,3-dicarboxylic	114
Anthraquinone-2-carboxylic	114
Fluorene-1-carboxylic	114
Naphthalene-1,6-dicarboxylic	114
Fluorene-9-carboxylic	112
Naphthalene-1,4,5,8-tetracarboxylic	111
1-Naphthylacetic	110
Anthracene-9,10-dicarboxylic	110
1-Naphthoic	108
1,1'-Binaphthyl-8,8'-dicarboxylic	108

 TABLE VI

 Relative Nucleating Ability of Sodium

 Salts of Fused-Ring Aromatic Carboxylic Acids

effect upon the nucleating ability (Table II). The data from 46 sodium salts indicate that nucleating ability usually is favored by *para* substitution (18 compounds, average,  $T_p = 124.2^{\circ}$ C.), followed by *ortho* (16 compounds, average  $T_p = 119.3^{\circ}$ C.), and then *meta* substitution (12 compounds, average  $T_p = 119.3^{\circ}$ C.). The effect of ring orientation appears to be less pronounced as the general nucleating ability of the substituent group decreases. A similar orientation effect is noted in the case of the three sodium pyridine carboxylates in which the ring nitrogen might be considered a pseudo substituent: sodium isonicotinate ("*para*,"  $T_p = 120^{\circ}$ C.) > sodium picolinate ("*ortho*,"  $T_p = 116.5^{\circ}$ C.) > sodium nicotinate ("*meta*,"  $T_p = 112.5^{\circ}$ C.).

This effect of ring orientation upon nucleating ability could allow the speculation that an electronic effect might be operating in heterogeneous nucleation. However, the inability to correlate the type of substituent group and a Hammett constant or group dipole moment with nucleating ability tends to preclude any significant electronic or polarization effect. One can only speculate on the effect of substituent group polarity upon the interfacial free energies. The order observed is due probably to a combination of a strong structural or steric effect that results in a suitable crystalline structure and surface for interaction for polypropylene and a weak, if any, electronic effect. Possibly somewhat related is the fact that of a series of related compounds the most symmetrical compound crystallizes the fastest.<sup>14,15</sup> This can be more likely explained through a favorable molecular symmetry rather than electronic effects.

Miscellaneous Aromatic Compounds. An examination of several miscellaneous arylalkyl acid salts (Table V) reveals that increasing the aliphatic character of sodium benzoate by introduction of aliphatic or ether linkages between the aromatic nucleus and the "insolubilizing" group reduces the nucleating ability. Thus sodium benzoate is superior to sodium phenylacetate,  $\beta$ -phenylpropionate, phenoxyacetate,  $\alpha$ -phenoxypropionate, or cinnamate. That aromatic character is not the only factor important in determining nucleating ability is illustrated by two examples: sodium triphenylacetate is an inferior nucleating agent compared to sodium diphenylacetate or phenylacetate. The nucleating ability of analogous dicarboxylates decreases as the ring progressively becomes more aromatic in character; sodium 1,2-cyclohexanedicarboxylate > cis-4-cyclohexene-1,2-dicarboxylate > phthalate, and sodium 1,4-cyclohexanedicarboxylate > terephthalate. Also the fact that sodium benzoate is superior to the benzene di-, tri-, tetra, and hexacarboxylates (Table V) indicates that nucleating ability may not be solely dependent upon insolubility or polar character.

**Fused Ring Aromatic Compounds.** A spectrum of effectiveness also exists among the sodium fused-ring aromatic carboxylates examined (Table VI). Most noteworthy is that the  $\beta$  or 2 isomer is superior to the corresponding  $\alpha$  or 1 isomer. The same behavior has been observed also in an analogous series of compounds not considered here.<sup>16</sup> This manifestation of a possibly more favorable molecular arrangement in the  $\beta$ -isomers for polymer–nucleating agent interaction has some precedent in the observed rates of crystallization of  $\beta$  and  $\alpha$  isomers of substituted naph-thalenes.<sup>15</sup>

### Effect of tert-Butyl Groups

Most of the substituent groups examined when introduced into the para ring position of sodium benzoate decreased its nucleating ability. *p-tert*-

Compound	<i>T</i> <sub>p</sub> , °C.
Sodium benzoate	131
Sodium <i>p-tert</i> -butylbenzoate	131.5
Basic aluminum dibenzoate	127
Basic aluminum di-p-tert-butylbenzoate	126
Potassium benzoate	125
Potassium <i>p-tert</i> -butylbenzoate	127.5
Sodium phenoxyacetate	118
Sodium <i>p-tert</i> -butylphenoxyacetate	127
Cupric benzoate	118
Cupric <i>p-tert</i> -butylbenzoate	122
Aluminum monobenzoate	117.5
Aluminum mono- <i>p-tert</i> -butylbenzoate	113
Nickelous benzoate	115
Nickelous <i>p-tert</i> -butylbenzoate	121
Sodium formate	113
Sodium pivalate	126

 TABLE VII

 Effect of tert-Butyl Groups on Nucleating Ability

Butyl, methyl, or the heavier halogen groups appear to have little effect (Table II). Introduction of a *p-tert*-butyl group into basic aluminum dibenzoate also appears to have little significant effect, but a methyl group reduces the nucleating ability considerably. The introduction of a tertiary butyl group into the *para* position of the ring enhances the nucleating ability of potassium benzoate, cupric benzoate, nickelous benzoate, and sodium phenoxyacetate (Table VII). The replacement of the hydrogen atom in sodium formate with a *tert*-butyl group (sodium pivalate) also increases the nucleating ability. The only case found in which a *tert*-butyl group decreased the nucleating ability was in aluminum monobenzoate.

## **Effect of Crystalline Structure**

Most likely the type of crystalline structure of the nucleating agent is of some importance in determining its effectiveness. Insufficient crystal structure data on the compounds examined are available to allow a firm conclusion. Polypropylene, sodium formate, and lithium benzoate all have monoclinic structures. Although sodium formate<sup>17</sup> has a better match of lattice parameters with polypropylene<sup>18</sup> than does lithium benzoate,<sup>19</sup> the latter is a much better nucleating agent. Measurements of the crystal structure of many of the compounds examined as well as determination of the relative degree of wetting of these compounds by various hydrocarbons would contribute substantially to a practical understanding of the heterogeneous nucleation process.

## SUMMARY AND CONCLUSIONS

A model nucleating agent for polypropylene might be envisioned as one consisting essentially of two parts: an organic group (solubilizing or "wetting" portion) and a polar group (insolubilizing portion). Such a model may be represented by organocarboxylic acid salts. The present work shows that a wide variation in effectiveness exists within the limits of this model. Many factors seem to affect heterogeneous nucleation of polypropylene crystallization, the most important appearing to be the chemical structure of the particular compound.

More specifically, sodium benzoate and basic aluminum dibenzoate are among the most ideal representatives of the model nucleating agent found so far for polypropylene. Aromatic organic groups are better constituents of the nucleating agent than are aliphatic groups. Salts of carboxylic acids are more effective than the free acids. Sodium salts are the most effective of the metal salts examined. Ring substituents generally reduce the nucleating ability, while substituents in the *para* position are better than the corresponding *ortho* or *meta* substituents. The presence of a tertiary butyl group, especially in the *para* position, frequently enhances the nucleating ability of intermediate or poor nucleating agents but does not improve that of a good nucleating agent. Increasing the aliphatic content of an aromatic carboxylate, for example by placing methylene groups between the aromatic ring and the carbonyl function, decreases nucleating ability. In aliphatic mono and dicarboxylates and alicyclic carboxylates those containing four to seven chain or ring carbon atoms are most effective. In fused-ring aromatic carboxylates those having the polar group in the 2 or  $\beta$  position are most effective.

These conclusions refer to nucleating agents in polypropylene and are not necessarily valid for other polymers. The model nucleating agent may be valid for other systems, but the order of effectiveness most likely is different from that of polypropylene.<sup>16</sup>

It is suggested that the nucleating ability of a particular material appears not to be an exclusive function of any one property or variable, but is probably the effective summation of many all operating at the same time.

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#### Résumé

Un agent de nucléation modèle pour la cristallisation du polypropylène est décrit. Une série de composés consistant principalement en sels d'acide organocarboxylique ont été évalués comme agents nucléants hétérogènes pour la cristallisation du polypropylène en mesurant leur effet sur la surfusion du polymère. Le benzoate de sodium et le dibenzoate basique d'aluminum sont parmi les meilleurs agents nucléants trouvés. Leur capacité à la nucléation de ces différents composés est discutée en termes de leurs propriétés structurales.

#### Zusammenfassung

Ein Modell-Keimbildungsmittel für die Polypropylenkristallisation wird beschrieben. Eine Reihe von Verbindungen, hauptsächlich organische Carbonsäuresalze, werden durch Messung ihres Einflusses auf die Unterkühlung des Polymeren auf ihre Wirksamkeit als heterogene Keimbildungsmittel für die Polypropylenkristallisation untersucht. Zu den wirksamsten Keimbildungsmitteln gehören Natriumbenzoat und basisches Aluminumdibenzoat. Die Keimbildungsfähigkeit der verschiedenen Verbindungen wird strukturmässig diskutiert.

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