

DTA Study of Heterogeneous Nucleation of Crystallization in Polypropylene*

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Synopsis

The effect of cooling, nucleation, and spherulitic growth rates on the properties of polypropylene is discussed briefly. A differential thermal analysis technique is described for evaluating the relative extent of heterogeneous nucleation that occurs in a particular polypropylene composition. The method is based upon a nucleating agent's ability to reduce the relatively large amount of supercooling that occurs upon crystallization of polypropylene. Compounds are shown to vary widely in their effectiveness as heterogeneous nucleating agents in polypropylene. The relationships between the degree of supercooling of a particular polypropylene composition and its relative clarity, tensile properties, density, and morphology are shown.

I. INTRODUCTION

The degree of crystallinity and the morphology of a polymeric composition must be controlled in order to obtain optimum physical properties and economics.¹ The spherulitic size, density, clarity, tensile properties, and impact resistance of polypropylene may be controlled by cooling rate from the melt.² It may be fabricated to give either an opaque, stiff, and relatively brittle object containing large spherulites by slow cooling such as that encountered with thick or large objects, or one may obtain a clear, tough material of lower modulus containing very small spherulites by very rapid cooling such as that encountered by a very thin object such as a film. A polymer's morphology and its degree of crystallinity are functions of the cooling rate, the overall rate of nucleation, and the spherulitic growth rate.³ Figure 1 shows the relative temperature dependencies of the rate of homogeneous nucleation and the spherulitic growth rate that are consistent with the observed behavior of polypropylene. At relatively low cooling rates at temperatures just below the polymer melting point (T_m) the spherulitic growth rate predominates over the nucleation rate, and few but large spherulites and relatively high crystallinity are obtained. At more rapid cooling rates, the large dependency of the nucleation rate on temperature becomes of importance, the nucleation rate predominates over the spherulitic growth rate, and many small spherulites with a resulting lower

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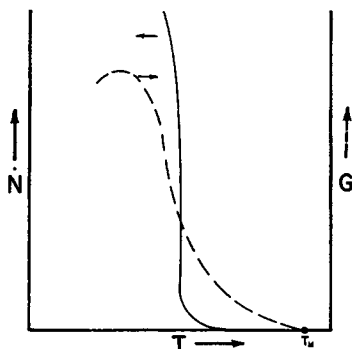


Fig. 1. Relative temperature dependencies of polypropylene nucleation rate \dot{N} and spherulitic growth rate G .

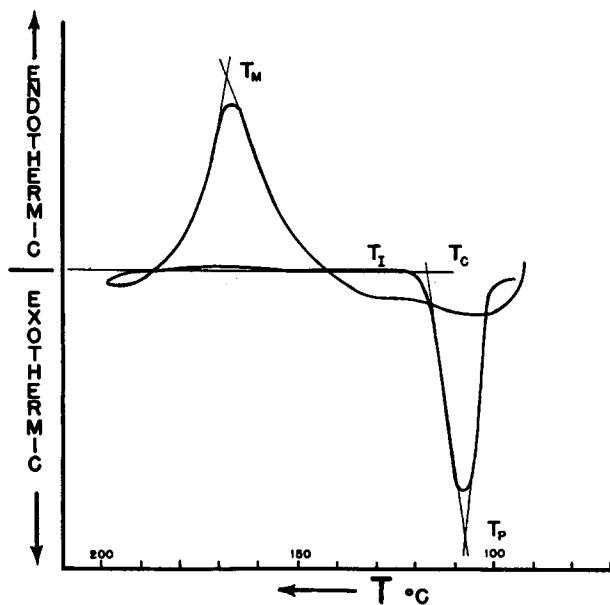


Fig. 2. Thermogram of melting and crystallization of polypropylene.

amount of crystallinity are obtained. (For polyethylene the relative positions of the curves are probably reversed.^{4,5} It is therefore very difficult to quench polyethylene sufficiently rapidly to obtain small spherulites and therefore relatively high clarity.) However, although rapid quenching of polypropylene produces a small spherulitic size, it also gives a product of lower crystallinity, and therefore often with less than optimum tensile properties. The amount of crystallinity may be increased by annealing—a time-consuming and uneconomical process undesirable from a commercial standpoint.

However, within limits and in the desirable temperature range, it is possible effectively to increase the overall rate of nucleation by the addition

of foreign materials that function as heterogeneous nuclei for polymer crystallization, while at the same time keeping the spherulitic growth rate relatively unchanged.⁶⁻¹⁶ This has the effect of moving the vertical part of the nucleation rate curve further to the right of the spherulitic growth rate curve. This change in relative rates of nucleation and spherulitic growth thus allows smaller spherulite size to be obtained at higher temperatures with heterogeneous nucleation than with homogeneous nucleation. Somewhat higher density also accompanies this decrease in spherulite size, also in contrast to that observed with homogeneous nucleation. Thus heterogeneous nucleation serves to increase the overall rate of crystallization and to increase the total amount of crystallinity.

Polypropylene exhibits a large degree of supercooling that may be detected readily by differential thermal analysis (DTA) techniques.¹⁷ Figure 2 shows a "closed-loop" thermogram of the melting and crystallization of a typical sample of polypropylene exhibiting about 60°C. of supercooling. The amount of this supercooling may be changed by cooling rate and by heterogeneous nucleation. We wish to show here how differential thermal analysis offers a rapid and sensitive analytical technique for evaluating the relative extent of heterogeneous nucleation in a particular polypropylene composition.

II. EXPERIMENTAL

DTA Instrument

Our DTA equipment shown schematically in Figure 3 was prepared by the research instrument shop of the Western Division of The Dow Chemical Company in Pittsburg, California. The sample cells are Pyrex glass and are 50 mm. long \times 6 mm. O.D. and contain a 2 mm. O.D. thermocouple well. The spacing between the well and the sample tube is quite uniform. The cells are heated in a circulating oil bath of 50 cStoke viscosity Dow Corning 200 polydimethylsiloxane fluid. The reference material also is 200 fluid. A controlled linear temperature decrease is obtained upon cooling by means of a Leeds and Northrup 10170 programmer coupled with a Leeds and Northrup Speedomax H strip-chart recorder and controller. The signal from the controller, modified through an electropneumatic converter, actuates a diaphragm motor valve that regulates the flow of cooling oil into the circulating oil bath surrounding the sample tubes. The differential thermocouple output is amplified by Hewlett-Packard Model 425A preamplifiers. Recording is achieved by means of a Moseley Model 136 Autograf $y, y-x$ recorder standardized against an ice-water mixture and boiling water or a constant voltage source with an output equivalent to 100°C. The recorder contains a compensator for room temperature drift.

Procedure

Dow Polypropylene 201 was used as the base polymer in all compositions. Compositions were prepared by prewarming the polymer and the nu-

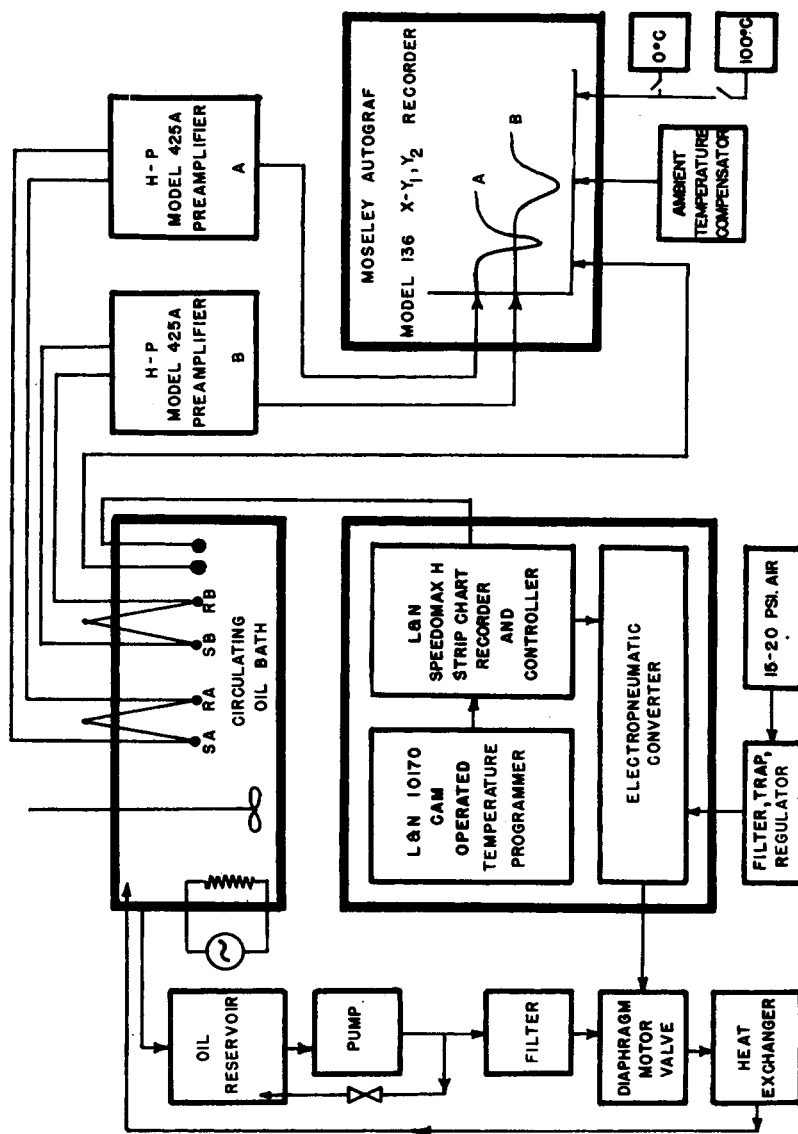


Fig. 3. Schematic diagram of DTA equipment.

cleating agent (0.25 wt.-%) for 5 min. at 150°C., followed by milling for 5 min. at 150°C. at a speed of 60–120 rpm in a Meili laboratory kneader, Type CK-1 (Fritz Meili Maschinenfabrik, Zurich). Coarse granules were obtained upon cooling the compositions to room temperature while mixing.

The polypropylene compositions were melted for 10 min. at 200°C. under vacuum in the sample tubes. Following insertion of the thermocouple well the tubes and their contents were maintained at 200°C. for an additional 10 min. This period of "relaxation" is sufficient to remove major orientation effects caused by the shear produced in the polymer melt upon insertion of the thermocouple well. Three characteristic temperatures were obtained upon cooling and resultant crystallization (Fig. 2). The initial temperature, T_i , at which the curve first deviates from the base line is a measure of the onset of crystallization. T_i is somewhat sensitive to shear-introduced orientation at the surface of the thermocouple well and to experimental technique and is reproducible to about ± 2 – 3°C . A second temperature referred to as the "constructed" temperature, T_c , is obtained at the intercept of tangents to the base line and the high temperature side of the exothermic peak. The peak temperature, T_p , occurs at the intercept of the tangents to the sides of the exothermic curve and is a measure of the temperature when the bulk of the polymer has crystallized. The peak temperature is reproducible to $\pm 1^\circ\text{C}$. and therefore will be used for the correlations to follow. The quantity $(T_c - T_p)$, i.e., the difference between the constructed temperature and the peak temperature, is a function of the overall rate of crystallization; the smaller the difference between these temperatures, the greater the rate of crystallization.

Effect of Cooling Rate

The peak temperature is a function of the cooling rate of the sample, (Fig. 4). The curve on the right shows the relative decrease in peak tem-

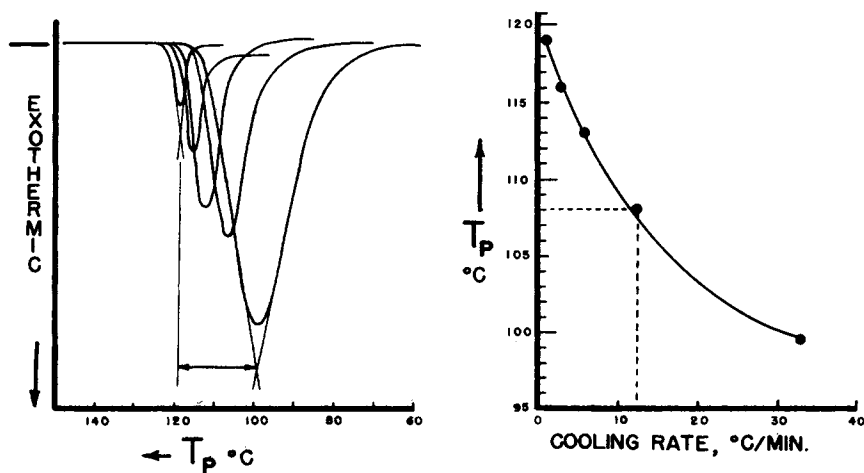


Fig. 4. Effect of cooling rate upon the supercooling of polypropylene.

perature (i.e., the increase in supercooling) obtained on this equipment with increasing cooling rate. The curves on the left show the same effect upon the shapes and areas of the thermograms, i.e., decreasing differential signal and area with slower rate of cooling. The equipment described gives a 19°C. difference in peak temperature between cooling rates of 1°C./min. and 33°C./min. Obviously close control of cooling rate is mandatory for reproducible results. All measurements were made at an arbitrary cooling rate of 12½°C./min. as indicated by the dashed line on the curve on the right.

III. RESULTS

Effect of Heterogeneous Nucleation upon Supercooling

Figure 5 shows thermograms of the crystallization of polypropylene and the same polypropylene containing a typical effective heterogeneous nucleating agent, aluminum dibenzoate. The increase in peak temperature (i.e., the reduced supercooling) occurring upon nucleation is at once apparent. Also apparent is the steeper slope on the high temperature side of the curve of the nucleated sample reflecting the occurrence of more rapid crystallization. The difference in peak heights here is due simply to sample size variations and not to effects of nucleation.

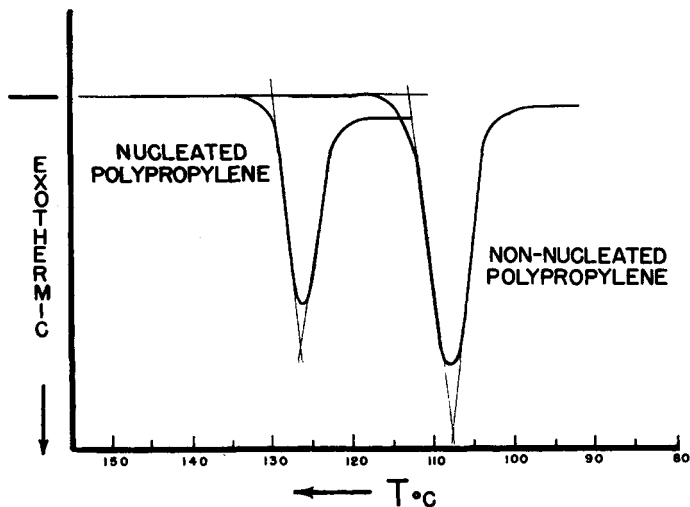


Fig. 5. Thermograms of crystallization of nucleated (with 0.25% aluminum dibenzoate) and nonnucleated polypropylene.

Effect of Concentration of Nucleating Agent

The peak temperature obtained upon heterogeneous nucleation is a function of the concentration of the nucleating agent. Figure 6 shows the increase in peak temperature associated with increasing concentration for one particular effective nucleating agent, aluminum dibenzoate. The greatest effects are observed at very low concentrations of nucleating agent.

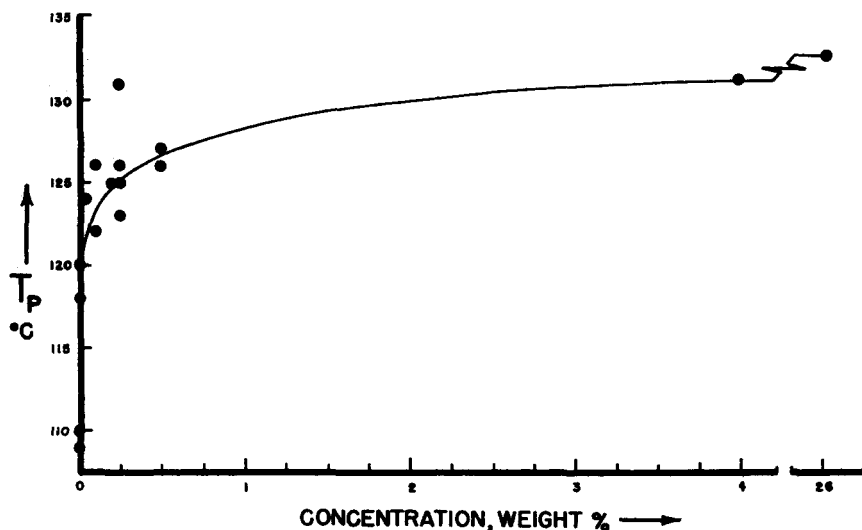


Fig. 6. Variation of peak temperature with concentration of nucleating agent (aluminum dibenzoate).

The discontinuity shown between the last two points represents approximately a sixfold increase in concentration. Errors due to possible concentration fluctuations in the samples were minimized by working at a concentration represented by a flatter part of the curve. By this technique over 240 compounds representing many different classes of both organic and inorganic compounds were examined as potential nucleating agents.

Effect of Heterogeneous Nucleation upon Physical Properties

The results of this work have revealed that compounds vary greatly in their effectiveness as nucleating agents. Figures 7 and 9–12 show least square plots of the relative average of various properties of these polypropylene compositions versus the peak DTA temperatures observed. Each point does not represent the effect of one particular nucleating agent but is the average effect obtained from as many as 24 compounds—on the

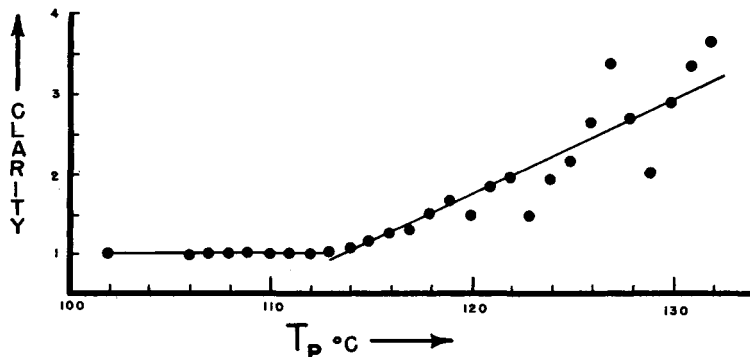


Fig. 7. Relationship of clarity and peak temperature.

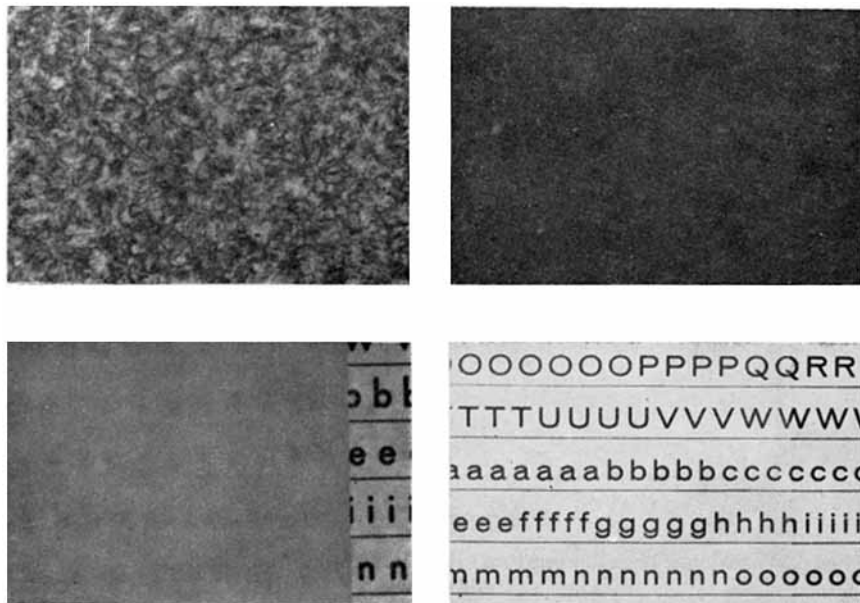


Fig. 8. Relationship of spherulitic size ($100\times$ magnification) and clarity for polypropylene (left) and nucleated polypropylene (right).

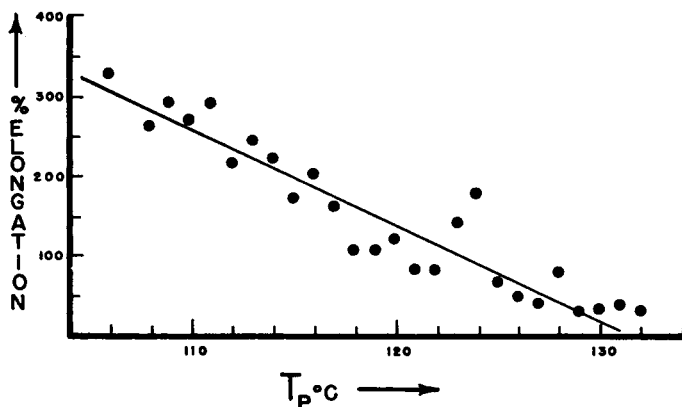


Fig. 9. Relationship of ultimate elongation and peak temperature.

average each point represents the averaged data from about eight or nine different compounds.

Clarity. Figure 7 shows a plot of the relative average clarity versus the peak temperature observed. The horizontal part of the curve represents complete opacity. Thus increased clarity is accompanied by higher peak temperatures (and therefore with less supercooling). The degree of clarity was determined by the relative size of figures that could be distinguished clearly at a distance of 3 ft. through a $\frac{1}{8}$ in. thick compression-molded slab. This relative clarity corresponds with transparency¹ or "see-through"¹⁸ and is related to spherulitic size. Figure 8 shows the relative spherulite

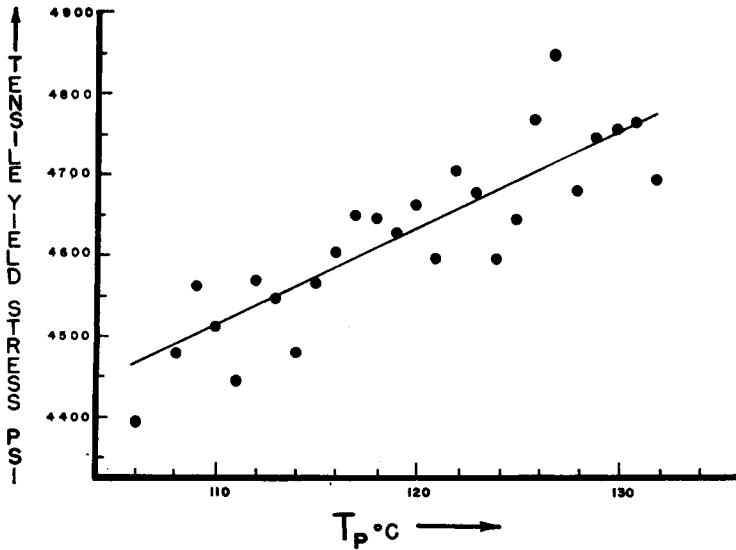


Fig. 10. Relationship of tensile yield stress and peak temperature.

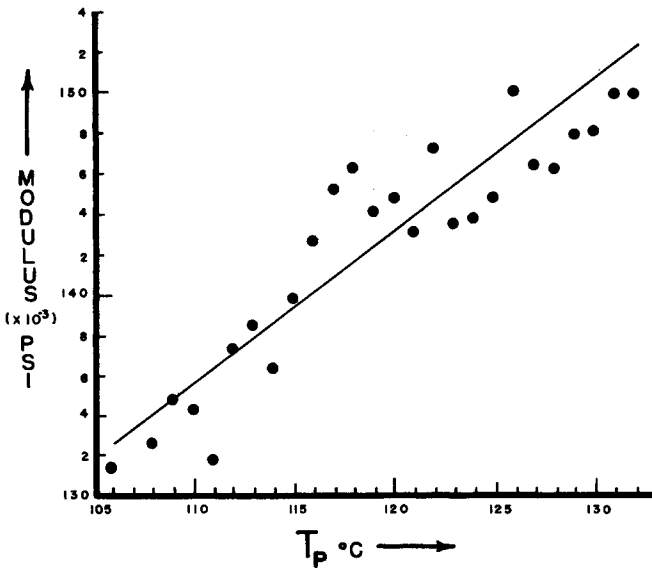


Fig. 11. Relationship of elastic modulus and peak temperature.

size and clarity associated with a sample of polypropylene on the left and a nucleated polypropylene sample on the right. At once apparent is the contrast between the opacity associated with the large coarse spherulites in the nonnucleated polypropylene and the clarity associated with the small spherulite size in the nucleated sample. These pictures together with the information in Figure 7 imply that high peak temperatures are also associated with small spherulite size.

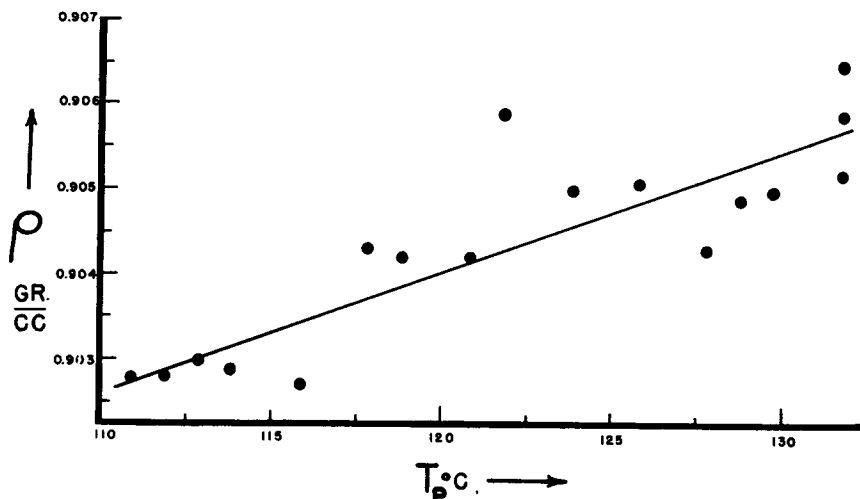


Fig. 12. Relationship of sample density and peak temperature.

Tensile Properties. Figures 9–11 show the relationships of the major tensile properties of nucleated polypropylene compositions and their DTA behavior. Figure 9 illustrates the relationship between per cent elongation and the peak DTA temperature. Decreasing elongation is associated with increasing peak temperature. A similar relationship also exists in which tensile yield strain decreases with increasing peak temperature. A plot of the relative average tensile yield stress versus peak temperature (Fig. 10) illustrates that higher tensile yield stress is associated with higher peak temperature, i.e., with better nucleation. Increasing elastic modulus and therefore increasing sample stiffness is associated with better nucleation and therefore with increasing DTA peak temperature (Fig. 11).

Density. Figure 12 illustrates the increase in density by 17 different nucleated polypropylene compositions associated with increasing peak temperature. This relationship reflects the increasing overall crystallinity resulting from increasing nucleating ability of the compound in question. Depending upon their nucleating ability the many foreign nuclei function to initiate many small spherulites that effectively “fill up” the interstices between spherulites before the spherulitic growth rate becomes too slow.

IV. DISCUSSION

The scatter of the points in Figures 7 and 9–12 from absolute linearity may be due to characteristic differences in the nucleating ability of each compound or to other somewhat less critical factors such as concentration fluctuations or impurities or to particle size differences. However, the clarity and tensile data shown were obtained on compression-molded samples approximately $\frac{1}{8}$ in. (125 mils) thick. It is experimentally difficult to prepare many samples of this thickness with exactly the same thermal history. As a result variations in clarity and in tensile properties due

to slight differences in quenching of the samples most likely account for the scatter. The DTA instrument, on the other hand, imparts a very reproducible thermal history to each sample. Thus, evaluations of the relative nucleating ability of various substances based upon DTA data are more reliable than tensile property evaluations.

Many classes of chemical compounds appear to function to some degree as nucleating agents for polypropylene crystallization, but, as the data indicate, a spectrum of nucleating ability exists. Among the more efficient nucleating agents (Table I) were alkali metal or aluminum salts of aromatic or alicyclic carboxylic acids. Salts of aliphatic mono- or dibasic acids or arylalkyl acids generally were of intermediate nucleating ability. The relative nucleating ability within these classes of compounds may be changed considerably by organic substituents and the combination of the particular acid and metal cation used. Inorganic compounds, though somewhat effective, were poor as nucleating agents when compared to the metal carboxylates.

TABLE I
Representative Nucleating Agents

Relative effectiveness		
Good	Intermediate	Poor
Aluminum dibenzoate	Sodium succinate	Alums
Potassium benzoate	Sodium glutarate	Silica
Sodium β -naphthoate	Sodium caproate	TiO ₂
Lithium benzoate	Sodium 4-methylvalerate	CaO, MgO
Sodium cyclohexanecarboxylate	Aluminum phenylacetate	Carbon black
Sodium cycloheptanecarboxylate	Sodium cinnamate	Clays

V. CONCLUSIONS

(a) The degree of supercooling of polypropylene is large and is easily and reproducibly measured by DTA techniques.

(b) The degree of supercooling of polypropylene, the polymer morphology, clarity, tensile properties, and the density may be altered by the presence of deliberately added heterogeneous foreign nuclei.

(c) Compounds vary widely in their effectiveness as heterogeneous nucleating agents in polypropylene.

(d) Differential thermal analysis is a rapid and sensitive means of evaluating the relative extent of this nucleation.

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Résumé

On discute brièvement de l'influence du refroidissement de la production de germes et des vitesses de croissance des sphérulites sur les propriétés du polypropylène. On décrit une technique d'analyse thermique différentielle pour évaluer l'étendue relative de la nucléation hétérogène qui a lieu dans une composition particulière de polypropylène. La méthode est basée sur une aptitude de l'agent de nucléation à réduire la quantité relativement importante de surfusion qui a lieu lors de la cristallisation du polypropylène. On montre que les composés varient fortement quant à leur efficacité comme agents de nucléation hétérogène dans le polypropylène. On montre les relations entre le degré de surfusion d'une composition particulière de polypropylène et sa clarté relative, ses propriétés de tension, sa densité et sa morphologie.

Zusammenfassung

Der Einfluss der Abkühlungs-, der Keimbildungs- und der Sphärolithwachstumsgeschwindigkeit auf die Eigenschaften von Polypropylen wird kurz diskutiert. Ein differentialthermoanalytisches Verfahren zur Ermittlung des relativen Ausmasses der heterogenen, in einer bestimmten Polypropylenmischung auftretenden Keimbildung wird beschrieben. Die Methode beruht auf der Fähigkeit eines Keimbildungsmittels zur Herabsetzung der relativ grossen, bei der Kristallisation von Polypropylen auftretenden Unterkühlung. Verschiedene Verbindungen besitzen eine stark unterschiedliche Wirksamkeit als heterogenes Keimbildungsmittel bei Polypropylen. Die Beziehung zwischen dem Unterkühlungsgrad einer bestimmten Polypropylenmischung und ihrer relativen Klarheit, ihren Zugeigenschaften, ihrer Dichte und Morphologie wird aufgezeigt.

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