

Heat and Entropy of Fusion of Polypropylene

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Synopsis

There are wide discrepancies in the literature values for the heat of fusion (ΔH_u) of isotactic polypropylene. A study was therefore made of the variables affecting ΔH_u as determined by differential thermal analysis. The results of this study show ΔH_u for 100% "crystalline" polypropylene to be 2400 cal./mole repeating unit with $2\sigma = 300$. The entropy of fusion is 5.4 e.u./repeating unit ($2\sigma = 0.3$). Thermal history, potential errors in sample-sensor contact as well as uncertainties in x-ray analysis for per cent crystallinity are discussed.

Introduction

The heat and entropy of fusion of a crystalline polymer can be determined experimentally from calorimetric data, from the thermal effects in differential thermal analysis (DTA), from the dependence of the melting point on pressure, and from the effect of diluents or comonomers on the melting point of the polymer. All of these methods have experimental uncertainties which can make it extremely difficult to get an accurate value for either the heat of fusion (ΔH_u) or the entropy of fusion (ΔS_u) of a crystalline polymer.¹⁻⁴ Thus, as may be seen from the data in Table I,

TABLE I
 Heat of Fusion Reported for Isotactic Polypropylene

Method	Year reported	Heat of Fusion ΔH_u		Reference
		cal./mole	cal./g.	
Differential thermal analysis (DTA)	1960	650	15.4	5
	1961	690	16.4	7
Temperature dependence of solubility	1957	660	15.7	6
Specific heat	1962	1470	35	8
	1960	1760	40	9
	1963	1890 \pm 200	45 \pm 5	4
Calculated from dT_m/dp	1962	1840	44	8
	1963	2225 ^a	53	4
Melting point depression	1958	2600	62	10

^a Reinterpretation of data in reference 10.

there are wide discrepancies in literature values for the heat of fusion of isotactic polypropylene.

DTA has a number of well known advantages for studying polymer transitions, and when correlated with other methods of analysis, it provides a powerful tool for determining valuable information. When applied to the melting process, DTA has the advantage of measuring directly the heat absorbed in the phase change. Conventionally, the heat of fusion of a material, e.g. polypropylene, is determined by comparing the area under the DTA endothermic "peak" with that of a standard sample. Although this comparison is in principal straightforward,¹¹ it can in practice be a source of error. This is discussed in greater detail below. The comparison gives a ΔH or heat of fusion for the sample under study. If the test sample is not 100% crystalline, then ΔH_u for 100% "crystalline" material can be calculated by the use of the formula:

$$\Delta H_u = \Delta H \times 100/X \quad (1)$$

where X is per cent crystallinity and ΔH is the heat of fusion of the sample under study. An obvious difficulty in obtaining an accurate value for ΔH_u for polypropylene lies in the uncertainty in determining the per cent crystallinity.

Experimental

Samples of isotactic polypropylene of 60–75% crystallinity were prepared in the laboratory by use of aluminum alkyl–transition metal catalysts. The properties of the polypropylene samples are summarized in Table II.

TABLE II
Polypropylene Samples Studied

Sample	Tensile strength, psi	Molecular weight	Heptane-insolubles, %
A	4200	310,000	86
B	4830	785,000	100
C	3920	520,000	84

The molecular weights were calculated from viscosity measurements using the Kinsinger equation. Samples A and C were unextracted samples, sample A having been prepared in the presence of diethyl zinc¹¹ for molecular weight control. The transition metal catalyst component was TiCl_3 . Sample C was prepared in the absence of a molecular weight control agent, using a TiCl_3 –0.33 AlCl_3 transition metal component. Sample B was a heptane-extracted sample. The differential thermal analysis measurements were made essentially by the procedure described by Ke^{5,12} and others.¹³ Two somewhat different techniques were used. For initial studies with samples A, B and C (Table II), a large (300–800 mg.) sample

was used. For the annealing study described below, a semimicro (~ 1 mg.) apparatus was used with polypropylene sample B. The 1 mg. samples were packed into 2 mm. O.D. glass capillary tubes which were placed in a cylindrical aluminum block heated by an 85 w. cartridge heater. Glass microbeads (acid- and solvent-washed and baked at $450^\circ\text{C}.$) were used for reference. Fine wire thermocouples, butt-welded and filed to a sharp point, were inserted into the exact center of the sample and reference masses. Heating rates of 9°C./min. were used throughout. (A 5°C./min. rate was used in the initial studies with large samples.) Reproducible rates were achieved through the use of a cam-driven Speedomax H proportional controller driving a Fincor reactor. Silver nitrate (Baker and Adamson), analyzed reagent grade, was used as the calibrating standard sample for most of the studies. The heat of fusion was taken as 17.7 cal./g.¹⁴ In the initial studies with 300–800 mg. samples, benzoic acid was used for calibration, the heat of fusion being taken as 33.9 cal./g.¹⁵ Silver nitrate was found superior to benzoic acid as a calibrant. Although the use of the latter material has been traditional in DTA experimentation, we found that partial sublimation occurred each time benzoic acid was heated through its melting point. This could introduce a serious source of error in DTA-determined heats of fusion on semimicro samples. As a further check on the semimicro technique, ΔH_u of polymethylene was determined and found to be 950 cal./mole CH_2 . This value agrees very well with the 930 cal./mole CH_2 reported by Wunderlich and Dole¹⁶ and 940 ± 30 cal./mole CH_2 reported by Quinn and Mandelkern.¹⁷

The crystalline fractions of the various polypropylene samples were determined by x-ray diffractometry by use of a flat fused sample in the symmetrical reflecting position. Care was taken to obtain a smooth diffracting surface and to avoid introducing preferred orientation of the crystals during sample preparation. This was accomplished by fusing polypropylene powder in a holder which consisted of a plane metal plate with an appropriate aperture. By means of a jig, the sample holder was held firmly against a piece of photographer's chromium-plated "ferrotype" plate. Polymer powder was then loaded into the aperture, and the assembly was heated to melt the powder, at the lowest practicable temperature. The polymer fused under its own weight in less than 5 min., after which the assembly was cooled slowly to room temperature in about 30 min. The ferrotype plate was separated from the fused polymer, leaving a very smooth and plane surface on the polymer sample. The polymer sample was then annealed by the same procedure as used for the DTA samples.

Diffractometer traces were obtained with radiation from a copper target. The range of 2θ between 8° and 31° was covered at a scanning rate of $1/3^\circ/\text{min.}$ Measurements of these traces were made for the integrated intensity A_c attributable to the amorphous fraction. The crystalline fraction, F_c , was calculated by the relationship

$$F_c = A_c / (A_c + KA_a) = 1 / [1 + K(A_a/A_c)] \quad (2)$$

where K is a constant determined in a separate experiment. A value of $K = 1.297$ was reported by Weidinger and Hermans,¹⁸ who used an amorphous standard consisting of a molten sample which presumably contained isotactic as well as atactic molecules. By a similar procedure, but with the use of a sample of atactic polypropylene at room temperature, a value of $K = 1.06$ was obtained in our laboratories.*

Results and Discussion

The crystalline content of the three polymer samples studied in the initial studies are listed in Table III. Values are given for $K = 1.06$ and $K = 1.297$.

TABLE III
Crystallinity of Polypropylene Samples According to Eq. (2)

Sample	A_a/A_c	F_c		Crystallinity, %
		$K = 1.06$	$K = 1.297$	
A	0.347	0.732	0.688	71 ± 3
B	0.482	0.645	0.616	63 ± 2
C	0.612	0.605	0.555	58 ± 4

The per cent crystallinity figure is based on an average of the $K = 1.06$ and $K = 1.297$ values. The results of the initial DTA measurements are summarized in Table IV.

TABLE IV
Heat of Fusion of Polypropylene Samples

Sample	Crystallinity, %	Observed ΔH , cal./g.	ΔH for 100% crystallinity, cal./g.
A	71	38; 41	57
B	63	34; 31; 31	51
C	58	40	69
			Avg. 59

The value of 59 cal./g. is equivalent to 2310 ± 300 cal./mole of repeating unit for ΔH_u of polypropylene. This value is in good agreement with 2370 cal./mole estimated by Schaeffgen¹⁹ and is in excellent agreement with the value of 2430 cal./mole obtained by one of us in another study.²⁰

As is well known, the crystallinity of a polypropylene sample is strongly dependent upon the polymer's thermal history. Unless sufficiently annealed, the polymer's melting point and heat of fusion can be low. Another potential source of error in differential thermal measurements is sample

* Determined by J. W. Harrison of Esso Research & Engineering Co., Analytical Div. A confirming value of 1.08 was obtained in the present study.

contact with the thermocouple. This source of error can be especially serious in micro work and where the polymer sample is of very high molecular weight. Moreover the contacting problem may be accentuated if the sample for analysis is available only as a molded pad or film. A study was therefore carried out to find a method for minimizing these sources of error. Sample B was chosen for these studies because of its high molecular weight. It was molded into a film before use. X-ray analysis showed the film sample to be 66% crystalline. Annealing for 48 hrs. at 150°C. did not change the x-ray crystallinity.

Pieces of sample B film were placed into the micro DTA sample tubes and the thermocouples embedded. The entire assembly was then heated in an annealing oven for various periods of time at either of two temperatures i.e., 127°C. and 150°C. After heat treatment the apparent ΔH was determined. As is evident from the data in Table V, heating time and temperature are extremely important when studying an irregularly shaped high molecular weight sample.

TABLE V
Heats of Fusion of Annealed Polypropylene

Annealing at 150°C.		Annealing at 127°C.	
Annealing time, hr.	Obs. ΔH , cal./g.	Annealing time, hr.	Obs. ΔH , cal./g.
0	13	0	13
2	20.2	6	13
4	20.4	24	12.9
4	23.4	48	22.2
6	24.9	72	42.9
48	38.0	120 ^a	41.0
72	37.5		

^a Some discoloration apparent indicating incipient degradation.

The terminal values of 38.0, 37.5, 42.9 and 41.0 cal./g. are equivalent to an average value of 1670 cal./mole with $\sigma = 100$ cal./mole. This indicates a heat of fusion of 2500 cal./mole for 100% crystalline polypropylene, the 2σ limits being ± 300 cal./mole. The need for adequate and uniform sample distribution in the tube and for positive contact with the thermocouple, as well as the requirement of adequate and uniform annealing may thus explain the wide variation in ΔH_u values previously reported in the literature and shown in Table I. Actually the spread of values observed in Table V encompass practically all of the values shown in Table I, even though only one sample (albeit treated differently) was used.

Representative thermograms are shown in Figure 1. It is significant that, aside from an increase in the observed ΔH , the heat treatment raises the apparent melting temperature and narrows the range of melting. This behavior, noted in a Marlex polyethylene, has been commented upon previously.²¹ Thus the effects of the heat treating are complex and could

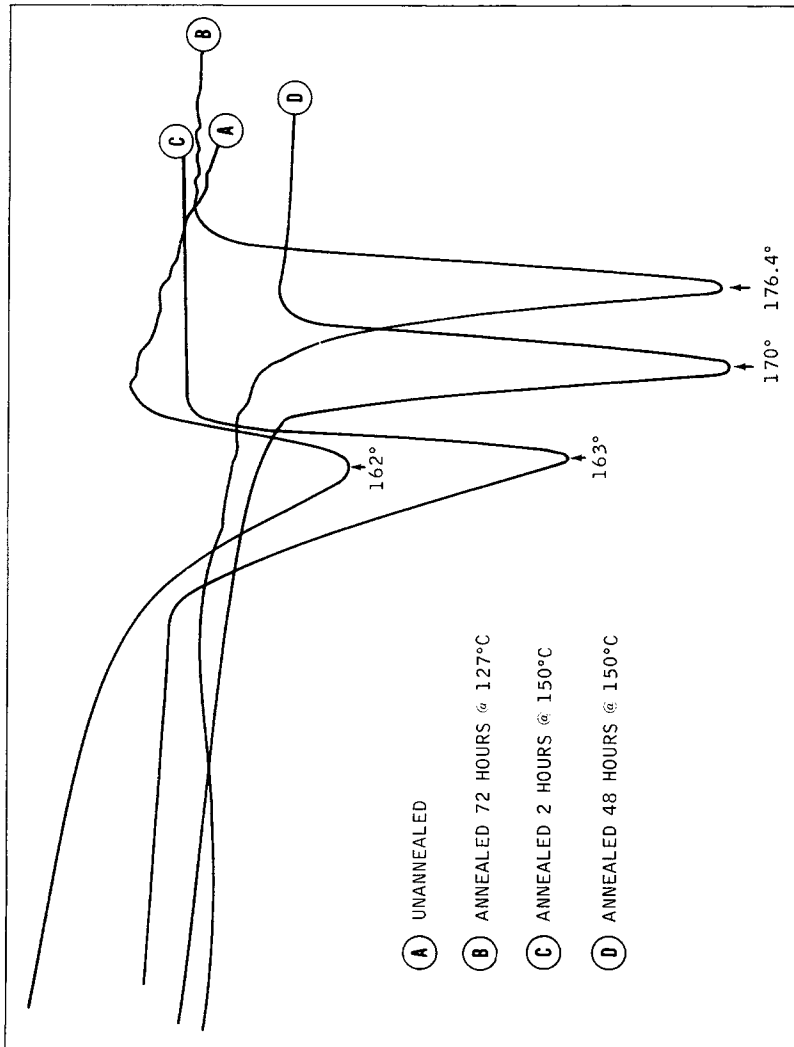


Fig. 1. Thermograms of annealed polypropylene.

reflect changes in overall crystallinity, in the crystallite size distribution, and in sample-sensor contact. The separation of the various effects is the subject of a continuing study in this laboratory. As noted previously, sample B had been extracted with *n*-heptane prior to analysis (100% heptane-insolubles) and consequently probably had a narrower molecular weight distribution than did the other samples. Both molecular weight and molecular weight distribution are important in determining crystallization kinetics.²²

In addition to the highly ordered crystalline component, there is a partially ordered paracrystalline or smectic component in semicrystalline polymers. This partially ordered component gives a rather diffuse x-ray diffraction pattern, from which contributions to both the crystalline and amorphous fractions are obtained by eq. (2). The paracrystalline polypropylene might also be expected to contribute to the fusion endotherm in DTA. It follows that errors thus introduced into the measurements for the crystalline fraction would be reduced by reducing the paracrystalline fraction. A convenient way of accomplishing this is by heat soaking below the melting point, preferably under conditions which reduce the paracrystallinity to a minimum. Furthermore, the errors introduced into the observed ΔH and the observed per cent crystallinity by the presence of paracrystallinity tend to compensate each other in the calculation of ΔH for 100% crystallinity. For the extensively heat-treated samples, the errors due to paracrystallinity have been assumed to be negligible.

Crystallization exotherms were also obtained for the samples described in Table V. The value of 2530 cal./mole ($2\sigma = 250$) calculated from these exotherms is in excellent agreement with the 2500 cal./mole obtained from the fusion endotherms.

The entropy of fusion of 100% "crystalline" polypropylene (ΔS_u) can be calculated from ΔH_u by means of the thermodynamic relationship

$$\Delta S_u = \Delta H_u / T_m$$

For an average value for ΔH_u of 2400 cal./mole, ΔS_u is 5.4 e.u. For comparison, the ΔS_u for poly-4-methyl-1-pentene is also about same.²³ In both cases ΔS_u per carbon is about 2.7 e.u. ($2\sigma = 0.3$ e.u.) as compared with a value of 2.3 e.u. for linear polyethylene.^{17,24}

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Résumé

Il existe de larges différences entre les diverses valeurs fournies par la littérature pour la chaleur de fusion, ΔH_u , du polypropylène isotactique. On a donc étudié par analyse différentielle thermique les variables qui influencent ΔH_u . Les résultats de cette étude montrent que, pour du polypropylène 100% cristallin ΔH_u vaut 2400 calories par mole d'unité de répétition avec $2\sigma = 300$. L'entropie de fusion est 5.4 u.e. par unité périodique ($2\sigma = 0.3$). On discute également l'histoire thermique, les erreurs possibles provenant du contact échantillon-élément sensible aussi bien que les incertitudes dans la détermination du pourcentage de cristallinité aux rayons-X.

Zusammenfassung

Zwischen den in der Literatur angegebenen Werten für die Schmelzwärme (ΔH_u) von isotaktischem Polypropylen existieren grosse Widersprüche. Es wurde daher eine Untersuchung der Variablen angestellt, die auf das durch Differentialthermoanalyse bestimmte ΔH_u Einfluss haben. Die Untersuchung ergibt ΔH_u für 100% "kristallines" Polypropylen zu 2400 Kalorien pro Mol Grundbaustein, mit $2\sigma = 300$. Die Schmelzentropie beträgt 5,4 e.u. pro Grundbaustein ($2\sigma = 0,3$). Thermische Vorgeschichte, mögliche Fehler beim thermischen Kontakt der Probe sowie Unsicherheiten der Röntgenanalyse für % Kristallinität werden diskutiert.

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