

Heterogeneous Nucleating Agents for the Crystallization of Isotactic Polystyrene

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Synopsis

A method for evaluating compounds as nucleating agents in isotactic polystyrene (IPS) is described that involves measuring the polymer heat of fusion by differential scanning calorimetry after a prescribed thermal history. Twenty-nine compounds are described that increase the overall crystallization rate of three IPS samples. In general, the effective compounds contain an aromatic nucleus, are polyfunctional, and are high melting. Most are organic nitrogen heterocyclics. The most effective nucleating agents are thymine, melamine, oxamide, 2-hydroxybenzimidazole, and 4-hydroxy-6,7-dimethylpteridine. The use of plasticizers such as butyl stearate, diisobutyl adipate, or paraffin oil with nucleating agents often results in a synergistic increase in crystallinity.

INTRODUCTION

The industrial fabrication and use of isotactic polystyrene (IPS) are presently restricted mainly because of its relatively slow overall crystallization rate.¹ If the rate could be increased sufficiently, it might be possible to introduce IPS commercially and take advantage of desirable properties attributed to the crystalline segments of the polymer such as its high heat distortion temperature (approximately 190°C) and good solvent resistance. Crystallinity is usually obtained by long-time annealing. The maximum rate of crystallization occurs about 75–95° above the heat distortion temperature of the amorphous polymer at approximately 175°C.^{1–8} It is thus necessary to achieve maximum crystallinity during a fabrication step or at least sufficient crystallinity at this stage so that distortion will be minimized during subsequent annealing. This paper describes (a) a number of compounds that effectively nucleate the crystallization of IPS and greatly increase its overall crystallization rate, and (b) a thermal method for evaluating the efficacy of compounds as nucleating agents in IPS.⁹

The physical properties of a semicrystalline polymer are functions of the degree and type of crystallinity that are present. The crystallinity depends upon the nucleation rate, spherulitic growth rate, and the polymer thermal history. For a given polymer the spherulitic growth rate is fixed by temperature, but crystallization may be considerably enhanced by control of thermal history and nucleation. The effects of thermal history, such as melting and annealing temperatures and time, cooling rates from the melt, supercooling, etc., upon crystallization (including related effects upon nucleation) have

been reported for IPS.^{2,3,5,6,10-14} The control of nucleation rate by use of heterogeneous nucleating agents has been considered in several reports of limited scope, but the increases observed in overall crystallization rates were much less than those described later in this paper. A patent claims 1,6-diphenyl-1,3,5-hexatriene as a nucleating agent when evaluated by x-ray diffraction and density techniques.¹⁵ Russian papers have described indigo, fluorescein, alizarin, quinacridone, and indanthrene as effective nucleating agents when evaluated by density changes or microscopically.¹⁶⁻²¹ A depolarized light intensity procedure²² was used to show the effectiveness of salts of organic carboxylic and sulfonic acids as nucleating agents.²³ Crystalline IPS itself has been described as an effective nucleating agent.¹⁶ The overall crystallization rate of IPS may also be enhanced by the use of plasticizers²⁴⁻²⁷ and shear-induced orientation.²⁸⁻³³

The present method used for evaluating the effectiveness of compounds as nucleating agents involves the measurement of changes in the polymer heat of fusion caused by the deliberate addition of the heterogeneous nuclei. The heat of fusion may be measured from the thermogram of the melting process using a differential scanning calorimeter (DSC) and is proportional to the amount of crystallinity present.^{34,35} The polymer and additive are intimately mixed; heated to a temperature sufficiently above the polymer melting point to remove prior thermal history, to ensure homogeneity, and to give reproducible data; quenched to the amorphous state; annealed at a suitable temperature and time; quenched; and then remelted while scanning in the DSC. Positive nucleation is considered to have occurred whenever the level of crystallinity (represented by the heat of fusion) observed during the initial crystallization process is higher than that of the neat polymer.

EXPERIMENTAL

Thermal Measurements

All thermal measurements were obtained using a Perkin-Elmer differential scanning calorimeter, Model DSC-1. The calorimeter sensitivity was calibrated with reagent tin metal. Mixtures were prepared by extended dry blending on mechanical rollers of coarse powders of IPS (less than 20 mesh particle size) with the finely powdered nucleating agents. Twenty to 30 mg of these mixtures or of neat polymer was sealed in aluminum pans and melted at 540°K for 5 min in the calorimeter. The molten specimens were quenched on Dry Ice followed by annealing on an aluminum block in a circulating air oven at 175°C for the desired length of time, usually 10 or 30 min. After completion of annealing the samples were again quenched on Dry Ice, inserted in the calorimeter, and covered with a sample holder cover. The melting behavior was recorded at an instrument sensitivity of 4 mcal/sec and a scanning rate of 20°C/min. The total endothermic area of the thermogram encompassing melting peaks at about 210°C and 220°C and often at about 190°C using a tangential baseline was obtained with a planimeter. The exact peak positions depend upon thermal history and orientation.^{10-12,14} The heat of fusion was calculated according to standard procedure³⁶ to a precision of ± 0.1 cal/g.

Polymer Characterization

The IPS samples were supplied by James K. Rieke and Frank L. Saunders of Dow Chemical U.S.A., Midland, Michigan. The three polymers used are described in Table I. Viscosity molecular weights were calculated from equations of Krigbaum³⁷ using viscosities obtained at 30°C in *o*-dichlorobenzene. GPC peak molecular weights were obtained in 0.05 wt-% solutions in tetrahydrofuran using a Waters ALC/GPC-501 liquid chromatograph equipped with five Waters Class B Styragel 4' × 3/8" O.D. columns of nominal exclusion limits 10³, 2–5000, 8.5 × 10³, 1.5–5 × 10⁴, and 10⁵ Å. Molecular weight calibration was carried out using atactic polystyrenes of narrow molecular weight distribution and was linear up to molecular weight 2.3 × 10⁶. Flow rates were 1.0 ml/min.

The solutions of polymer C were prepared by dissolving the polymer in hot *o*-dichlorobenzene, 4.2%, containing 0.25% 2,6-di-*t*-butyl-*p*-cresol, followed by dilution to 0.05% in tetrahydrofuran. These solutions of high molecular weight polymer often partially plugged the columns resulting in effective flow rates of 0.36–0.46 ml/min. The plugged columns usually could be cleared by reverse flushing with neat solvent. Molecular weight distributions were broad with \bar{M}_w/\bar{M}_n estimated to be larger than 3.5. The atactic content was defined as the amount of polymer removed by methyl ethyl ketone during 24 hr in a Soxhlet extractor. The molecular weights of the atactic fractions were 1.7–1.8 × 10⁴. Spherulitic radial growth rates were obtained using a Leitz Ortholux microscope equipped with polarizing optics and a hot stage. Specimens were melted at 270–275°C for 60 sec followed by rapid transfer to the hot stage set at 175°C.

Table I lists values for the observed heats of fusion after 10 and 30 min annealing at 175°C and the maximum values obtained after long-time annealing. Complete crystallization curves for the neat polymers were obtained from measurements on many specimens annealed at periodic intervals. Also included in Table I are the rates of crystallization calculated from the linear portions of the crystallization curves, i.e., the maximum slope of the curves. Induction periods are defined as the times when the crystallization curves first deviated from the initial baselines. The lengths of time necessary to achieve maximum attainable crystallinity and the overall crystallization rates were also obtained from crystallization curves and are included in Table I. All crystallization rates are expressed in relative units of cal g⁻¹ hr⁻¹.

RESULTS AND DISCUSSION

There is at present no practical a priori way of selecting a good nucleating agent for polymer crystallization. Many desirable properties of a good nucleating agent have been listed.³⁸ Unfortunately, a spectrum of effectiveness exists in the nucleating ability of compounds possessing these properties. Screening of compounds representing various chemical classes for their effectiveness must be carried out. The described thermal method was found satisfactory for the initial rapid screening of approximately one thousand compounds. All evidence of thermal history was completely removed at the melting temperature 267°C. The method becomes somewhat unreliable for evaluating very effective nucleating agents or very fast crystallizing speci-

TABLE I
 Polymers Used

Polymer	Molecular weight		Atactic content, %	G_i , μ /mind	Induction period, min ^e	Linear rate of crystallization, cal g ⁻¹ hr ^{-1e}	Time to maximum crystallinity, min ^e	Overall rate of crystallization, cal g ⁻¹ hr ^{-1e}	ΔH_f , cal/g		
	\bar{M}_η^a	\bar{M}_p^b							f	Maximum ^e	
A	3.71×10^5	4.05×10^5	29.5	0.27	20	2.9	160	2.0	0.0	0.45	5.4
B	6.40×10^5	7.80×10^5	23.2	0.16	0.0	12.0	71	3.5	0.4	0.70	4.2
C	3.95×10^6	2.60×10^6	19.9	0.26	25	0.36	>1500	0.22	0.0	0.05	>5.5
		5.70×10^{6c}									

^a Viscosity molecular weight.

^b GPC peak molecular weight.

^c Two peaks observed.

^d Spherulitic growth rate at 175°C.

^e At 175°C.

^f After 10 min at 175°C.

^g After 30 min at 175°C.

mens that may crystallize further during the analytical procedure. False high values of fusional heats may be obtained under these conditions as evidenced by an exotherm at about 150–160°C during the DSC scanning at 20°C/min. The exotherm reflects the rapid crystallization of the specimens due to increased chain mobility enhanced by the elevated temperatures. The crystallinity of such specimens is better determined by other methods such as a calibrated density gradient bath.

An unusually slow crystallizing polymer, C, was selected for initial evaluations. The GPC curve of this polymer showed a binodal distribution composed of two high molecular weight peaks in a molecular weight ratio of 2.2. (Since this work was completed, other work suggests caution whenever a high molecular weight "hump" or binodal distribution is observed using a linear calibration, especially when the MWD of the samples lies beyond the linear portion of the calibration curve.³⁹ The possibility that a GPC analytical peculiarity rather than a genuine binodal distribution is actually being observed must be considered.) A relatively high concentration of nucleating agent, 3–5%, was selected to compensate for possible heterogeneity in mixing, particle size differences, unknown concentration effects, or deleterious impurities. Further screening of promising compounds was affected using fast crystallizing polymers of lower and more practical molecular weight, A and B, and a nucleating agent concentration of 1%. Subsequent experiments confirmed that good nucleating agents were effective at concentrations of 0.05 wt-% and lower if homogeneously dispersed in the polymers. The most effective nucleating agents found for IPS crystallizations are listed in Table II roughly in order of their decreasing effectiveness. The values of the heats of fusion are averages of two to five determinations. Most compounds are organic nitrogen heterocyclics, contain an aromatic nucleus, are polyfunctional, and are relatively high melting. All the nucleating agents melt above 200°C; twenty of twenty nine, above 300°C. Occasionally significant, but reproducible, differences between the ΔH_f values for the three polymers were observed (e.g., isonicotinic acid, 2,5-pyridine dicarboxylic acid, theobromine, and ethylenethiourea). The reason for the differences is not known.

Compounds effective as heterogeneous nucleating agents in other semicrystalline polymers were not always equally effective in IPS. None of over two hundred metal organocarboxylates and sulfonates and none of over one hundred metal organochelates tested showed any effect as heterogeneous nucleating agents in IPS. These compounds have been reported to be effective nucleating agents in IPS²³ and polypropylene.^{23,38,40,41} Two phthalic acids claimed to be effective nucleating agents in IPS²³ were poor when examined by the present method. Isophthalic acid (ΔH_f : in polymer A, <0.3 cal/g; in B, <0.2; and in C, 3.4) and terephthalic acid (ΔH_f : in polymer A, <0.2 cal/g; in B, 1.2; and in C, 1.6) were relatively poor nucleating agents. Phthalic acid was completely ineffective. Many high-melting organonitrogen heterocyclics such as substituted benzimidazoles and indazoles have been reported as effective nucleating agents for the crystallization of vinylidene chloride–vinyl chloride copolymers.⁴² Only melamine and 2-hydroxybenzimidazole were effective in IPS.

The effective nucleating agents greatly decrease the induction periods of crystallization and increase the linear rate of crystallization. This is illus-

TABLE II
 Effective Nucleating Agents for Isotactic Polystyrene

Compound	In polymer	ΔH_f , cal/g		
		A ^a	B ^a	C ^b
Thymine (5-methyluracil)		4.5	4.6	4.1
2-Hydroxybenzimidazole		4.1	4.5	4.2
Oxamide		4.5	3.4	4.6
4-Hydroxy-6,7-dimethylpteridine		4.5	4.3	3.6
Melamine		4.6	3.2	4.3
4-Methylsculetin (6,7-dihydroxy-4-methylcoumarin)		4.2	4.5	3.4
2,4,6-Triaminopyrimidine		4.5	3.5	4.0
4,6-Diamino-5-nitropyrimidine		3.9	4.1	3.5
Isonicotinic acid		5.7	1.0	4.7
3-Cyano-4,6-dimethyl-2-hydroxypyridine		4.1	3.0	4.2
4-Nitroimidazole		3.0	3.5	4.5
2,5-Pyridinedicarboxylic acid		2.2	4.4	4.1
4,5-Diaminopyrimidine		<3.1	1.8	5.3
Lumazine (2,4-pteridinediol)		4.2	2.1	3.9
2-Amino-5,6-dimethyl-4-pyrimidinol		2.4	4.3	3.0
Theobromine (3,7-dimethylxanthine)		3.6	1.4	4.3
2-Imidazolidinethione (ethylenethiourea)		1.9	<1.5	5.1
8-Mercaptopurine		3.1	2.0	3.3
6-Azauracil (as triazine-3,5-(2H,4H)-dione)		2.4	2.1	3.7
6,7-Dimethylumazine (6,7-dimethyl-2,4-pteridinediol)		2.6	1.3	4.0
2-Hydroxy-6-methylpyridine-3-carboxylic acid		1.0	3.4	3.4
<i>p</i> -Hydroxybenzoic acid hydrazide		1.7	2.1	3.9
Phthalazine-1,4-dione (phthalic acid hydrazide)		1.4	2.2	3.2
Trithiocyanuric acid (<i>s</i> -triazine-2,4,6-trithiol)		1.2	2.0	3.2
4-Aminopyrazolo(3,4- <i>d</i>)pyrimidine		1.2	1.7	3.4
2,5-Dichloroterephthalic acid		1.8	1.2	3.1
2,4-Dihydroxy-6-methylpyrimidine (6-methyluracil)		1.9	1.0	3.1
4-Hydroxy-2-mercaptopteridine		1.6	1.1	3.1
Uracil (2,4-(1H,3H)pyrimidinedione)		1.0	1.5	3.2

^a Concentration 1.0 wt-%; annealed at 175°C for 10 min.

^b Concentration 3–5 wt-%; annealed at 175°C for 30 min.

trated by data from crystallization curves of IPS containing two of the best nucleating agents, thymine and melamine, Table III. The use of these compounds as nucleating agents completely eliminated the induction period of 25 min observed for the neat polymer. Samples containing thymine could not be quenched sufficiently rapidly using Dry Ice to give zero crystallinity. The linear rates of crystallization were 15–18 times faster in the presence of the nucleating agents; overall rates, 17–19 times faster. The effectiveness of these nucleating agents in increasing the density of nuclei and thus decreasing the effective spherulite size is illustrated in Figure 1 for a sample nucleated with thymine.

A combination of plasticizer and nucleating agent was found often to enhance crystallinity more than would be expected from the use of plasticizer or nucleating agent separately. For example, the use of 5% plasticizer such as paraffin oil, butyl stearate, or diisobutyl adipate with nucleating agents as melamine, ethylenethiourea, or isonicotinic acid gave ΔH_f values 5–14% higher than when the plasticizer was absent. Mixtures containing the above nucleating agents and 5% dibutyl sebacate, 1-chloronaphthalene, or dioctyl

TABLE III
Crystallization of Nucleated IPS at 175°C

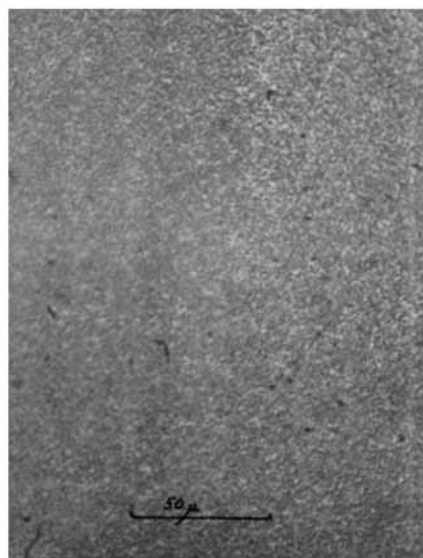
Compound ^a	Induction period, min	Linear rate of crystallization, cal g ⁻¹ hr ⁻¹	Time to maximum crystallization, min	Maximum ΔH_f , cal/g	Overall rate of crystallization, cal g ⁻¹ hr ⁻¹
Melamine	0.0	6.5	80	5.1	3.8
Thymine	0.0 ^b	5.3	60	4.1	4.1

^a One-half wt-% in polymer C; $T_m = 540^\circ\text{K}$ for 3 min.

^b At time 0; $\Delta H_f = 1.0$ cal/g.



(a)



(b)

Fig. 1. Effect of nucleation on spherulite size of IPS: (a) polymer B annealed at 175°C for 169 min; (b) polymer B containing 0.25% thymine and 5% butyl stearate; annealed at 160°C for 5 min. Calibration markers are 50 microns.

phthalate showed less synergistic effect. The use of 5% tritolyol phosphate or dibutyl phthalate with these nucleating agents was detrimental to crystallinity resulting in 5–16% less ΔH_f than with the nucleating agents alone.

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