

# Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules

## IV. Polypropylene

Umesh Gaur and Bernhard Wunderlich

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. 12181*

The heat capacity of polypropylene from 0 K to 600 K is reviewed on the basis of measurements on 20 samples reported in the literature. The crystallinity dependence is critically evaluated and a set of recommended data for completely crystalline and amorphous polypropylene are derived. The effect of tacticity on the heat capacity is also evaluated. Entropy, enthalpy, and Gibbs energy functions are calculated. This paper is the fourth in a series of publications which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: Atactic; crystal; crystallinity; density; enthalpy; entropy; fusion; Gibbs energy; glass transition; heat capacity; isotactic; linear macromolecule; melt; polypropylene; syndiotactic.

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## 1. Introduction

This is the fourth paper in a series of discussions of heat capacities of linear macromolecules. In the preceding papers [1,2,3],<sup>2</sup> the heat capacities of selenium, polyethylene and a series of polyoxides were analyzed. In this paper the heat capacity of polypropylene, the simplest organic linear macromolecule with a side group has been critically analyzed. In subsequent publications, the analysis of heat capacities of groups of more complicated linear macromolecules will be reported.

## 2. Heat Capacity of Polypropylene

### 2.1. Introduction

Polypropylene derives from polyethylene by substituting a methyl group for a hydrogen atom on every second carbon atom. The repeating unit of polypropylene is  $\text{CH}_2\text{-CHCH}_3$ -(formula weight 42.08). The chemical structure is complicated by the possibility of stereo isomers of which the simplest are atactic, isotactic, and syndiotactic. Atactic polypropylene, which has random placement of the methyl groups on either of the two isomeric positions, has no crystallinity. Isotactic polypropylene, which has sterically identical placement of the methyl groups over long sequences, ideally over the whole molecule, is quite crystalline ( $w^c = 0.45\text{-}0.65$ ). Finally, syndiotactic polypropylene has sterically an alternating placement of methyl groups. It has a different crystal structure than the isotactic isomer. Samples with a crystallinity  $w^c = 0.2\text{-}0.5$  have been reported. All three stereochemical modifications of polypropylene have been analyzed for heat capacity.

The most common crystal structure of isotactic polypropylene is monoclinic (P2<sub>1</sub>/c). The molecular chains form a 2\*3/1 helix along the crystallographic *c*-axis. The unit cell contains 4 chains and 12 repeating units. The unit cell parameters have been determined by Turner-Jones *et al.* [4].

$$a = 0.666 \text{ nm} \quad b = 2.078 \text{ nm} \quad c = 0.649 \text{ nm} \quad \beta = 99.62^\circ$$

The crystalline density is  $0.946 \text{ Mg m}^{-3}$  at 298 K which corresponds to the packing fraction of 0.66 [5].

Syndiotactic polypropylene has successive repeating units of isomorphous, anticlinal configuration [5]. The crystal structure is orthorhombic, of space group C22<sub>2</sub>. The helix axes (4\*2/1) coincide with the twofold screw axes. The unit cell parameters have been determined by Natta [6].

$$a = 1.450 \text{ nm} \quad b = 0.560 \text{ nm} \quad c = 0.740 \text{ nm}$$

The crystalline density is  $0.930 \text{ Mg m}^{-3}$  at 298 K which corresponds to a packing fraction of 0.65 [5].

The density of amorphous, isotactic polypropylene has been established by Wilski [7] to be  $0.8554 \text{ Mg m}^{-3}$  (packing fraction 0.60). The density of amorphous, syndiotactic polypropylene has been reported by Danusso *et al.* [8] to be  $0.858 \text{ Mg m}^{-3}$  (packing fraction 0.60). For atactic polypropylene Wilski [7] has reported a value of  $0.8554 \text{ Mg m}^{-3}$  for the density of an x-ray amorphous sample, which is the same as the density of isotactic amorphous polypropylene.

The equilibrium melting temperature of isotactic polypropylene is still somewhat uncertain. Extrapolated melting temperatures from 455 to 493 K have been reported. The best esti-

mate of equilibrium melting temperature is 460.7 K [5]. Heats of fusion of isotactic polypropylene from 2.7 to  $10.9 \text{ kJ mol}^{-1}$  have been reported. An average value of  $6.94 \pm 0.76 \text{ kJ mol}^{-1}$  has been derived from more reliable direct calorimetric measurements [5]. An estimate of the equilibrium heat of fusion of  $4.4 \text{ kJ mol}^{-1}$  for syndiotactic polypropylene has been reported by Gee and Melia [16].

The average value of the glass transition temperature for atactic, isotactic, and syndiotactic polypropylene have been reported to be 260 K, 265 K, and 265 K, respectively [9]. In this work 260 K has been used as the glass transition temperature for amorphous polypropylene.

### 2.2. Literature Data of the Heat Capacity of Polypropylene

Twenty five investigations of the heat capacity of isotactic, syndiotactic, and atactic polypropylene have been reported in the literature. Heat capacity of thirtyfour samples of various crystallinities have been measured over a wide range of temperature.

All investigations were critically evaluated in terms of sample characterization, experimental technique used, error limits, and accuracy of representation of data. It was found that only 11 of the 25 investigations met our standards of acceptable data (discussed in ref. [1]). These investigations are listed in table 1. These contain heat capacity data on 20 samples of isotactic, syndiotactic, and atactic polypropylene. These samples cover a broad range of crystallinity from 0.1 to 0.65. Fourteen investigations which did not contain acceptable data were not included in further analyses. These are listed in table 2, along with brief comments on the reasons for exclusion from this study.

Table 1 lists, chronologically, all the investigations from which data were retrieved. Each sample has been given a number, which is in accordance with the file numbers of our data bank. The temperature region over which the determination of heat capacity was carried out is given in kelvins. The experimental technique used by the investigators and their claimed experimental uncertainties are listed. A review of various experimental techniques used for measuring heat capacities of linear macromolecules was given in reference [1]. Sources of data (tables, graphs or curve fitted functions) are also listed. If the data were in tabular form, but not in temperature intervals desired by us, (0.1 K intervals below 1 K, to 10 K intervals at higher temperatures), the data were interpolated. The spline function technique (discussed in ref. [1]) was used to determine the interpolated heat capacity values at desired temperatures.

Characterization of the samples is also given in table 1. Commercial names and origin of the sample are given. Molecular weight and brief thermal history of the sample, if reported by the investigators, is also listed. Key characterization parameter useful for our analysis is the crystallinity of the samples. If the density at 298 K was reported, the weight fraction crystallinity was recalculated as

$$w^c = \left( \frac{\rho_c}{\rho} \right) \left( \frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \quad (1)$$

where  $\rho$ ,  $\rho_c$  and  $\rho_a$  are densities of the semicrystalline, completely crystalline, and completely amorphous states, respectively. X-ray crystallinities of  $0.16 \pm 0.04$  and  $0.46$  have been

<sup>2</sup>Numbers in brackets refer to literature references in section 5.

reported for atactic (sample 9) and isotactic (sample 11) polypropylenes, respectively. These x-ray crystallinities differ considerably from weight fraction crystallinities reported for other samples. The data on these samples also showed significant deviations from other samples in crystallinity extrapolations (discussed in Sec. 2.3) when x-ray crystallinities were used. Since the data on these samples are quite good and are the only data sets available from 10 to 80 K, their crystallinities were reevaluated. A crystallinity of 0.1 was estimated for the atactic sample 9 which is similar to sample 34 in its atactic content. A crystallinity of 0.65 was estimated for the isotactic sample 11. The average of crystallinities of isotactic samples 6, 13, 21, 28, 29, and 50 is 0.65.

The heat capacity data on various polypropylene samples retrieved from the literature are given in tables A1 to A6. Tables A1 to A6 have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. The data below the glass transition temperature on various samples are given in table A1. The data between the glass transition and melting temperatures for isotactic and syndiotactic polypropylene samples are given in tables A2 and A3, respectively. The heat capacity data for molten isotactic and syndiotactic polypropylene are listed in table A4. The data for atactic polypropylene above the glass transition temperature are given in table A5. Finally, table A6 contains low temperature data for one sample of isotactic polypropylene. Since only one set of data is available for polypropylene below 5 K, no further analysis of heat capacity values below 5 K was made.

### 2.3. Recommended Data on Heat Capacity of Amorphous, Crystalline, and Molten Polypropylene

To determine the heat capacity of the completely crystalline and the completely amorphous polypropylene (referred to hereafter as crystalline and amorphous polypropylene), the data on various atactic, isotactic, and syndiotactic polypropylene were plotted as a function of crystallinity ( $w^c$ ) at each temperature between 10 and 350 K and curve fitted into the two phase model equation

$$C_p = w^c C_p^c + (1 - w^c) C_p^a \quad (2)$$

where  $C_p^c$  and  $C_p^a$  are the heat capacity of crystalline and amorphous polypropylene. In the preliminary plotting, all atactic, isotactic, and syndiotactic samples fell on a straight line with the exception of data on atactic samples above the glass transition. The data on atactic samples were higher than the isotactic and syndiotactic samples. This observation indicates that the two phase model for linear extrapolation is not applicable to atactic samples above the glass transition. This is probably because remaining crystallinity of the atactic samples begins to melt above the glass transition and the heat capacity data have a heat of fusion associated with it.

The heat capacity data were then replotted excluding atactic samples above  $T_g$ . The results of the extrapolations are shown in table 3 and selected plots are shown in figure 1. The extrapolated data are plotted in figure 2. Also listed in table 3 are the RMS deviation at each temperature and the sample number for which data were excluded. All samples excluded showed

large deviations from the curve fitted line. The excluded points fall generally in the temperature region where the performance of the particular calorimetry is of limited accuracy. Sample 21 does not fit the extrapolations over the entire range. Its deviations are probably due to erroneous presentation of the data in the literature (data on sample 20 of the same publication fit quite well).

The heat capacity of crystalline polypropylene obtained from crystallinity extrapolations were further smoothed as follows: Heat capacity values from 10 to 100 K were curve fitted into the equation

$$C_p = \exp [0.241028 (\ln T)^3 - 3.01364 (\ln T)^2 + 13.5529 (\ln T) - 18.7621] \text{ J mol}^{-1} \text{ K}^{-1} \quad (3)$$

The RMS deviation was 0.4%. Data from 80 to 250 K were curve fitted into the equation

$$C_p = \exp [0.121683 (\ln T)^3 - 1.90162 (\ln T)^2 + 10.727 (\ln T) - 17.6875] \text{ J mol}^{-1} \text{ K}^{-1} \quad (4)$$

The RMS deviation was 0.8%. The data from 230 to 350 K were curve fitted into the equation

$$C_p = 1.5912 \cdot 10^6 T^{-2} + 0.3837 T - 64.551 \text{ J mol}^{-1} \text{ K}^{-1} \quad (5)$$

The RMS deviation of the data from eq. (5) was 1.7%. The smoothed values from 10 to 90 K, obtained from eq. (1), from 100 to 230 K, obtained from eq (4) and from 240 to 350 K obtained from eq (5) are given in table 4.

The heat capacity values for crystalline polypropylene in the temperature region from 350 K to the melting temperature (460.7 K) were obtained using the eq (5). The plot of eq (5) from 350 to 460.7 K is shown in figure 2. This was compared to the data of crystalline polyethylene, which also shows an inverse quadratic upward increase at temperatures close to the melting. The upward increase for polypropylene starts at somewhat lower temperature than for polyethylene. The upward increase is mainly due to the C-H bending vibrations. The increase starts at lower temperature in case of polypropylene due to C-CH<sub>3</sub> rotation, stretching and bending vibrations, which begin to get excited at lower temperature.

The heat capacity of amorphous polypropylene obtained from the crystallinity extrapolations below the glass transition temperature were further smoothed as follows: Heat capacity values from 10 to 60 K were curve fitted into the equation

$$C_p = \exp [0.327068 (\ln T)^3 - 3.688 (\ln T)^2 + 14.7469 (\ln T) - 18.4281] \text{ J mol}^{-1} \text{ K}^{-1} \quad (6)$$

The RMS deviation was 1.0%. Data from 50 to 180 K were curve fitted into the equation

$$C_p = \exp [7.42669 \cdot 10^{-3} (\ln T)^3 - 0.189318 (\ln T)^2 + 2.10843 (\ln T) - 3.06991] \text{ J mol}^{-1} \text{ K}^{-1} \quad (7)$$

The RMS deviation was 0.7%. Data from 160 to 260 K were curve fitted into the equation

$$C_p = \exp [7.27139 \cdot 10^{-2} (\ln T)^3 - 0.711627 (\ln T)^2 + 2.31907 (\ln T) + 0.77926] \text{ J mol}^{-1} \text{ K}^{-1} \quad (8)$$

The RMS deviation was 1.1%. The smoothed values from 10 to 60 K, obtained from eq (6), from 70 to 170 K, obtained from eq (7), from 180 K to 260 K and from eq (8) are given in table 5.

Table 1. Heat capacity measurements of polypropylene

Investigator	Sample no. characterization	Temperature range(K)	Experimental technique (claimed uncertainty)	Source of data <sup>a</sup>
Wilkinson and Dole (1962) [11]	29. Isotactic $\bar{M}_V=640,000$ $\rho=0.9100 \text{ Mg m}^{-3}$ $w^C=0.63$	240-480	Adiabatic (1%)	240-370 K : Equation(1) 450-480 K : Table <sup>b</sup>
	34. Atactic $\bar{M}_V=22,000$ $\rho=0.8667 \text{ Mg m}^{-3}$ $w^C=0.1$	220-480	Adiabatic (1%)	220-240 K : Table <sup>b</sup> 270-300 K : Equation(2) 450-480 K : Equation(3)
Dainton, Evans, Hoare and Melia (1962) [12]	9. Atactic 57% atactic content(IR) $w^C=0.1^d$	22-310	Adiabatic (1%)	Table
	11. Isotactic $w^C=0.65^d$	22-310	Adiabatic (1%)	Table
Hellwege, Knappe and Wetzel (1962) [13]	28. Isotactic Average data for two commercial samples Hostalen PPH $\rho=0.912 \text{ Mg m}^{-3}$ Hostalen PPH $\rho=0.910 \text{ Mg m}^{-3}$ $w^C=0.64$ (Farbw. Hoechst)	310-390	Adiabatic (1%)	Graph
Passaglia and Kevorkian (1963) [26]	3. Atactic $\bar{M}_V=15,700$ $\rho=0.8562 \text{ Mg m}^{-3}$ $w^C=0.03$	90-480	Adiabatic (0.5%)	Table <sup>b</sup>
	6. Isotactic $\bar{M}_V=140,000$ $\Delta H_f=5.26 \text{ kJ mol}^{-1}$ $w^C=0.66$	90-490	Adiabatic (0.5%)	Table <sup>b</sup>
Slonimskii and Godovskii (1965) [14]	24. Isotactic Average of eight samples $\rho=0.908 \pm 0.001 \text{ Mg m}^{-3}$ $\Delta H_f=3.87 \text{ kJ mol}^{-1}$ $w^C=0.60$	290-510	Unreported	290-380 K : Equation(4) 460-510 K : Equation(5)
Gee and Melia (1968) [15]	40. Syndiotactic Annealed at 405 K for 72 h. Syndioindex=2.85 $\bar{M}_V=8,900$ $\rho=0.889 \text{ Mg m}^{-3}$ $\Delta H_f=2.85 \text{ kJ mol}^{-1}$ $w^C=0.45$	180-460	DSC (2%)	180-260 K : Equation(6) 280-320 K : Graph 430-460 K : Table
Gee and Melia (1969) [16]	41. Syndiotactic Annealed at 408 K for 2 h. Syndioindex=1.8 $\bar{M}_V=31,200$ $\rho=0.875 \text{ Mg m}^{-3}$ $\Delta H_f=1.13 \text{ kJ mol}^{-1}$ $w^C=0.25$	180-450	DSC (2%)	180-260 K : Equation(6) 270-350 K : Graph 420-450 K : Equation(7)

Table 1. Heat capacity measurements of polypropylene--Continued

Investigator	Sample no. characterization	Temperature range(K)	Experimental technique (claimed uncertainty)	Source of data <sup>a</sup>
	42. Syndiotactic Annealed at 408 K for 2 h Syndioindex=2.0 $\bar{M}_v=28,800$ $\rho=0.879 \text{ Mg m}^{-3}$ $\Delta H_f=1.58 \text{ kJ mol}^{-1}$ $w^c=0.31$	180-450	DSC (2%)	180-260 K : Equation(6) 280-330 K : Graph 420-450 K : Equation(7)
	43. Syndiotactic Annealed at 408 K for 2 h Syndioindex=2.3 $\bar{M}_v=23,400$ $\rho=0.883 \text{ Mg m}^{-3}$ $\Delta H_f=1.76 \text{ kJ mol}^{-1}$ $w^c=0.37$	180-450	DSC (2%)	180-260 K : Equation(6) 280-350 K : Graph 420-450 K : Equation(7)
	44. Syndiotactic Annealed at 408 K for 2 h. Syndioindex=2.7 $\bar{M}_v=20,000$ $\rho=0.887 \text{ Mg m}^{-3}$ $\Delta H_f=2.01 \text{ kJ mol}^{-1}$ $w^c=0.42$	180-450	DSC (2%)	180-260 K : Equation(6) 280-230 K : Graph 420-450 K : Equation(7)
Gee and Melia (1970) [17]	20. Isotactic Melt cryst. $w^c=0.5$	200-500	DSC (2%)	200-260 K : Equation(8) 290-380 K : Graph 450-500 K : Equation(9)
	21. Isotactic Solution cryst. $\rho=0.912 \text{ Mg m}^{-3}$ $\Delta H_f=6.65 \text{ kJ mol}^{-1}$ $w^c=0.65$	200-500	DSC (2%)	200-260 K : Equation(10) 290-380 K : Graph 450-500 K : Equation(9)
Smit (1972) [18]	15. Isotactic <sup>c</sup> Granular $w^c=0.41$	190-570	DSC (1%)	190-310 K : Graph 460-570 K : Equation(11)
	13. Isotactic shear cryst. $w^c=0.67$	190-570	DSC (1%)	190-310 K : Graph 460-570 K : Equation(11)
Bares and Wunderlich (1973) [19]	26. Atactic $\bar{M}_n=15,000$ $\rho=0.867 \text{ Mg m}^{-3}$	320-390	DSC (1%)	Table
	27. Isotactic Profax (Hercules Co.)	450-600	DSC (1%)	Table
Salinger and Cordell (un- published) [20]	50. Isotactic $\rho=0.912 \text{ Mg m}^{-3}$ $w^c=0.65$	0.5-4.0	Heat pulse (unreported)	Equation(12)

<sup>a</sup>Equations cited as sources of data are tabulated separately in table 1a.

<sup>b</sup>Data interpolated using the spline function technique to give heat capacities at every ten degree intervals.

<sup>c</sup>Several small endothermic melt transitions analogous to the ones in liquid crystals have been reported. The transitions fall just outside the limits of the measurement. The data was averaged over these transitions.

<sup>d</sup>Crystallinity values have been estimated. The estimates are just outside the error limits of X-ray crystallinity reported by the authors (see text).

Table 1a. Source of data<sup>a</sup>

Equation (1)	$C_p = -0.3669 + 0.00242t(^{\circ}\text{C})$ (RMS=0.7%) <sup>b</sup>	cal g <sup>-1</sup> K <sup>-1</sup>
Equation (2)	$C_p = 0.51 + 0.00207t(^{\circ}\text{C})$ (RMS=1%) <sup>b</sup>	cal g <sup>-1</sup> K <sup>-1</sup>
Equation (3)	$C_p = 0.648 + 0.004t(^{\circ}\text{C})$ (RMS=1%) <sup>b</sup>	cal g <sup>-1</sup> K <sup>-1</sup>
Equation (4)	$C_p = 0.36 + 0.0023t(^{\circ}\text{C})$ <sup>b</sup>	cal g <sup>-1</sup> K <sup>-1</sup>
Equation (5)	$C_p = 0.3688 + 0.00141t(^{\circ}\text{C})$ <sup>b</sup>	cal g <sup>-1</sup> K <sup>-1</sup>
Equation (6)	$C_p = 0.235 + 0.00476t$ <sup>b</sup>	J g <sup>-1</sup> K <sup>-1</sup>
Equation (7)	$C_p = 1.220 + 0.0034T$ <sup>b</sup>	J g <sup>-1</sup> K <sup>-1</sup>
Equation (8)	$C_p = 0.128 + 0.00509T$ <sup>b</sup>	J g <sup>-1</sup> K <sup>-1</sup>
Equation (9)	$C_p = 1.24 + 0.00304T$ <sup>b</sup>	J g <sup>-1</sup> K <sup>-1</sup>
Equation (10)	$C_p = 0.284 + 0.00423T$ <sup>b</sup>	J g <sup>-1</sup> K <sup>-1</sup>
Equation (11)	$C_p = 50.974 + 0.1372T$ (RMS dev. = 1%) <sup>c</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
Equation (12)	$C_p = \exp[-0.130693(\ln T)^3 + 0.249189(\ln T)^2 + 0.0816695(\ln T) + 5.41896]T^3$ (RMS dev. = 4.4%) <sup>d</sup>	erg g <sup>-1</sup> K <sup>-1</sup>

<sup>a</sup>Equation numbers correspond to the equations in table 1.

<sup>b</sup>Equation reported by the authors.

<sup>c</sup>Authors graphical data was curve fitted into the equation.

<sup>d</sup>Authors tabulated data was curve fitted into the equation.

Table 2. Investigations not included in this study

Reference	Reason(s) for exclusion
Mikhailov, Fainberg, and Gorbacheva (1959) [21]	Only single values of heat capacities reported for heptane extracted fractions
Wilski (1960,1966) [22,23]	Average heat capacities determined with a drop calorimeter have been reported.
Tautz, Glück, Hartmann and Leuteritz (1963,1964) [24,25]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Steere (1966) [27]	Heat capacities per unit volume have been reported. These values are not directly comparable to the data presented here.
Arutyunov and Bil (1966) [28]	Heat capacity reported in the melting region at various pressures (1-680 bar). Values are somewhat higher than the values reported here.
Dragan (1971) [30]	Data reported in arbitrary units
Gul, Penskaya, Zanemonets and Zanina (1972) [29]	Data reported in the melting region only. Values could not be read accurately from too small graphs.
Park and Uhlmann (1973) [32]	Large deviations from data reported here.
Frazer, Whitwell, and Miller (1974) [33]	Heat capacity measurements have been reported on uncharacterized polypropylene monofilaments. Data could not be read accurately from too small graphs.
Bashirov, et al. (1975, 1976) [34,35]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Anderson and Sundquist (1975) [31]	Pressure dependence of heat capacity of polypropylene was determined from simultaneous measurements of thermal conductivity and diffusivity at 300 K in the pressure range 0-25 k bar. $C_p(25 \text{ kbar})/C_p(0)$ is 0.93 and 0.86 for isotactic and atactic polypropylene.

The crystallinity extrapolated heat capacity values of amorphous polypropylene show a sharp increase from 260 to 280 K. This is followed by a small linear portion from 280 to 300 K. Beyond 300 K the extrapolated data shows a large upward slope. The sharp increase from 260 to 280 K is due to the glass transition. The large upward slope above 300 K is not a heat capacity effect, but caused by contributions from changes in crystallinity. Thus, only the extrapolated amorphous heat capacity values from 280 to 300 K represent the true heat capacity of molten polypropylene.

To determine the recommended heat capacity data for molten polypropylene, the data of all samples were plotted. Agreement between samples from various laboratories was very good with the exception of samples 34 and 26. These two atactic samples show larger deviations than the error limits. Both samples were taken from the same batch and were thus not included in further analysis. Heat capacity data on samples 3, 6, 13, 15,

20, 21, 24, 27, 29, and 40-44 were averaged at each temperature from 420 to 600 K. The averaged data from 420 to 600 K and the amorphous data from 280 to 300 K obtained from crystallinity extrapolations was curve fitted into the equation

$$C_p = 0.151291 T + 42.956 \text{ J mol}^{-1}\text{K}^{-1} \quad (9)$$

The RMS deviation was 2.5%. The curve fitted equation and the data are plotted in figure 3. Equation (9) was used to calculate the heat capacity of molten polypropylene from 260 to 600 K. These values are listed in table 5. The difference in the heat capacity between the extrapolated melt value and the crystalline heat capacity at the glass transition is  $23.54 \text{ J mol}^{-1}\text{K}^{-1}$ . According to Wunderlich's rule [10] of constant heat capacity change at  $T_g$  ( $\Delta C_p$ /mole of beads =  $11.3 \text{ J g}^{-1}\text{K}^{-1}$ ), this corresponds to two beads.

Table 3. Heat capacity vs. crystallinity: Results of curve fitting data into the equation  $C_p = w^c \cdot C_p(\text{cryst.}) + (1-w^c)C_p(\text{am.})$

T(K)	$C_p(\text{cryst.})$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	$C_p(\text{am.})$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	RMS (%)	Samples not included
10	0.5543	1.075		
20	3.554	5.122		
30	7.120	8.574		
40	10.20	11.94		
50	13.00	15.22		
60	15.67	18.21		
70	18.24	21.02		
80	20.83	23.71		
90	23.80	25.67	1.4	
100	26.51	28.21	1.2	
110	28.59	31.16	0.4	
120	30.94	33.07	0.9	
130	33.16	35.39	0.8	
140	35.37	37.73	0.7	
150	37.68	39.53	1.1	
160	39.41	41.38	1.2	
170	42.26	43.09	1.6	
180	43.31	45.48	1.0	40-44
190	45.47	47.40	0.9	13,15,40-44
200	47.47	50.53	1.3	13,15,21
210	49.30	52.58	1.1	3,13,15,21
220	52.33	53.84	1.1	3,13,21
230	54.08	55.84	0.9	3,13,15,21
240	55.75	58.62	0.6	3,13,15,21, 24
250	56.53	61.05	0.5	13,15,21,24
260	55.63	66.01	0.8	13,15,21
270	59.61	75.01	1.7	
280	61.57	82.00	2.0	
290	64.90	83.76	2.6	
300	70.39	84.11	2.5	21
310	73.03	87.49	2.5	21
320	74.03	92.88	2.1	21
330	76.38	98.30	2.4	21
340	79.11	103.3	3.2	21
350	82.12	109.2	3.1	21

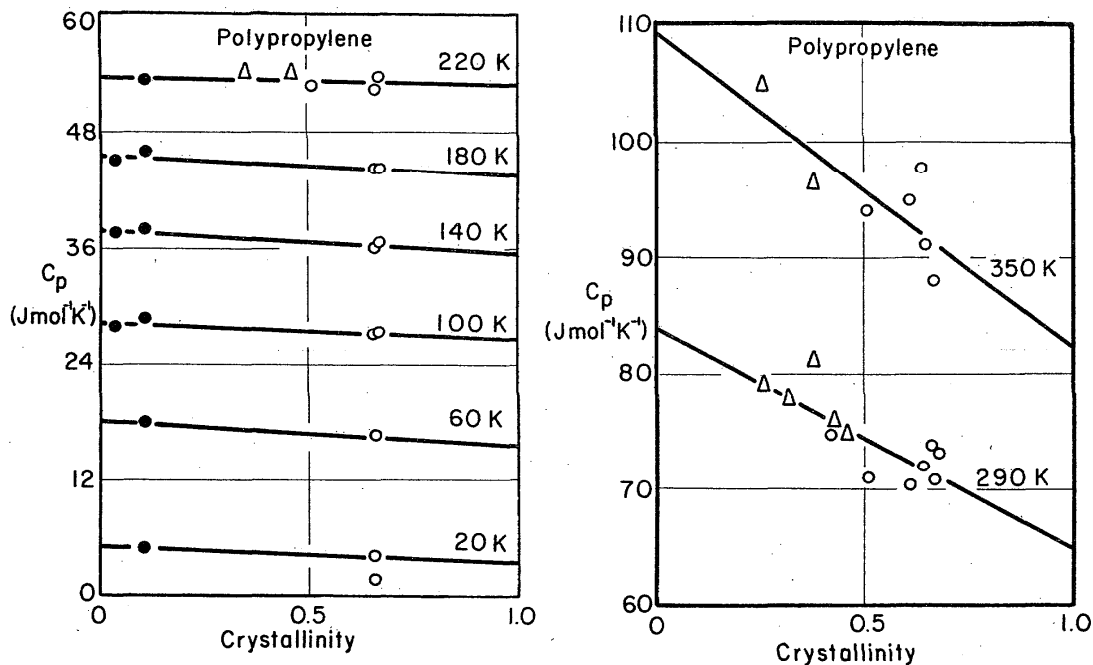


FIGURE 1. Heat capacity of polypropylene as a function of crystallinity at various temperatures, open circles: Isotactic polypropylene filled circles: Atactic polypropylene, triangles: Syndiotactic polypropylene.

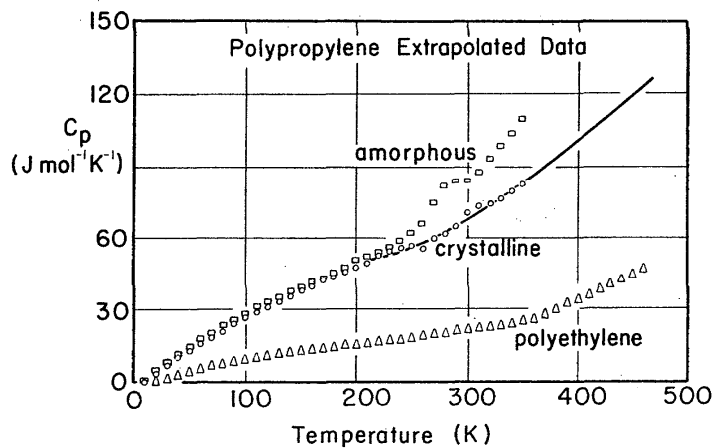


FIGURE 2. Crystallinity extrapolated heat capacity of amorphous and crystalline polypropylene. The drawn-out curve represents the best estimate for the heat capacity of crystalline polypropylene between  $T_c$  and  $T_m$ . The increase is similar to the heat capacity increase of crystalline polyethylene also shown in the figure.



Table 4. Recommended thermodynamic data of crystalline polypropylene<sup>a</sup>

T(K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H_T^C - H_0^C$ (J mol <sup>-1</sup> )	$S_T^C$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$-(G_T^C - H_0^C)$ (J mol <sup>-1</sup> )
0.0	0.0	0.0	0.0	0.0
10.0	0.5538	1.099	0.1342	0.2419
20.0	3.572	20.43	1.354	6.638
30.0	7.065	73.81	3.470	30.28
40.0	10.20	160.5	5.942	77.18
50.0	13.02	276.8	8.526	149.4
60.0	15.67	420.3	11.14	247.7
70.0	18.27	590.0	13.75	372.2
80.0	20.90	785.8	16.36	522.7
90.0	23.65	1008.	18.98	699.3
100.0	26.25	1258.	21.60	902.2
110.0	28.69	1532.	24.22	1131.
120.0	31.03	1831.	26.82	1386.
130.0	33.28	2153.	29.39	1667.
140.0	35.45	2496.	31.94	1974.
150.0	37.57	2862.	34.46	2306.
160.0	39.64	3248.	36.95	2663.
170.0	41.68	3654.	39.41	3045.
180.0	43.68	4081.	41.85	3451.
190.0	45.66	4528.	44.27	3882.
200.0	47.63	4994.	46.66	4336.
210.0	49.59	5481.	49.03	4815.

Table 4. Recommended thermodynamic data of crystalline polypropylene<sup>a</sup>--Continued

T(K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H_T^C - H_O^C$ (J mol <sup>-1</sup> )	$S_T^C$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$-(G_T^C - H_O^C)$ (J mol <sup>-1</sup> )
220.0	51.54	5986.	51.38	5317.
230.0	53.50	6511.	53.72	5842.
240.0	55.16	7056.	56.03	6391.
250.0	56.83	7616.	58.32	6963.
260.0	58.75	8193.	60.58	7557.
270.0	60.87	8791.	62.84	8175.
273.15	61.59	8987.	63.56	8377.
280.0	63.18	9411.	65.09	8814.
290.0	65.64	10055.	67.35	9477.
298.15	67.76	10602.	69.21	10036.
300.0	68.24	10725.	69.62	10161.
310.0	70.95	11420.	71.90	10869.
320.0	73.77	12144.	74.20	11600.
330.0	76.68	12896.	76.52	12353.
340.0	79.67	13678.	78.85	13130.
350.0	82.73	14490.	81.20	13930.
360.0	85.86	15333.	83.58	14754.
370.0	89.04	16207.	85.97	15602.
380.0	92.27	17114.	88.39	16474.
390.0	95.55	18053.	90.83	17370.
400.0	98.87	19025.	93.29	18290.
410.0	102.2	20030.	95.77	19236.
420.0	105.6	21069.	98.28	20206.
430.0	109.0	22143.	100.8	21201.
440.0	112.5	23250.	103.4	22222.
450.0	116.0	24393.	105.9	23268.
460.0	119.5	25570.	108.5	24340.
460.7	119.7	25654.	108.7	24416.

<sup>a</sup>The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

## 3. Thermodynamic Functions

Thermodynamic functions for amorphous and crystalline polypropylene have been derived from the heat capacities. These are listed in tables 4 and 5.  $H_0$  and  $S_0$  refer to zero point enthalpy and residual entropy of the polymer. Details of the integrations have been reported earlier in reference [1].

At 0 K the residual amorphous entropy was found to be  $1.89 \text{ J mol}^{-1}\text{K}^{-1}$ . A value of  $2.59 \text{ J (mol of CH}_2\text{)}^{-1}\text{K}^{-1}$  was reported earlier for polyethylene [2]. Note that amorphous polypropylene shows a much lower residual entropy at 0 K than polyethylene ( $1.89$  for  $\text{CH}_2\text{CH (CH}_3\text{)}$ ) as compared to  $5.18$  for  $\text{CH}_2\text{CH}_2$ ).

Table 5. Recommended thermodynamic data of amorphous polypropylene<sup>a</sup>

T(K)	$C_p$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	$H_T^a - H_0^a$ ( $\text{J mol}^{-1}$ )	$S_T^a - S_0^a$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	$H_T^a - H_0^c$ ( $\text{J mol}^{-1}$ )	$S_T^a$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	$-(G_T^a - H_0^c)$ ( $\text{J mol}^{-1}$ )
0.0	0.0	0.0	0.0	4239.	1.89	-4239.
10.0	1.076	2.311	0.2848	4241.	2.18	-4219.
20.0	5.077	32.62	2.225	4271.	4.12	-4189.
30.0	8.721	102.1	4.995	4341.	6.89	-4134.
40.0	11.89	205.4	7.945	4444.	9.84	-4051.
50.0	15.01	339.8	10.93	4578.	12.82	-3937.
60.0	18.36	506.4	13.96	4745.	15.85	-3794.
70.0	20.91	701.8	16.97	4940.	18.86	-3620.
80.0	23.54	924.2	19.93	5163.	21.82	-3417.
90.0	26.07	1172.	22.85	5411.	24.74	-3184.
100.0	28.51	1445.	25.72	5684.	27.62	-2922.
110.0	30.85	1742.	28.55	5981.	30.44	-2632.
120.0	33.11	2062.	31.33	6301.	33.22	-2314.
130.0	35.30	2404.	34.07	6643.	35.96	-1968.
140.0	37.42	2767.	36.77	7006.	38.66	-1595.
150.0	39.48	3152.	39.42	7391.	41.31	-1195.
160.0	41.48	3557.	42.03	7796.	43.92	-768.9
170.0	43.43	3981.	44.60	8220.	46.49	-316.8
180.0	45.35	4425.	47.14	8664.	49.03	160.7
190.0	47.44	4889.	49.65	9128.	51.54	663.6
200.0	49.63	5374.	52.13	9613.	54.03	1191.
210.0	51.92	5882.	54.61	10121.	56.50	1744.
220.0	54.31	6413.	57.08	10652.	58.97	2321.
230.0	56.80	6968.	59.55	11207.	61.44	2923.
240.0	59.40	7549.	62.02	11788.	63.91	3550.
250.0	62.10	8157.	64.50	12396.	66.39	4201.
260.0(T <sub>g</sub> )	64.92	8792.	66.99	13031.	68.88	4878.
260.0	82.29	8792.	66.99	13031.	68.88	4878.
270.0	83.80	9622.	70.13	13861.	72.02	5582.
273.15	84.29	9891.	71.12	14130.	73.01	5814.
280.0	85.32	10468.	73.20	14707.	75.09	6318.

Table 5. Recommended data of amorphous polypropylene --Continued

T(K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H_T^a - H_O^a$ (J mol <sup>-1</sup> )	$S_T^a - S_O^a$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H_T^a - H_O^c$ (J mol <sup>-1</sup> )	$S_T^a$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$-(G_T^a - H_O^c)$ (J mol <sup>-1</sup> )
290.0	86.83	11328.	76.22	15568.	78.11	7084.
298.15	88.07	12046.	78.66	16285.	80.55	7734.
300.0	88.34	12204.	79.19	16443.	81.08	7880.
310.0	89.86	13095.	82.11	17334.	84.00	8705.
320.0	91.37	14001.	84.99	18240.	86.88	9560.
330.0	92.88	14923.	87.82	19162.	89.71	10443.
340.0	94.39	15859.	90.62	20098.	92.51	11354.
350.0	95.91	16811.	93.38	21050.	95.27	12293.
360.0	97.42	17777.	96.10	22016.	97.99	13259.
370.0	98.93	18759.	98.79	22998.	100.7	14252.
380.0	100.5	19756.	101.5	23995.	103.3	15273.
390.0	102.0	20768.	104.1	25007.	106.0	16319.
400.0	103.5	21795.	106.7	26034.	108.6	17392.
410.0	105.0	22837.	109.3	27076.	111.1	18490.
420.0	106.5	23895.	111.8	28134.	113.7	19615.
430.0	108.0	24967.	114.3	29206.	116.2	20764.
440.0	109.5	26055.	116.8	30294.	118.7	21939.
450.0	111.0	27158.	119.3	31397.	121.2	23138.
460.0	112.6	28276.	121.8	32515.	123.7	24362.
460.7	112.7	28355.	121.9	32594.	123.8	24416.
470.0	114.1	29409.	124.2	33648.	126.1	25611.
480.0	115.6	30557.	126.6	34796.	128.5	26884.
490.0	117.1	31720.	129.0	35959.	130.9	28181.
500.0	118.6	32899.	131.4	37138.	133.3	29502.
510.0	120.1	34092.	133.8	38331.	135.7	30847.
520.0	121.6	35301.	136.1	39540.	138.0	32215.
530.0	123.1	36525.	138.4	40764.	140.3	33607.
540.0	124.7	37764.	140.8	42003.	142.6	35021.
550.0	126.2	39018.	143.1	43257.	144.9	36459.
560.0	127.7	40287.	145.3	44526.	147.2	37920.
570.0	129.2	41572.	147.6	45811.	149.5	39404.
580.0	130.7	42871.	149.9	47110.	151.8	40910.
590.0	132.2	44186.	152.1	48425.	154.0	42439.
600.0	133.7	45515.	154.4	49754.	156.2	43990.

<sup>a</sup>The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

#### 4. Conclusions

The heat capacity of polypropylene from 0 to 600 K has been reviewed on the basis of 20 measurements reported in the literature. The crystallinity dependence has been critically evaluated and a set of recommended heat capacity, enthalpy, entropy, and Gibbs energy data for completely crystalline and amorphous polypropylene have been derived. In addition, we have arrived at the following conclusions.

1. The heat capacity of crystalline polypropylene is a smooth function of temperature from 0 to 280 K. The steeper slope above 280 K increases the heat capacity of the crystalline polypropylene to that of the amorphous polypropylene at about 430 K. The heat capacity of amorphous polypropylene is also a smooth function of temperature from 0 to 230 K. The increasing slope above 230 K can be associated with the glass transition. The heat capacity of molten polypropylene is a linear function of temperature to 600 K.

2. Up to temperatures close to melting, the heat capacity of amorphous polypropylene is higher than the heat capacity of

crystalline polypropylene. Differences are, however, less than 5% over the temperature range of 150 to 200 K.

3. The two phase model for linear extrapolation of heat capacities is applicable to isotactic, atactic and syndiotactic polypropylene below the glass transition (260 K). However, above the glass transition the model is not applicable to atactic polypropylene. Beyond 310 K, the heat capacity of amorphous polypropylene obtained from linear extrapolations have to be corrected for changes in crystallinity with temperature.

4. The change in heat capacity at the glass transition fits the rule of constant  $\Delta C_p$ .

5. At 0 K the residual amorphous entropy is  $1.89 \text{ J mol}^{-1} \text{ K}^{-1}$ .

6. The change in tacticity influences mainly the crystallinity of the sample and this, in turn, changes the heat capacity. However, the change in heat capacity is in agreement with the change of crystallinity. This seems to indicate that the change from the helical crystal structure in isotactic polypropylene to a planar zig-zag crystal structure in syndiotactic polypropylene does not change the heat capacity significantly.

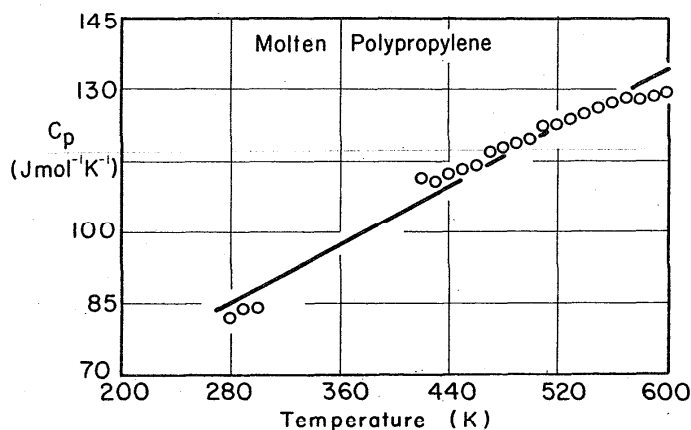


FIGURE 3. Heat capacity of molten polypropylene. The data point from 280 to 300 K are amorphous heat capacity values obtained from crystallinity extrapolations (table 3). The data points from 420 to 600 K are the averaged data on molten samples (tables A4 and A5). The drawn-out line represents the recommended data [eq. (9)].

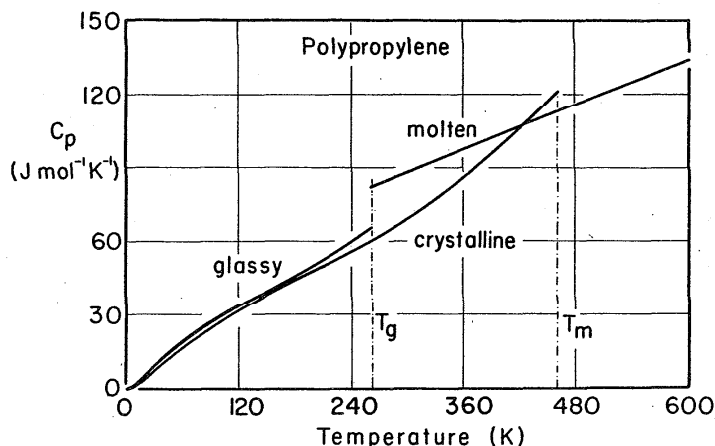


FIGURE 4. Recommended data of the heat capacity of crystalline, amorphous, and molten polypropylene.

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