

DSC Studies of Tactic Polypropylenes: The Correlation of Polymer Stereochemistry with Thermal Properties

DAVID R. BURFIELD* and PATRICK S. T. LOI, *Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia*,
YOSHIHARU DOI, *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan*, and
JIRÍ MEJZÍK, *Chemopetrol, Research Institute of Macromolecular Chemistry, 656 49, Brno, Czechoslovakia*

Synopsis

A large number of polypropylene samples, of isotacticities spanning the range 0.35 to 1.00 mm, have been examined by differential scanning calorimetry (DSC) in order to establish a calorimetric index for determining stereostructure. Crystallization studies show that the crystallization onset temperature decreases in step with reduced isotacticity. However, samples prepared with supported catalysts show significantly lower crystallization onset temperatures than those from conventional catalysts which is believed to be due to differences in the inter- or intramolecular distribution of stereodeflects. Furthermore, whole and fractionated samples cannot be fitted by one calibration curve. However, the enthalpy of crystallization is found to be related to the isotacticity by an equation of the form: $\log \Delta H = m \log(\text{isotacticity}) + c$. This relationship is found to be applicable to samples from all types of catalysts examined and to both whole and fractionated samples. Fusion curves have been determined for "as received" as well as conditioned and annealed samples but the melting temperatures are not found to be a reliable guide to isotacticity. The respective enthalpies of fusion are found to follow the same logarithmic relationship stated above and thus can also be used as a basis for a calorimetric isotactic index. Examination of glass transition and related heat capacity data does not provide any clear-cut alternative index.

INTRODUCTION

Calorimetric studies have proved of immense value in probing the morphology of polymers. These techniques may also be used to provide indirect information on the microstructure of macromolecules. Thus recently¹⁻⁴ we have employed differential scanning calorimetry (DSC) to examine tactic polypropylene (PP) samples. The importance of these studies lies in the fact that industrial PP catalysts provide polymers of varying stereostructure of which only the isotactic form is currently of commercial significance. DSC analysis potentially provides a rapid and simple technique for characterizing this polymer. The earliest calorimetric studies of PP sought to establish a relationship between the polymer melting point and isotacticity.⁵⁻⁷ However, whereas the melting point of the sample generally increases with isotacticity, the correlation is poor for unfractionated samples and in any case the results are dependent on the thermal

* Present address: 431, High Road, Chilwell, Nottingham NG9 5EA, England.

history of the material. In an alternative approach Tolchinskii et al.⁸ were able to establish a correlation between the enthalpy of fusion and the % amorphous (atactic) content. The drawback of this method is that the melting curves are generally very broad and consequently the precise area is difficult to define. Again the pretreatment of the sample can significantly affect the observed results.

An alternative approach to calorimetric studies of PP is to monitor the process of polymer crystallization rather than fusion. This has a threefold advantage: (i) preheating of the sample to the melt erases previous thermal history, (ii) crystallization onset temperatures are very reproducible, and (iii) the crystallization curves are generally well defined and thus the enthalpy of crystallization may be measured with some degree of precision. In recent preliminary reports it has been shown that both the crystallization onset temperature (T_c) and the enthalpy of crystallization (ΔH_c) may be correlated with the stereostructure of the polymer. This study documents a more complete calorimetric study which includes data on fusion phenomenon and glass transition parameters as well as a more comprehensive treatment of the crystallization data. The calorimetric data are correlated with the stereostructure as determined by ¹³C-NMR so as to provide calibration of calorimetric procedures for tacticity measurement.

EXPERIMENTAL

Materials

Polypropylene samples spanning the isotacticity range 0.35 to 1.00 mm were of varying molecular weight and were obtained from a variety of sources including both laboratory and commercial plant preparations. Methods for laboratory syntheses have been described or referenced in earlier publications.^{1,9,10} Certain laboratory samples were purified by reprecipitation as described elsewhere⁹ whereas other samples were fractionated by hot heptane extraction into heptane insoluble (HI) and heptane soluble (HS) fractions.⁴

Characterization

Polymer isotacticities were determined by ¹³C-NMR measurements using a JEOL FX-200 spectrometer on 15 to 30 w/v % dichlorobenzene solutions at 140°C, as earlier described.^{11,12} DSC measurements were made with a Perkin-Elmer DSC-2C instrument calibrated at 10°C/min against indium (156.63°C) and zinc (419.5°C). For highly isotactic samples the instrument was used in the normal mode and calorimetric data obtain over the range 47 to 197°C for both heating and cooling runs. Samples of low isotacticity were examined over the extended range -53 to 197°C with the instrument equipped with an Intra-cooler II two-staged cooling unit and dry-box assembly.

Polymer samples were prepared for examination either "as received" or after pressing at 197°C into thin films. The powdered polymer or discs cut from the thin films were encapsulated in standard aluminium sample pans before introducing into the calorimeter at 27°C. Samples were normally examined in the following threefold sequence. An initial heating run to the maximum temper-

ature of 197°C at a scan rate of 20°C/min. The sample was held at the maximum temperature for 5 min before programmed cooling at 20°C/min to the minimum temperature. Finally, after holding for 5 min at the minimum temperature the sample was rescanned up to the maximum temperature at the same heating rate. All calorimetric parameters were calculated with the Perkin-Elmer standard TADS program.

In certain cases samples were conditioned in the sample pans before running. For this purpose sample pans were inserted into a glass tube which was subsequently pumped out under high vacuum and thermostatted in an oil-bath at the required elevated temperature. After annealing, samples were allowed to cool to room temperature before removal from the vacuum environment.

Glass transition data were acquired using the following procedure. With the DSC instrument in sub-ambient mode, the samples were introduced at a cell temperature of 47°C. The sample was subsequently heated to 197°C and isothermed for 5 min before quenching at 320°C/min to -48°C. The sample was then scanned over the range from -48 to 97°C at 20°C/min. The value of T_g and C_p was calculated using the standard TADS program.

RESULTS AND DISCUSSION

Characteristic Thermal Behavior of Tactic Polypropylenes

It is probably helpful at the outset to describe the typical behavior of various tactic polypropylenes on heating and cooling cycles. Highly isotactic PP, without preconditioning, shows a somewhat broad fusion curve with T_{\max} value of about 167°C and an enthalpy of fusion of nearly 29 cal/g (Fig. 1). Annealing of the sample at elevated temperatures reduces the breadth of the fusion curve and raises both T_{\max} and enthalpy of fusion. By contrast, the HS stereoblock polymer of much lower overall isotacticity shows a pronounced glass transition (not readily observable in the highly isotactic samples) and a broad but much smaller melting transition at a much reduced temperature. The crystallization curves for the same samples are shown in Figure 2. For the highly isotactic sample the onset of crystallization occurs at about 121°C and the enthalpy of crystallization is close to 26 cal/g which is somewhat less than the value for the initial fusion process. As would be expected the stereoblock polymer begins to crystallize at much lower temperatures and with a reduced enthalpy of crystallization.

In general, the crystallization process is more clearly defined than fusion—the curves are narrower, have less ambiguous baselines and show more reproducible onset temperatures. It was partly this reason that lay behind the proposal to use crystallization parameters as indices of tacticity.¹

Preliminary Investigations

A number of preliminary investigations were carried out to delineate the optimum conditions for the major study. Earlier, it has been shown³ that variation in sample size has a small but nevertheless significant effect on the observed values of transition temperatures and enthalpies. Consequently throughout this study a uniform mass of 5 ± 0.5 mg was employed. The repro-

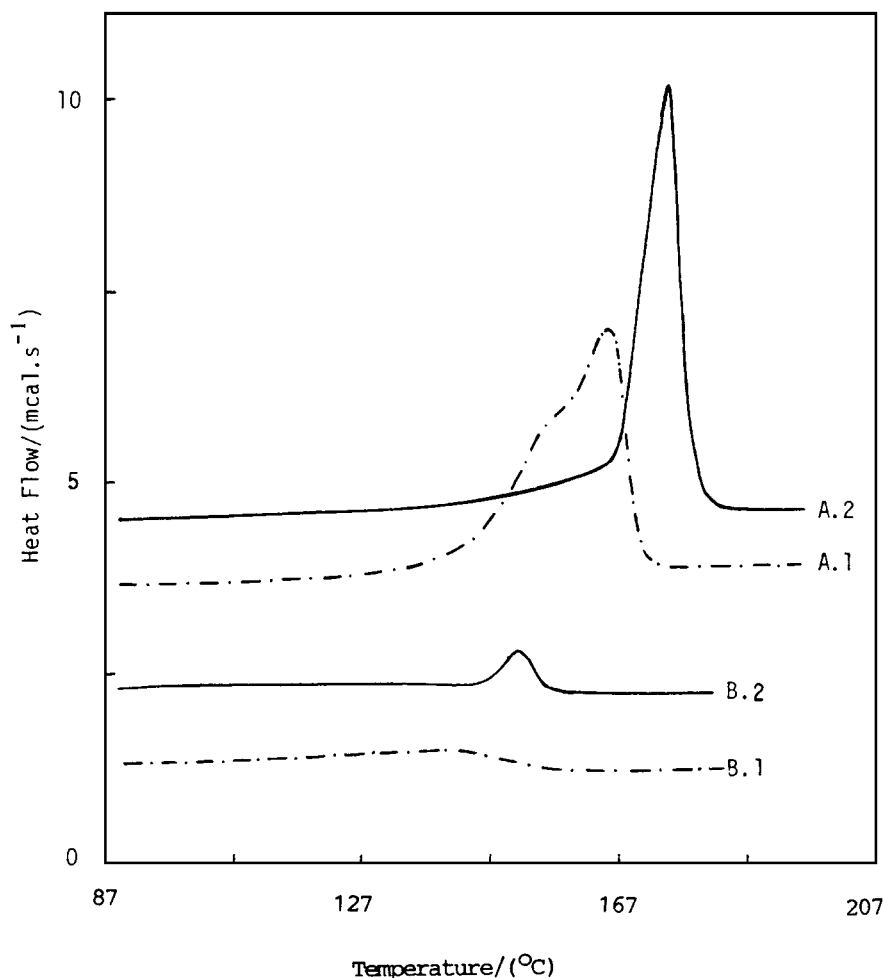


Fig. 1. Typical fusion curves for: A—highly isotactic ($mm = 1.0$) and B—stereoblock ($mm = 0.58$) polypropylene. A.1—without pretreatment; A.2—annealed at 162°C , B.1—without pretreatment, B.2—annealed at 137°C .

ducibility of the crystallization data is illustrated in Table I for the same sample run repetitively in the instrument and for three separate preparations of a sample run sequentially. It is apparent from the first series of runs that the instrument reproducibility is very high since the series of five onset temperature measurements are all bracketted within 0.1°C . Preparation of a series of fresh samples slightly increases the observed spread but the T_c values still lie within a 0.5°C range and the average of the enthalpy values lies within $\pm 1\%$. The discrepancy could point to slight inhomogeneities in the samples or to differences in packing or positioning of the sample pan. However, it should be noted that this reproducibility is obtained under optimum conditions with well-defined thermal curves and highly isotactic samples.

To further investigate the importance of sample preparation, a series of 12 pairs of samples was prepared. Each pair consisted of a powdered sample and

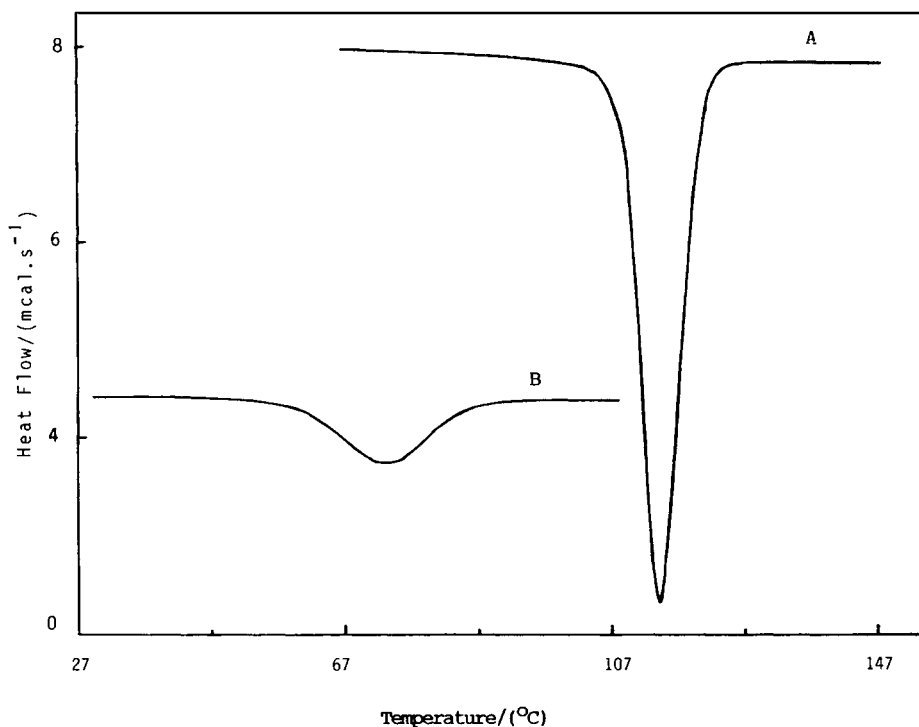


Fig. 2. Typical crystallization curves for: A—highly isotactic ($mm = 1.00$) and B—stereoblock ($mm = 0.58$) polypropylene.

a film sample derived from the same polymer batch. The sample pairs were then analyzed in both heating and cooling modes under identical conditions after an initial annealing at elevated temperatures to provide a uniform thermal history. On average, over the 12 samples, the films were found to give enthalpies of fusion and crystallization of about 2% higher than the powdered samples. On heating runs the value of T_{max} was found to be about 1°C lower for the film

TABLE I
Measurement Reproducibility

Sample	T_c ($^{\circ}\text{C}$)	ΔH_c (cal/g)
B.5 ^a	119.36	
	119.29	
	119.31	
	119.29	
	119.30	
MP.381 (A) ^b	120.0	-22.3
(B)	120.0	-22.4
(C)	120.5	-22.1

^a Same preparation, run repetitively.

^b Three separate sample preparations.

samples, whereas, for crystallization, film samples gave T_c values which were on average 0.5°C higher. These results imply, as might be expected, that the film samples are in better thermal contact with the sample pan than the powdered samples. However, the results are not grossly different and because of the need to run "as received" samples, powder sample preparation was normally used.

The advantage of polymer characterization by crystallization measurement lies in the possibility of erasing the thermal memory by annealing at elevated temperatures. It has been suggested that the standardized treatment temperature of 197°C is insufficient for highly crystalline polymers so in order to check this the behavior of samples pretreated at both 197°C and 217°C were compared. Table II summarizes the crystallization data for five different PP samples pretreated for 5 min at 197°C and 217°C respectively. Since there is no significant difference between the two sets of results the lower temperature was preferred so as to minimize the possibility of degradation.

Anomalous Crystallization Curves

During the course of the DSC examination of nearly 70 PP samples a small number of the polymers were found to exhibit completely anomalous crystallization curves. Examples of these are illustrated in Figure 3. (It is worth noting that significant differences are not observable in the form of the fusion curves for these samples and hence the crystallization examination is more diagnostic.) Curve A (B.6) is a PP sample prepared in the laboratory in the presence of excessively high transfer agent concentration ($\text{ZnEt}_2 = 600 \text{ mmol/L}$). Purification of this sample by multiple reprecipitation restores the usual symmetrical crystallization curve and modifies the crystallization parameters as summarized in Table III. It is evident in this case that the polymer contains some impurity, possibly a zinc derivative, which acts to nucleate the initial crystallization. Thus one reprecipitation reduces the onset temperature of crystallization by as much as 8°C . Further purification however has little additional effect illustrating that the nucleating impurity is fairly readily removed. Exactly analogous behavior was observed with a second sample from a similar background (Table III). It is also interesting that the process of purification has a very significant effect on the enthalpy of fusion of the initial run. Thus for PP sample B.8 ΔH_m

TABLE II
The Effect of Pretreatment Temperature on Crystallization Parameters

Sample	Temperature of pretreatment			
	197°C		217°C	
	ΔH_c (cal/g)	T_c ($^\circ\text{C}$)	ΔH_c (cal/g)	T_c ($^\circ\text{C}$)
B.6 (R2)	14.9	116.7	14.9	116.5
B.7	16.8	115.5	16.9	115.5
B.8 (R2)	16.5	114.5	16.8	114.5
B.9 (R)	16.0	114.3	16.1	114.0
B.11 (R2)	17.1	114.2	17.3	114.0

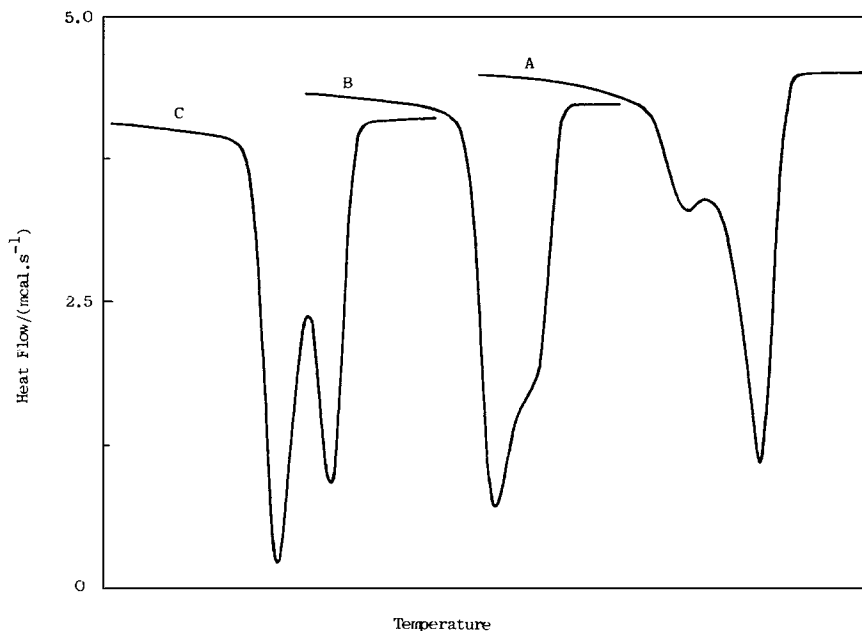


Fig. 3. Examples of anomalous crystallization curves. A—Sample B.6; B—Sample MP.362(HI), C—Sample MP.381.

increases in value from about 13 to 18 cal/g after two reprecipitations. Whereas, this might partially be accounted for by the loss of low molecular weight non-crystallizing polymer, the magnitude of the effect suggests that the removal of the nucleating impurity significantly alters the course of the crystallization. Thus although the impurity enhances the onset of crystallization the equilibrium extent of crystallinity is reduced.

Curve C in Figure 3 shows a startling dual exotherm which was only encountered for this polymer (MP.381). However, whereas this crystallization curve could be reproduced using the same sample, other samples from the same batch showed no such effect. Clearly in this case the initial sample was contaminated with an impurity which was not homogeneously distributed throughout

TABLE III
The Effect of Purification on Crystallization and Fusion Parameters

Sample	ΔH_c (cal/g)	T_c (°C)	ΔH_m (cal/g)	T_{max} (°C)
B.6	15.8	124.4	14.7	151.7
B.6 (R)	14.7	116.3	16.4	151.5
B.6 (R2)	14.9	116.7	18.0	151.9
B.8	14.9	123.5	13.3	155.9
B.8 (R)	16.4	114.0	15.1	156.9
B.8 (R2)	16.5	114.5	17.9	156.9

Polymer preparation $TiCl_3$ -AA/ Al_iBu_3 / $ZnEt_2$, $[ZnEt_2] = 600$ mmol/L; Purified by reprecipitation: R = $\times 1$, R2 = $\times 2$.

the bulk of the sample. This is in contradistinction to the effect illustrated in Curve A which was readily reproducible. A more detailed study was made with a second sample prepared in identical fashion to MP.381. This sample (MP.379) showed a significant shoulder on the crystallization curve. In this case the sample was first heptane extracted to yield the HI fraction which was subsequently extracted for 20 h with acidified alcohol. DSC examination of these samples showed that the shoulder was progressively removed on purification to yield the usual symmetrical curve. However, a concurrent determination of catalyst residues showed no significant differences in the titanium (18 to 26 ppm) and the aluminium content (31 to 40 ppm) of the polymer. This implies that in this case nucleating impurities distinct from catalyst residues are operative.

It is evident from these above examples that impurities present in PP samples can have a very significant effect on the crystallization parameters particularly on the onset temperature. Such effects would invalidate the use of the onset temperature as a possible index of stereostructure. However, such examples are not numerous and can in any case be readily detected from the shape of the thermal curve. Accordingly, in the calibrations reported below any samples displaying anomalous thermal curves were omitted from consideration.

Crystallization Parameters as Indices of Isotacticity

Crystallization Onset Temperature. These DSC studies have confirmed that the crystallization onset temperature (T_c) of pure PP samples is highly reproducible and it was for this reason that T_c was initially proposed as an index of isotacticity.¹ Elsewhere, in detailed isothermal crystallization studies, Martuscelli et al.^{13,14} have confirmed the dependence of the crystallization behavior on the stereoregularity of the polymer chain and have shown that the overall rate of crystallization, at a given temperature, decreases with increase in stereochemical defects. Thus for samples cooled at a standard rate from the melt it would be expected that the temperature of the onset of crystallization should be related to the rate of crystallization and hence the stereoregularity of the polymer chain. Whereas the initial results¹ suggested a simple relationship between T_c and isotacticity a more comprehensive study, embodying polymers prepared from widely different catalyst systems, reveal the more complex relationship shown in Figure 4. From the curve it appears that polymers prepared from conventional and supported catalysts show distinct crystallization behavior. Thus polymers derived from $\text{TiCl}_4/\text{MgCl}_2/\text{EB}$ catalysts invariably show lower crystallization temperatures for a given polymer isotacticity.

There would appear to be several possible reasons for the above discordant behavior: level of catalyst residues, variation in MW or MWD, differences in distribution of stereodefects, and other chain irregularities. At first sight the effect of catalyst residues seems a plausible explanation since supported catalysts operate at much lower catalyst concentrations and lead to reduced contamination of the polymer. The lower T_c value for supported PP would thus be a consequence of less nucleation by impurities. However, the observation that repetitive purification of the polymers derived from conventional catalysts does not reduce T_c would appear to mitigate against this explanation.

Another important difference between polymers derived from the two catalyst types is in the area of molecular size of the macromolecules. Thus in recent

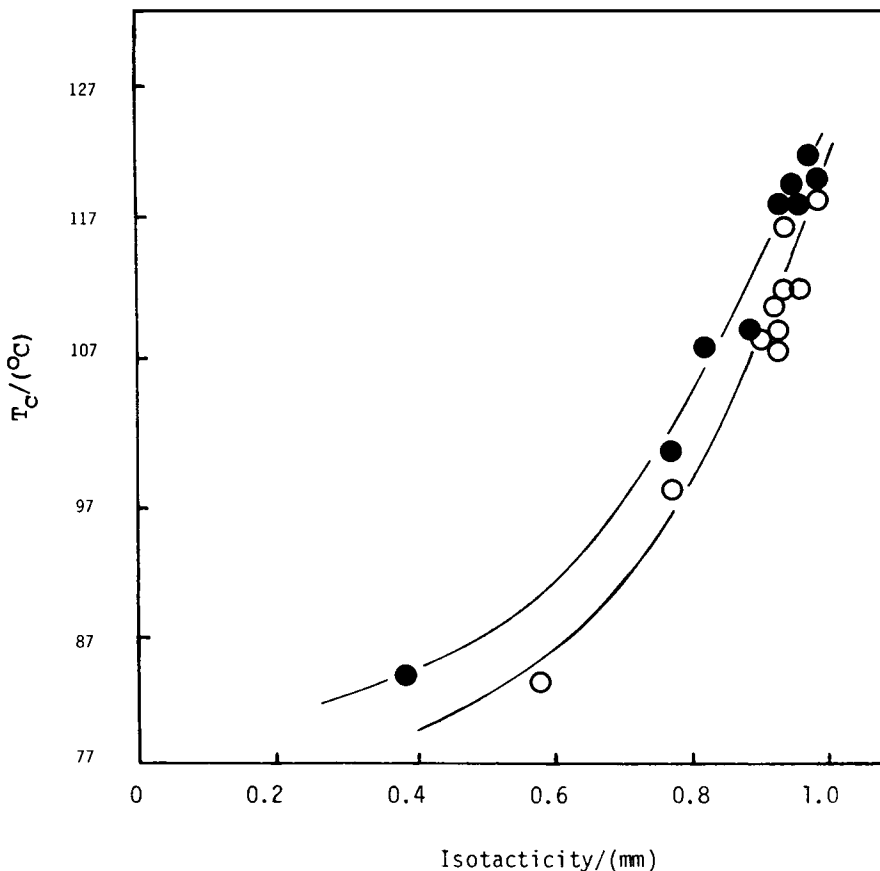


Fig. 4. Correlation of crystallization onset temperature with isotacticity. Polypropylene samples prepared from: ●—conventional, ○—supported catalysts.

preparative studies with both types of catalyst, under similar experimental conditions, it was observed that polymers derived from supported catalyst showed both lower molecular weight and much narrower MWD.⁹ In order to probe the influence of these effects samples of similar stereostructure but different MW characteristics were examined. The results (Table IV) are displayed for a series of polymers derived from both conventional and supported catalysts. An overall examination of both series reveals that the \bar{M}_n value has little apparent effect on T_c over a fivefold range. However, the supported catalyst with MWD values in the range 3.4 to 4.4 does show lower mean T_c values than the polymers prepared from conventional catalysts which have MWD in the range of 6 to 9. However, this observation is not conclusive as it does not separate differences in MWD from differences in catalyst type. On balance it would appear that the effect of molecular weight is probably minor.

Differences in the polymers derived from the two catalyst systems are to be found in the microstructure of the polymer. Thus, supported catalysts tend to produce polymers rich in unsaturated chain ends, since transfer with monomer is the predominant transfer step. Furthermore, the supported catalysts are very

TABLE IV
The Influence of Molecular Weight on Crystallization Behavior

Sample	mm (NMR)	\bar{M}_n^a ($\times 10^{-3}$)	\bar{M}_w/\bar{M}_n	T_c ($^{\circ}\text{C}$)
<i>Conventional catalyst</i> ^b				
MHP.9	0.95	142	6-9	116
MP.348 (HI)	0.95	140		117
MP.343 (HI)	0.95	93		121
MP.380 (HI)	0.95	34		120
				Mean = 119 \pm 2
<i>Supported catalyst</i> ^c				
D.15	0.94	338	3.4	112
D.16	0.93	162	4.3	112
D.17	0.94	108	3.8	109
D.18	0.92	89	3.6	111
D.19	0.94	65	4.4	112
				Mean = 111 \pm 1

^a Determined by GPC.

^b $\text{TiCl}_3(\text{TAC144})/\text{AlEt}_2\text{Cl}/\text{Diglyme}$.

^c $\text{TiCl}_4/\text{MgCl}_2/\text{EB}/\text{AlEt}_3$.

regioselective and show few if any irregular linkages of propylene units, whereas between 2 to 7 mol % of propylene unit inversion is usually detectable in the ^{13}C -NMR of atactic PP derived from conventional Ti or V based catalysts. However, it would seem unlikely that differences in the structure of the chain end would have a significant effect on crystallization behavior and the absence of monomer inversion should lead to enhanced crystallizability—the opposite of the observed effect—and hence these explanations should be discounted.

Probably, the most likely explanation on the differences in crystallization behavior is related to variation in the distribution of stereochemical defects. Thus although PP samples may have the same overall isotacticity the nonisotactic units may be distributed differently and hence lead to variation in crystallizability. Such an effect of distribution of stereochemical defects on crystallizability has been demonstrated earlier by Martuscelli et al.^{13,14} In this context it seems likely that supported catalysts are characterized by greater uniformity in active sites and that this in turn leads to the production of a more uniform distribution of stereodeflects in the polymers. This in turn would be expected to lead to polymers with less tendency to crystallize than their apparently structurally equivalent counterparts in which the defects are concentrated in certain parts of the chain or more likely in certain chains. This would rationalize the discrepancies observed in Figure 4 and explain why polymers derived from supported catalysts show lower T_c values. It is probably also worth noting that the two curves in Figure 4 appear to converge as the isotacticity approaches unity and this would be expected if the difference in behavior is related to the distribution of defects.

A consequence of the above observations is that it is not possible to obtain a unique calibration curve relating the value of T_c to polymer isotacticity. As

an added complication it should also be noted that the data in Figure 4 were derived from samples that had been grossly fractionated into HI and HS fractions by hot heptane extraction. The use of whole samples with fractions of very mixed stereostructure shows large divergence from the calibration. A typical set of crystallization curves for the various fractions of a given polymer sample is shown in Figure 5. It is readily apparent that the crystallization curve for the whole sample lies in an intermediate position between the HI and HS fractions as might be expected but the shift in T_c is not directly additive. This is illustrated in Table V which summarizes the crystallization parameters for the three fractions. The crystallization temperature of the whole sample (114.2°C) corresponds to an NMR triad isotacticity of 0.94 according to the calibration curve (Fig. 4) whereas the actual value is about 0.84. This wild

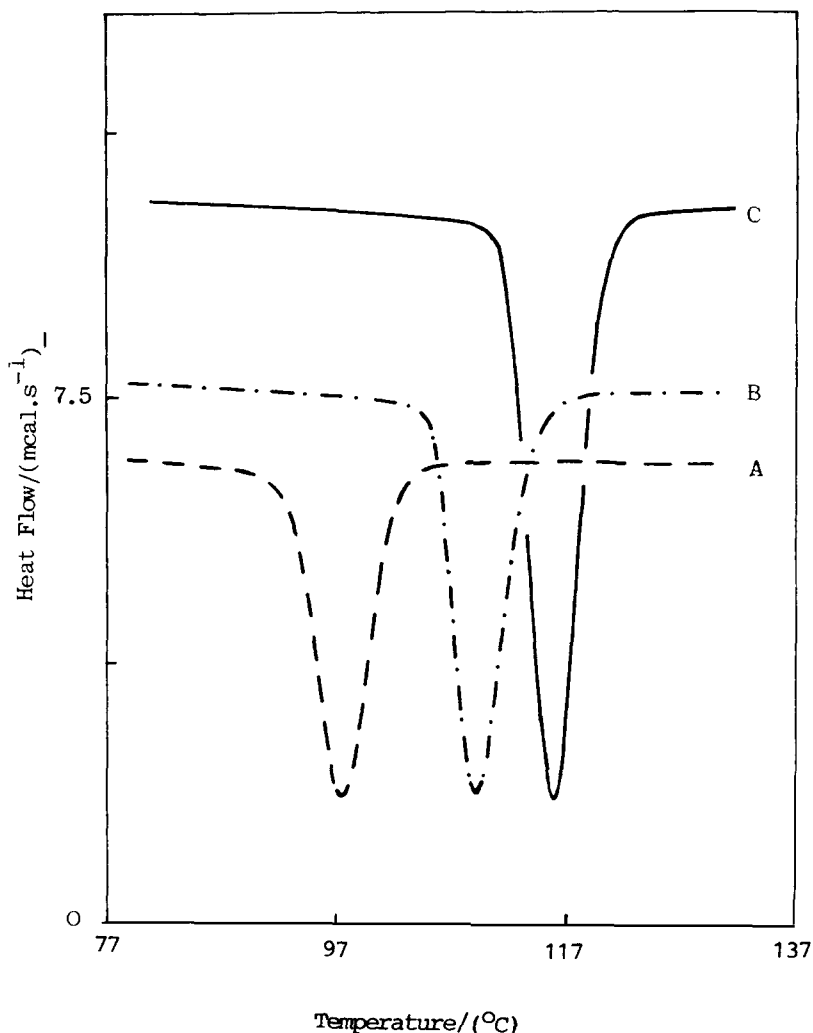


Fig. 5. Crystallization curves for polypropylene fractions and whole samples. A—Heptane soluble, B—Whole sample, C—Heptane insoluble.

TABLE V
Crystallization Parameters for a Fractionated Polymer Sample

Sample	w_s^a	mm (NMR)	T_c (°C)	T_{\min} (°C)	T^b (°C)	ΔH_c (cal/g)
B.11	1	0.84	114.2	109.2	5.0	-17.1
B.11 (HI)	0.32	1.00	120.5	115.9	4.6	-24.5
B.11 (HS)	0.68	0.77	102.0	97.3	4.7	-13.5

^a Weight fraction of whole sample.

^b Difference between T_c and T_{\min} .

discrepancy demonstrates that in the case of a mixture of polymers of grossly different stereoregularity the observed crystallization onset temperature is more representative of the fraction of higher isotacticity. At the same time it is interesting to observe that the breadth of the crystallization curves, as measured by the difference between the onset and minimum temperatures, is quite close for all three fractions (Table V). This would appear to indicate that the crystallization process is a cooperative one, the sample crystallizing as a whole rather than in discrete fractions. The effect of stereoblock polymer is thus to inhibit the crystallization of the more regular isotactic polymer chains.

Enthalpy of Crystallization. In view of the difficulties outlined previously for employing the crystallization onset temperature as index of isotacticity it was thought worthwhile to investigate the possible relationship of the enthalpy of crystallization to this parameter. This would still have the advantage discussed earlier of removal of the thermal history of the initial sample by cooling from the melt. Examination of the enthalpy data shows that there is a correlation between isotacticity and the enthalpy of crystallization (ΔH_c) with the latter value decreasing from about 25 cal/g for highly isotactic samples to as little as 2 cal/g for samples of mm = 0.35. Interestingly, a plot of ΔH_c vs. isotacticity (Fig. 6) shows a similar shape to the analogous onset temperature plot but without distinction between polymers from supported and conventional catalysts. The lack of discrimination in the case of enthalpy measurements may be rationalized if the onset temperature measurements are related to the *rate* of crystallization whereas the enthalpy measurements effectively measure the *extent* of crystallization. Conceivably the latter parameter is less sensitive to variations in the distribution of stereodefects.

An added bonus of the use of enthalpy measurements is that the enthalpies of crystallization are approximately additive. For additive enthalpies we should expect a relationship such as:

$$\Delta H_{c_{\text{whole}}} = w_{\text{insol}} \times \Delta H_{c_{\text{insol}}} + w_{\text{sol}} \times \Delta H_{c_{\text{sol}}} \quad (1)$$

where, w_{insol} and w_{sol} represent the weight fractions of the insoluble and soluble fractions respectively. Application of this equation to the data summarized in Table V leads to a calculated value of $\Delta H_{c_{\text{whole}}} = -17.0$ cal/g which is very close to the experimental value of -17.1 cal/g observed for the whole sample. Thus it can be seen that correlation of the enthalpy of crystallization with isotacticity (Fig. 6) leads to an alternative method of tacticity determination by DSC mea-

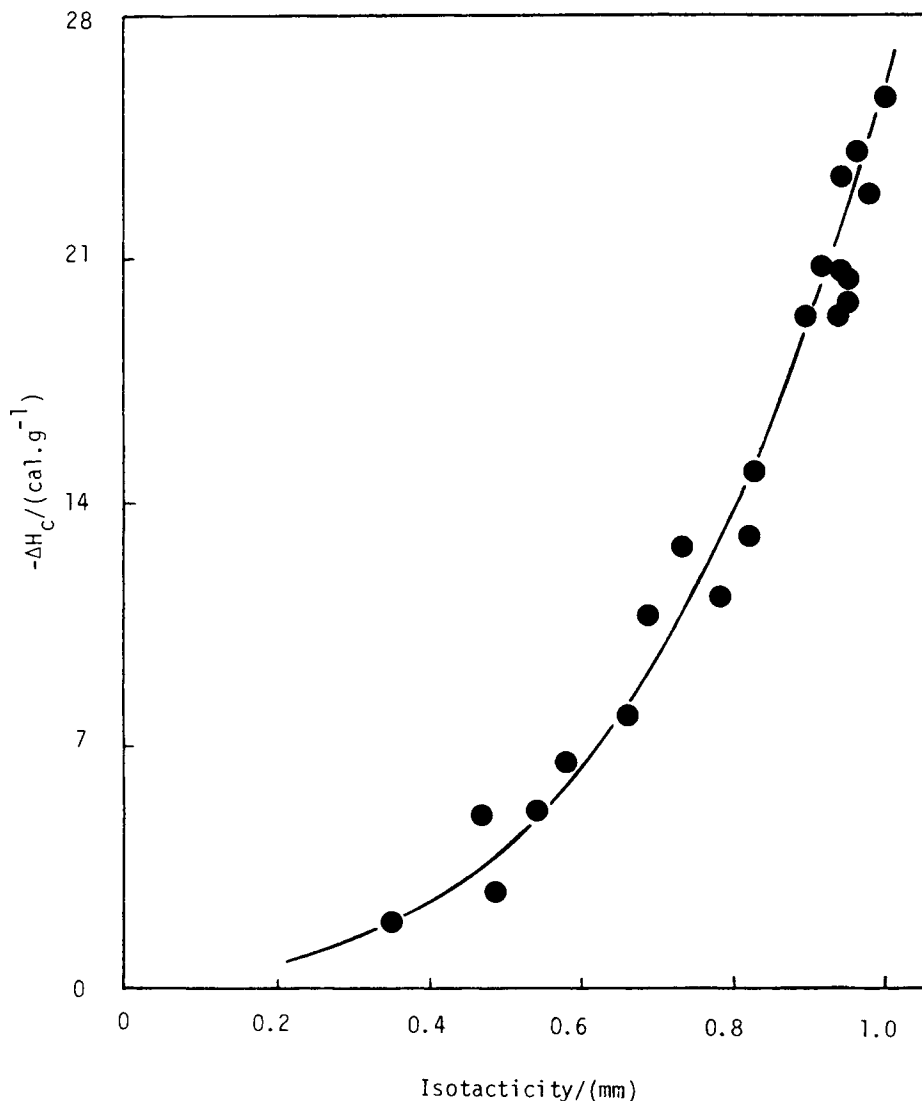


Fig. 6. Correlation of enthalpy of crystallization with isotacticity.

surement. This method has certain advantages in that: (i) there is little difference in behavior of polymers from various catalyst types, (ii) both whole and fractionated samples may be accommodated, and (iii) the enthalpy of crystallization may be measured more accurately than the onset temperatures with samples of low isotacticity.

The crystallization data are capable of further manipulation since it has been shown that the enthalpy of crystallization is related to the sequence run length of crystallizable units in the polymer chain. Thus the relationship

$$\Delta H_c = kP^n \quad (2)$$

where k is a constant, P the fraction of crystallizable units, and n the critical sequences for crystallization, has been shown to be applicable to ethylene sequences in EP polymers¹⁵ in LDPE^{16,17} and vinyl chloride copolymers.¹⁷

In the case of PP, if it is assumed that only the isotactic units are involved in crystallization then it is possible to show⁴ that eq. (2) may be expressed in the form

$$\log(\Delta H_c) = \log k + n/3 \log(mm) \quad (3)$$

where mm is the triad tacticity. The application of this equation to the current data is shown in Figure 7 where the anticipated linear correlation is observed. The slope of the plot corresponds to a critical run sequence of $n = 8$ isotactic units. Interestingly, all samples including fractionated and whole polymers ap-

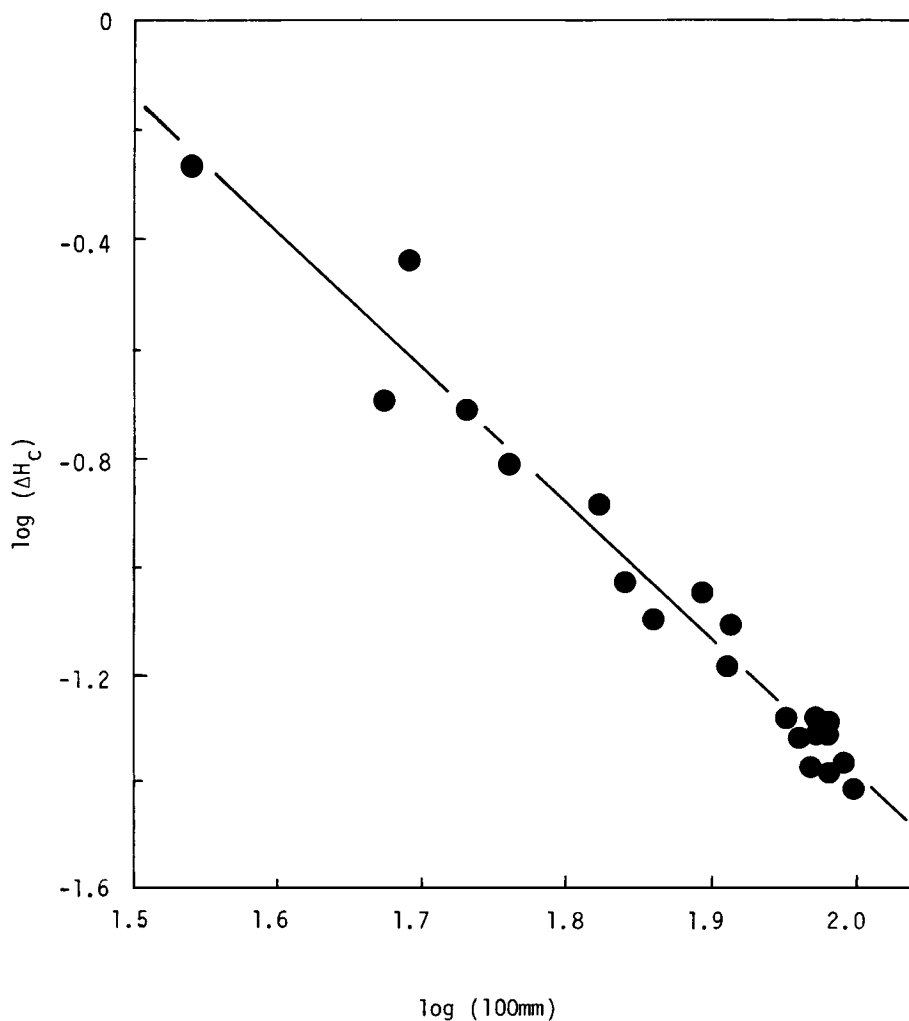


Fig. 7. Double logarithmic plot of enthalpy of crystallization vs. isotacticity.

pear to fall on the same line and consequently this could be a useful calibration for relating isotacticity to enthalpy of crystallization.

Fusion Parameters as Indices of Isotacticity

The Fusion Temperature. The earliest attempts to characterize tactic polypropylene by calorimetry involved the measurement of crystalline melting points.⁴⁻⁶ The main difficulty in this approach is that the form of the fusion curves and hence the measured fusion temperatures are dependent on the thermal history of the sample. To obviate this difficulty the samples were preconditioned by a standardized heat-cool cycle or by annealing at elevated temperatures some 5 to 20°C below the predetermined melting point. A second difficulty concerns the definition of the melting point. In this work two distinct temperatures were measured, the maximum temperature (T_{\max}) and the onset temperature (T_{ons}), the latter being derived from the intercept of the tangent to the steepest gradient of the leading edge of the fusion curve with the baseline of the thermal curve.

Typical fusion temperatures for a selection of PP samples, prepared from a wide variety of catalyst types, are recorded in Table VI. Clearly the fusion temperatures are dependent on tacticity and generally the most highly isotactic

TABLE VI
Fusion Temperatures of Preconditioned and Annealed Samples

Sample	Catalyst	mm	Onset temperature (°C)		Maximum temperature (°C)	
			Conditioned	Annealed	Conditioned	Annealed
B.11 (HI)	A	1.00	154.6	166.4	163.0	174.4
B.6 (HI)	A	0.98	148.4	148.8	161.2	159.3
B.14 (HI)	A	0.96	155.3	153.5	163.8	162.3
L.52 (HI)	B	0.95	146.3	148.2	158.3	157.9
MP.384 (HI)	F	0.95	150.5	169.2	162.7	176.2
L.50 (HI)	B	0.94	146.8	147.3	159.4	158.1
B.21 (HI)	C	0.94	149.3	165.5	158.9	172.1
D.17	H	0.94	143.9	147.6	158.3	157.2
D.18	H	0.92	144.5	148.0	157.7	157.0
B.5 (HI)	B	0.89	150.5	170.9	162.5	179.7
L.52	B	0.82	143.4	147.8	159.4	156.6
B.23 (HI)	D	0.82	123.5	170.9	135.3	173.7
D.2	H	0.78	121.6	132.5	145.5	139.6
L.50	B	0.73	144.0	147.6	160.0	156.7
B.10 (HS)	A	0.69	124.5	147.4	138.2	153.6
MHP.177 (HS)	G	0.66	120.8	143.7	136.1	151.0
B.20 (HS)	E	0.58	101.7	145.5	139.8	151.8
L.52 (HS)	B	0.54	100.0	131.6	126.4	138.4
D.12	J	0.49	92.3	—	146.7	—
D.50 (HS)	B	0.47	113.6	132.7	150.8	140.2
LD.11	I	0.35	96.8	131.2	117.9	137.5

A: TiCl_3 .AA/ $\text{Al}(\text{Bu})_3$ / ZnEt_2 , B: TiCl_3 ./AA/ $\text{Al}(\text{Bu})_3$, C: TiCl_4 / MgCl_2 /EB/ $\text{Al}(\text{Bu})_3$ / ZnEt_2 , D: VCl_3 / $\text{Al}(\text{Bu})_3$, E: TiCl_4 / MgCl_2 /EB/ $\text{Al}(\text{Bu})_3$, F: TiCl_3 (TAC-144)/ AlEt_2Cl /Diglyme, G: TiCl_3 (TAC-144)/ AlEt_3 , H: TiCl_4 /EB/ MgCl_2 / AlEt_3 , I: $\text{Ti}(\text{OC}_4\text{H}_9)_2$ / AlEtCl_2 , J: $\text{Ti}(\text{OC}_4\text{H}_9)_2$ / AlEt_2Cl .

samples have the highest melting points. However, there are a significant number of inconsistencies. For example, samples B.5 and B.23 with isotacticities of only 0.89 and 0.82 show the highest melting points. The most likely reason for this apparent discrepancy is that these samples have much higher molecular weights than the samples of higher isotacticity. (GPC \bar{M}_n values indicate a factor of $\times 10$). This supposition is supported by the analysis of samples of similar tacticity but with wide variations in molecular weight (Table VII). It is evident from these data that the fusion temperature increases with molecular weight.

The effect of annealing is, as expected, to raise both the maximum and onset fusion temperatures. At the same time the breadth of the fusion curve, as measured by the difference between the two temperatures (ΔT), is narrowed. Thus for the preconditioned samples ΔT ranges from 8 to 54°C compared to 3 to 11°C for the annealed samples. In the case of the annealed samples the onset temperature is probably less characteristic of the material since it is significantly affected by the chosen annealing temperature. Thus the observed onset temperature is usually close to the annealing temperature.

From the perspective of determining isotacticity, fusion temperatures do not seem likely to form a useful criteria since the observed temperatures are crucially dependent on the thermal history or treatment of the sample as well as other factors, particularly molecular weight. In this respect this approach would appear to have the same limitation as the solvent extraction method¹⁸ which has been shown^{4,19} to be dependent on both polymer stereoregularity and molecular weight.

The Enthalpy of Fusion. An alternative approach to the use of melting temperatures is to employ the enthalpy of fusion (ΔH_m) as an indicator of isotacticity. The implication here is that ΔH_m is a measure of crystallinity which in turn is dependent on the isotactic content of the sample. However, this method is not without difficulty since the measured heat of fusion is dependent on the thermal history of the sample. Furthermore, determination of a precise baseline for the fusion curve is somewhat arbitrary.

In this work three distinct measurements of the heat of fusion were made. These were derived from: (i) the "as received" sample, (ii) the sample after cooling from the melt, and (iii) the sample after annealing at an elevated temperature. As anticipated the highest enthalpies were obtained with samples

TABLE VII
The Effect of Molecular Weight on Fusion Temperatures

Sample	mm	$\bar{M}_n^a (\times 10^{-3})$	Maximum temperature	
			First run	Conditioned
D.15	0.94	338	165.5	162.3
D.16	0.93	162	160.8	160.4
D.17	0.94	108	154.0	156.3
D.18	0.92	89	154.5	156.3
D.19	0.94	65	153.6	157.0

^a Determined by GPC.

annealed at an elevated temperature and the values ranged from 31.5 cal/g for $mm = 1.00$ to as little as 1.7 cal/g for $mm = 0.35$. The enthalpies of the samples "as received" were however frequently greater than that of the samples cooled from the melt, indicating an annealing of the samples during storage.

The data from these measurements have been analyzed by the relationship analogous to eq. (3) and the results are shown in Figure 8 and summarized in Table VIII. It is clear that the fusion data provide a reasonably good fit to eq. (3) with the best correlation being provided by the data from the conditioned samples and the worst resulting from the "as received" samples. This is to be anticipated since the "as received" samples will have a much less uniform thermal history than the conditioned samples. It can be seen that further annealing of the sample does not improve the correlation and this finding is consistent with recently published results which show that polymer film annealing does

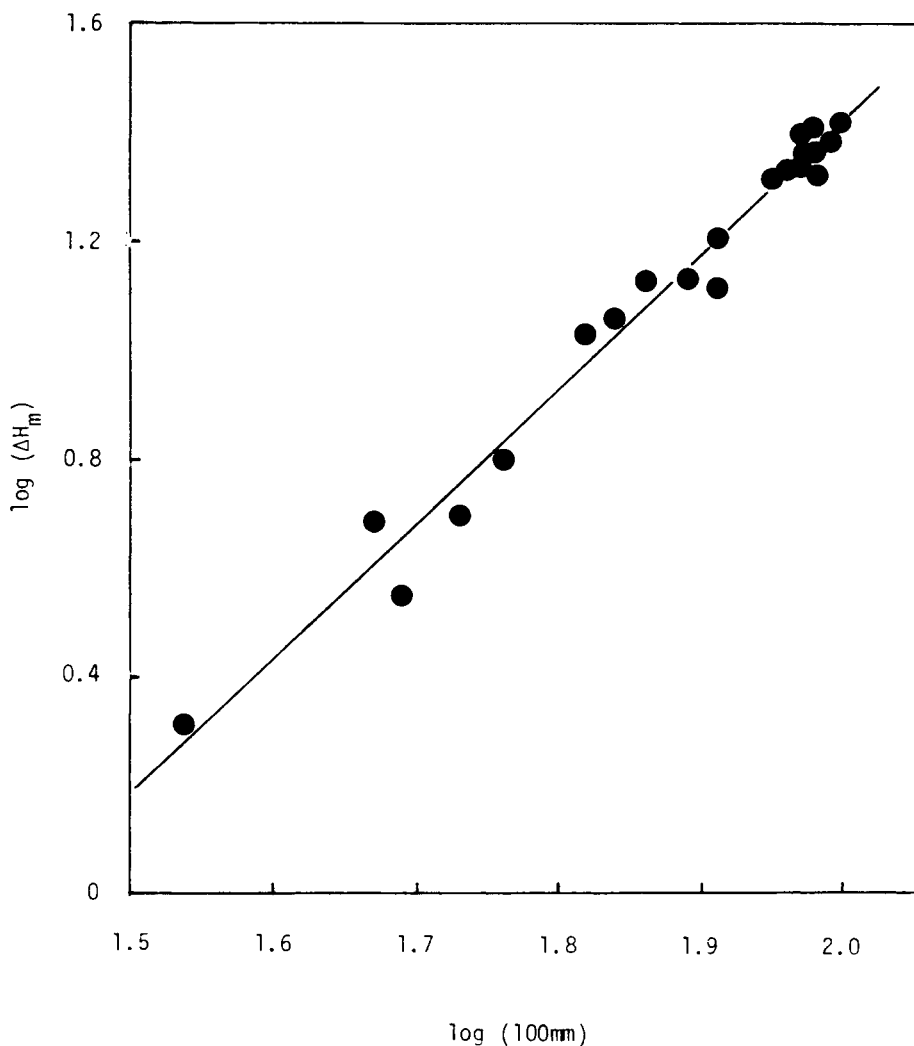


Fig. 8. Double logarithmic plot of enthalpy of fusion of conditioned samples vs. isotacticity.

TABLE VIII
Summary of the Data from Double Logarithm Plots of Enthalpy versus Isotacticity

	$\log k$	$n/3$	Correlation coefficient
<i>Fusion</i>			
"As received"	-4.53 ± 0.31	2.99 ± 0.17	0.971
Conditioned	-3.51 ± 0.15	2.46 ± 0.08	0.990
Annealed	-4.31 ± 0.23	2.91 ± 0.12	0.985
<i>Crystallization</i>			
From the melt	-3.62 ± 0.2	2.50 ± 0.10	0.983

not improve the precision of PP stereoregularity determination from IR measurements.²⁰ Interestingly, the measurements derived from the fusion analysis of the conditioned samples is very close to that derived from the crystallization data (Table VIII).

Glass Transition Parameters as Indices of Isotacticity

The Glass Transition Temperatures. Earlier calorimetric studies² have shown that the glass transition temperature (T_g) of PP is dependent on the stereoregularity of the macromolecule with the isotactic structure having a value some 12 to 14°C below the syndiotactic and atactic configurations. In principle therefore, the value of the T_g could be used as an indicator of PP stereostructure. In practice there are two difficulties: (i) the glass transition temperature of highly isotactic polymers is indistinct because of the high crystallinity of the material, and (ii) the glass transition temperature is also markedly affected by the molecular weight.² Thus, for atactic samples, values of T_g ranging from -24 to -7°C have been determined for polymers in the molecular weight range 3.8 to 754×10^3 .

In this work the observed midpoint T_g values of the samples were found in the range -19 to -3°C , however, there does not appear to be any clear correlation between the T_g and the isotacticity. This almost certainly reflects the wide range of molecular weights which characterize the samples.

The Heat Capacity. Potentially, the change in heat capacity (ΔC_p) associated with the glass transition temperature may be used as an indirect measure of polymer crystallinity and hence isotacticity. Thus ΔC_p is proportional to the amount of amorphous material present in the polymer sample, i.e., $\Delta C_p = k'w_a$ where, w_a is the weight fraction of the amorphous material and k' is a constant. Similarly, it follows that $\Delta H_m = k''w_c$, where w_c is the weight fraction of crystalline material and k'' a constant. Since $w_a + w_c = 1$, it can be readily shown that

$$\Delta H_m = k'' - k''\Delta C_p/k' \quad (4)$$

Consequently a plot of ΔH_m vs. ΔC_p should be linear. This indeed proves to be the case (Fig. 9) although the plot does exhibit considerable scatter. The extrapolated value of ΔC_p when $\Delta H_m = 0$ is found to be approximately 0.116

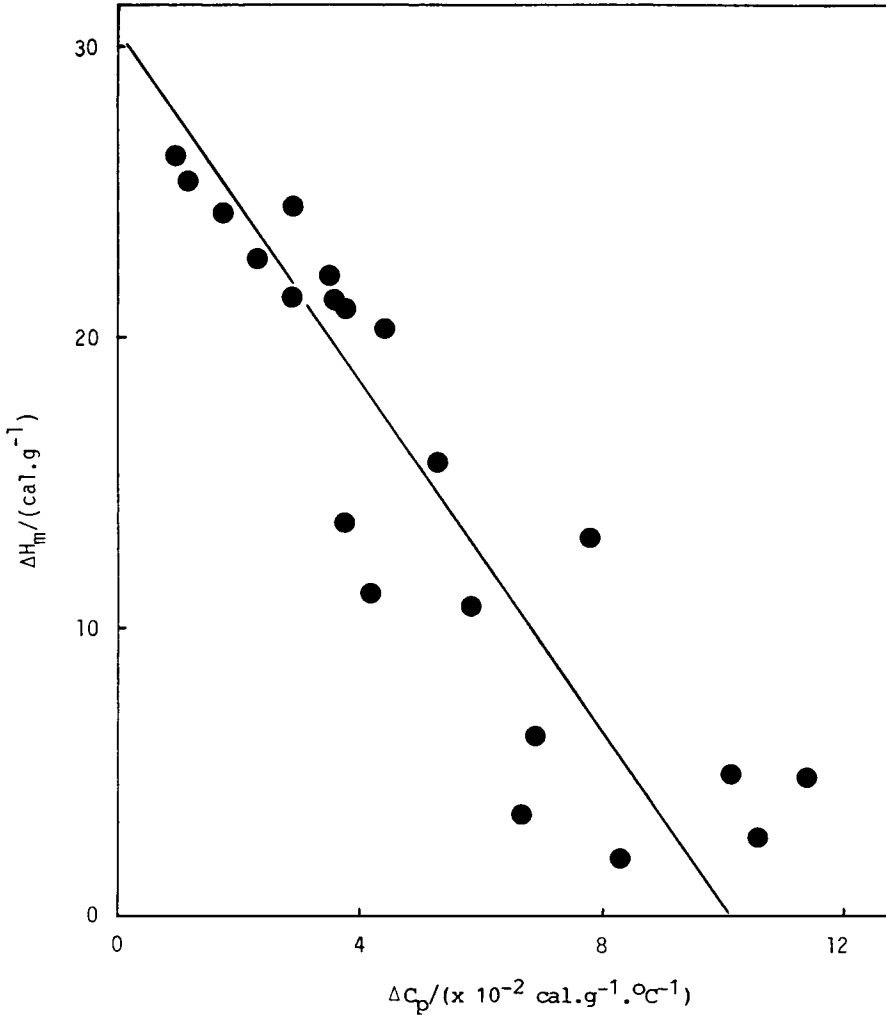


Fig. 9. Correlation of enthalpy of fusion with change in heat capacity at the glass transition.

cal/g°C which is within the range 0.114 to 0.129 cal/g°C determined by previous workers.²¹⁻²⁴

The degree of scatter in the results is probably a consequence of the difficulty of accurate measurement of the heat capacity change in these samples. Such imprecision mitigates against the use of heat capacity data as an index of isotacticity.

CONCLUSION

Calorimetric methods provide considerable potential in the evaluation of the stereoregularity of PP. The methods are rapid, require only small samples, and are reasonably precise. The best indices of isotacticity are provided by enthalpy data from either the fusion or crystallization processes. In both cases double

logarithmic plots of ΔH vs. isotacticity are found to be linear over the range of tacticities from 0.35 to 1.00 mm. These indices are applicable to both fractionated and whole samples and are not appreciably affected by wide variations in molecular weight.

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