

# Unbiased Evaluation of Literature Data on Equilibrium Melting Temperature and Enthalpy of Fusion of Perfectly Syndiotactic Polypropylene

PITT SUPAPHOL\*

The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chulalongkorn 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand

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**ABSTRACT:** The thermodynamic properties of highly syndiotactic polypropylene (PP) were reevaluated based on the data taken from the literature. The thermodynamic equilibrium melting temperature of a perfectly syndiotactic PP, which was estimated based on the Flory theory for the depression of the melting point in random copolymers, was 168.0°C. However, it was found to be 174.2°C when a linear extrapolation was attempted on a plot of the observed equilibrium melting temperature against the syndiotacticity level. The thermodynamic enthalpy of fusion of a perfect crystal of fully syndiotactic PP was estimated to be 8.7 kJ mol<sup>-1</sup>, and the average value of the literature data was 7.8 kJ mol<sup>-1</sup>. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1603–1609, 2001

**Key words:** syndiotactic polypropylene; thermodynamic property; equilibrium melting temperature; enthalpy of fusion

## INTRODUCTION

The syndiotactic form of polypropylene (s-PP) was first synthesized in the early 1960s by Natta et al.<sup>1,2</sup> based on the AlEt<sub>2</sub>Cl/VCl<sub>4</sub> catalyst systems along with anisole as an electron donor. Pertinent publications regarding the synthesis of s-PP based on the traditional Ziegler–Natta catalysis were given in detail by Natta et al.<sup>3</sup> and later by Boor and Youngman.<sup>4,5</sup> Even though the resulting polymer possessed a fair level of syndiotactic content, it contained too high a level of regioirregular defects (e.g., head to head/tail to tail type defects). As a result, the properties of the obtained polymer were quite difficult to control, and this was the reason why the first generation s-PP was largely viewed as a laboratory curiosity.

The second generation s-PP was successfully synthesized in 1988 when Ewen et al.<sup>6</sup> reported that highly stereoregular and regioregular s-PP can be polymerized using a catalyst system composed of isopropylidene(*cyclo*-pentadienyl)(9-fluorenyl)zirconium or hafnium dichloride and methylaluminumoxane. The discovery of these new metallocene catalyst systems provided a new route for the production of s-PP with much improved purity and yields, which led to renewed interest in both scientific research and industrial applications. In terms of scientific research, there were a number of publications relating to various aspects of the physical properties of s-PP. Many of these studies up to 1994 were reviewed and discussed in a publication by Rodriguez-Arnold et al.<sup>7</sup>

Among these scientific studies, the thermal behavior of s-PP was also of focal interest and was reported by various laboratories.<sup>8–20</sup> Preliminary

\* E-mail: ps@sunsv1.ppc.chula.ac.th.

**Table I** Molecular Characterization, Equilibrium Melting Temperature ( $T_m^0$ ), and Enthalpy of Fusion ( $\Delta H_f^0$ ) Data of s-PP Taken from Literature and Estimated Equilibrium Melting Temperature for 100% Syndiotactic s-PP Sample [ $(T_m^0)_{100\%}$ ]

1	2	3	4	5	6	7	8	9	10	11
Data Source	$M_w$ ( $\times 10^3$ )	$M_w/M_n$	[%rrrrr]	[%rrr]	[%r]	$T_m^0$ ( $^{\circ}\text{C}$ )	Method	$\Delta H_f^0$ (kJ mol $^{-1}$ )	$(T_m^0)_{100\%}$ ( $^{\circ}\text{C}$ )	$(T_m^0)_{100\%}$ ( $^{\circ}\text{C}$ ) <sup>a</sup>
Ziegler-Natta catalyzed s-PP										
Boor and Youngman <sup>4,5,8</sup>	—	—	—	—	—	161.0	log $\chi_c$ versus $1/T_m$ (DTA/density) <sup>b</sup>	(2.9) <sup>c</sup>	—	—
Miller and Seeley <sup>9,10</sup>	—	—	—	64.4	71.7	158.8	Hoffman-Weeks (DSC@40/-)	(3.1) <sup>c</sup>	—	—
Metallocene catalyzed s-PP										
Galambos et al. <sup>11</sup>	—	—	95.0	—	—	171.0	Gibbs-Thomson (DSC@20/density)	(4.4) <sup>d</sup>	—	—
Hafka and K�onnecke <sup>12</sup>	98	2.2	—	92.4	95.3	151.0	Hoffman-Weeks (DSC@20/WAXD)	8.3	159.9	160.5
	129	2.3	—	93.3	96.0	155.0	Hoffman-Weeks (DSC@20/-)	—	—	163.3
	52	2.3	81.4	85.6	91.9	(134.9)	Hoffman-Weeks (DSC@10/-)	—	—	(150.5)
	77	2.9	88.8	92.2	95.4	(149.9)	Hoffman-Weeks (DSC@10/-)	—	—	(159.1)
	96	2.9	91.5	94.9	96.9	165.9	Hoffman-Weeks (DSC@10/-)	—	—	172.4
	115	2.7	88.6	91.8	95.1	152.9	Hoffman-Weeks (DSC@10/-)	—	—	162.8
	152	2.1	91.4	95.1	97.0	163.9	Hoffman-Weeks (DSC@10/-)	—	—	170.2
	164	2.2	92.1	94.8	96.8	165.9	Hoffman-Weeks (DSC@10/WAXD)	7.0	173.5	172.7
	173	2.0	91.5	95.4	97.2	169.9	Hoffman-Weeks (DSC@10/-)	—	—	175.9
	228	2.4	93.2	96.2	97.6	(181.9)	Hoffman-Weeks (DSC@10/-)	—	—	(187.3)
	266	2.6	94.5	96.7	98.0	(185.9)	Hoffman-Weeks (DSC@10/-)	—	—	(190.5)
	164	2.2	92.1	94.8	96.8	168.0	Hoffman-Weeks (DSC@10/-)	—	—	174.9
Marigo et al. <sup>14</sup>	12	1.2	85.0	91.0	94.0	(147.5)	Hoffman-Weeks (DSC@10/-)	—	—	(159.6)
Rodr�guez-Arnold et al. <sup>15,16</sup>	17	1.1	86.0	91.0	94.0	150.7	Hoffman-Weeks (DSC@10/WAXD)	7.6 <sup>e</sup>	163.3	162.9
	23	1.1	88.0	93.0	95.0	159.3	Hoffman-Weeks (DSC@10/WAXD)	7.8 <sup>e</sup>	169.8	169.8
	23	1.1	88.0	93.0	95.0	158.0	Gibbs-Thomson (DSC@10/WAXD)	7.8 <sup>e</sup>	168.5	168.5
	29	1.1	86.0	91.0	94.0	153.6	Hoffman-Weeks (DSC@10/WAXD)	7.6 <sup>e</sup>	166.3	166.0
	37	1.1	86.0	92.0	94.0	155.2	Hoffman-Weeks (DSC@10/WAXD)	7.7 <sup>e</sup>	167.8	167.7
	46	1.1	86.0	92.0	94.0	158.1	Hoffman-Weeks (DSC@10/WAXD)	8.2 <sup>e</sup>	170.1	170.8
	59	1.1	86.0	92.0	94.0	157.1	Hoffman-Weeks (DSC@10/WAXD)	7.4 <sup>e</sup>	170.4	169.7
	85	1.1	86.0	92.0	94.0	157.0	Hoffman-Weeks (DSC@10/WAXD)	7.9 <sup>e</sup>	169.4	169.6
	85	1.1	86.0	92.0	94.0	160.0	Gibbs-Thomson (DSC@10/WAXD)	7.9 <sup>e</sup>	172.5	172.8
	158	1.2	87.0	92.0	95.0	155.2	Hoffman-Weeks (DSC@10/WAXD)	8.0 <sup>e</sup>	165.2	165.5
	281	1.2	87.0	92.0	95.0	156.6	Hoffman-Weeks (DSC@10/WAXD)	8.0 <sup>e</sup>	166.7	167.0
Uehara et al. <sup>17</sup>	94	2.3	89.1	—	97.2	157.0	Hoffman-Weeks (DSC@10/-)	—	—	162.7
	96	2.0	87.3	—	97.1	156.0	Hoffman-Weeks (DSC@10/-)	—	—	161.9
	96	2.1	87.3	—	96.5	155.0	Hoffman-Weeks (DSC@10/-)	—	—	162.1
	109	1.9	88.6	—	97.2	156.0	Hoffman-Weeks (DSC@10/-)	—	—	161.7
	180	3.0	93.6	—	97.5	163.0	Hoffman-Weeks (DSC@10/density)	(5.4) <sup>f</sup>	170.8	168.2
	202	1.8	94.5	—	98.0	170.0	Hoffman-Weeks (DSC@10/density)	(5.2) <sup>f</sup>	176.2	174.3

Schmidtke et al. <sup>18</sup>	239	2.3	91.0	97.0	—	166.0	Hoffman-Weeks (SAXS@10/SAXS)	7.7	—	
	239	2.3	91.0	97.0	—	(176.0)	Gibbs-Thomson (SAXS@10/SAXS)	7.7	—	
De Rosa et al. <sup>19</sup>	164	—	92.5	—	—	164.0	Hoffman-Weeks (DSC@2.5/-)	—	—	
	213	—	94.2	—	—	168.0	Hoffman-Weeks (DSC@2.5/-)	—	—	
	228	—	95.0	—	—	170.0	Hoffman-Weeks (DSC@2.5/-)	—	—	
	266	—	95.8	—	—	172.0	Hoffman-Weeks (DSC@2.5/-)	—	—	
Supaphol and Spruiell <sup>20</sup>	133	3.6	74.6	83.7	88.3	148.3	Hoffman-Weeks (DSC@20/-)	—	173.3	
	165	2.2	77.1	87.3	91.4	146.1	Hoffman-Weeks (DSC@20/-)	—	163.7	
	165	3.5	75.3	85.1	90.0	146.4	Hoffman-Weeks (DSC@20/-)	—	167.2	
	171	2.1	74.6	84.4	89.2	146.4	Hoffman-Weeks (DSC@20/-)	—	169.0	
	195	3.7	74.6	83.1	87.4	146.6	Hoffman-Weeks (DSC@20/-)	—	173.7	
Average								7.8 ± 0.3	168.7 ± 4.1	168.0 ± 4.5

<sup>a</sup> Calculated based on the Flory theory for the depression of the melting temperature in copolymers using either a corresponding  $\Delta H_f^o$ -value or the average value of 7.8 kJ mol<sup>-1</sup>, respectively.

<sup>b</sup> It should be read, for example, the method of obtaining  $T_m^o = \log \chi$  versus  $1/T_m$ ; the method of obtaining  $T_m$  and/or  $\Delta H_f = \text{DTA}$  (where possible, the heating rate used is also reported); and the method of obtaining the absolute crystallinity,  $\chi_c = \text{density}$ . It is worth noting that  $\Delta H_f^o = \Delta H_f/\chi_c$ , DSC@40, 20, etc.; thermal behavior observed at a heating rate of 40 or 20°C min<sup>-1</sup>, etc.

<sup>c</sup> The authors estimated the  $\Delta H_f^o$  values based on data given by Boor and Youngman.<sup>4</sup> After careful reevaluation, the correct value should be  $3.1 \pm 0.4$  kJ mol<sup>-1</sup>.

<sup>d</sup> The extrapolated value (as reported), whereas the average value of  $\Delta H_f^o$  recalculated (based on their data listed in table I in Galambos et al.<sup>11</sup>) based on  $\Delta H_f/\chi_c$  is  $5.1 \pm 0.5$  kJ mol<sup>-1</sup>.

<sup>e</sup> Taken directly from the data listed in table 4.1 in Rodriguez-Arnold.<sup>16</sup>

<sup>f</sup> Recalculated values based on the data listed in table 2 in Uehara et al.<sup>17</sup>

observation of these results revealed that the equilibrium melting temperature ( $T_m^o$ ) is strongly dependent on the syndiotacticity level of the sample studied. The estimated values of the enthalpy of fusion ( $\Delta H_f^o$ ) vary widely. Estimation of the equilibrium  $T_m^o$  for a 100% syndiotactic s-PP sample [( $T_m^o$ )<sub>100%</sub>] gave anomalous<sup>9,10,13</sup> and debatable<sup>19,20</sup> results. Consequently, the purpose of this article is twofold: it is a critical review of the literature data and an unbiased evaluation of the  $\Delta H_f^o$  and ( $T_m^o$ )<sub>100%</sub> values based on these data.

## EXPERIMENTAL

### Compilation of Literature Data

Table I summarizes in chronological order the  $T_m^o$  (column 7) and the  $\Delta H_f^o$  (column 9) data of s-PP samples, as well as corresponding molecular characterization information (columns 2–6) that was reported in the literature.<sup>8–20</sup> It should be noted that only the data reported by Boor and Youngman<sup>4,5,8</sup> and Miller and Seeley<sup>9,10</sup> were measured on s-PP samples that were polymerized based on Ziegler-Natta catalysis whereas the rest of the data<sup>11–20</sup> were measured on s-PP samples produced by metallocene catalysis. The method for determining the  $T_m^o$  along with the method for obtaining the thermal information shown in the parentheses (i.e., the melting temperature  $T_m$  and/or heat of fusion  $\Delta H_f$ ) and/or the method for measuring the absolute crystallinity ( $\chi_c$ ) are also reported in column 8 in Table I. It should be noted that the heating rate used to obtain thermal information is also given if known (e.g., DSC@20 is equivalent to saying that the thermal behavior was observed using a DSC at a heating rate of 20°C min<sup>-1</sup>).

The most commonly used approaches for obtaining the  $T_m^o$  are the Gibbs-Thomson<sup>21</sup> and Hoffman-Weeks<sup>22</sup> extrapolation methods. It is not the intention of this article to describe these two methods in detail; therefore, interested readers are urged to consult with either the original<sup>21,22</sup> or related<sup>23</sup> publications. In short, the Gibbs-Thomson equation predicts a linear relationship between the  $T_m$  and the reciprocal value of the crystal thickness  $1/l_c$  whereas the Hoffman-Weeks equation predicts a linear relationship between the  $T_m$  and the crystallization temperature  $T_c$ . In order for these methods to be used effectively, the effects of crystal thickening and/or superheating need to be minimized and this can

be done through a proper experimental scheme used to measure the  $T_m$ . For the DSC technique, these effects can be minimized by using a moderate heating rate (i.e., ca. 5 to ca. 20°C min<sup>-1</sup>) and an optimal sample size (i.e., ≤7 mg).

The  $\Delta H_f^o$  can be obtained based on the relation  $\Delta H_f^o = \Delta H_f / \chi_c$ , where the  $\Delta H_f$  is for finite thickness crystals (crystallized at an arbitrary  $T_c$ ). Based on column 8 in Table I, three methods were used to arrive at the  $\chi_c$ : density,<sup>4,11,17</sup> WAXD,<sup>12,13,15,16</sup> and SAXS.<sup>18</sup> As discussed later, different methods for measuring the  $\chi_c$  value have a strong affect on the resulting value of the  $\Delta H_f^o$ .

### Analysis and Discussion of Literature Data

According to Table I, the syndiotacticity level (as determined by the racemic pentad content [%rrrrr]) of the s-PP samples studied ranged from 74.6 to 95.8% (column 4) with the exclusion of the data determined for Ziegler–Natta catalyzed s-PP samples.<sup>4,5,8–10</sup> The resulting  $T_m^o$  value ranged from 146.1 to 172.0°C (column 7) with the exception of the data in parentheses. It is worth noting that because the syndiotacticity level of the s-PP samples polymerized using Ziegler–Natta catalysis were apparently low<sup>4,5,8–10</sup> and because a small amount of isotactic PP (i-PP) crystals were present in WAXD patterns,<sup>9,10</sup> the resulting  $T_m^o$  values estimated for these s-PP samples may be questionable.

In Table I the  $\Delta H_f^o$  is in the range of 5.1–8.3 kJ mol<sup>-1</sup> (column 9), and the average value is 7.3 ± 1.0 kJ mol<sup>-1</sup>. (Data measured for Ziegler–Natta catalyzed s-PP samples<sup>4,5,8–10</sup> are excluded.) As mentioned previously, the method used to obtain the  $\chi_c$  value has a strong affect on the resulting value of the  $\Delta H_f^o$ . This can be proven by closer examination of the  $\Delta H_f^o$  data listed in column 9. It is evident that when the density was used to calculate the  $\chi_c$  value, the resulting  $\Delta H_f^o$  value ranged from 5.1 to 5.4 kJ mol<sup>-1</sup>; however, it ranged from 7.0 to 8.3 kJ mol<sup>-1</sup> when WAXD was used to obtain the  $\chi_c$  value. This can only be interpreted as the  $\chi_c$  value calculated from the density data being greater than that obtained from the WAXD data. This may be explained by a hypothesis that the crystallinity content calculated from the density is higher than that obtained from the WAXD data due to contributions from the interfacial layer.<sup>24</sup> Consequently, the  $\Delta H_f^o$  value obtained from using the density as the means to calculate the  $\chi_c$  may not be totally accurate. With this in mind, the average value of

the  $\Delta H_f^o$  (calculated without the data whose  $\chi_c$  value was based on the density measurement) of 7.8 ± 0.3 kJ mol<sup>-1</sup> may be more meaningful.

A critical comment should also be made on the  $\Delta H_f^o$  values reported by Boor and Youngman<sup>4,5,8</sup> and Miller and Seeley.<sup>9,10</sup> Both groups calculated and reported their  $\Delta H_f^o$  value based on the original  $\Delta H_f$  and  $\chi_c$  data reported by Boor and Youngman.<sup>4</sup> In their original publication, Boor and Youngman<sup>4</sup> assumed amorphous<sup>25</sup> and unit cell<sup>1,2</sup> densities (denoted  $\rho_a$  and  $\rho_c$ , respectively) of 0.854 and 0.90 g mL<sup>-1</sup>, respectively. Based on the most recent data,<sup>26,27</sup> the  $\rho_c$  value was calculated to be 0.930 g mL<sup>-1</sup> whereas the  $\rho_a$  value stands as previously noted. Based on this information, the correct  $\Delta H_f^o$  value for the original data of Boor and Youngman<sup>4</sup> should be 3.1 ± 0.4 kJ mol<sup>-1</sup>, which is equal to the recalculated value used by Miller and Seeley.<sup>9,10</sup>

The estimated  $T_m^o$  values summarized in Table I exhibit a strong correlation with the syndiotacticity level of the s-PP samples studied. In an attempt to correlate the dependence of the observed  $T_m^o$  values as a function of syndiotacticity level, Miller<sup>28</sup> modified the original Flory theory for the depression of the melting point in copolymers<sup>29,30</sup> to be used in this manner. The model assumes that a s-PP chain has a random arrangement of syndiotactic dyads, which are crystallizable, and isotactic ones, which are not crystallizable and are totally excluded from the crystals. Mathematically, this model reads

$$\frac{1}{T_m^o} - \frac{1}{(T_m^o)_{100\%}} = -\left(\frac{R}{\Delta H_f^o}\right) \ln p_r, \quad (1)$$

where  $(T_m^o)_{100\%}$  and  $\Delta H_f^o$  are for a 100% syndiotactic s-PP sample,  $R$  is the universal gas constant, and  $p_r$  is the fraction of the monomer units that are syndiotactically bonded. In a practical sense,  $p_r$  is replaced by the racemic dyad content [%r].

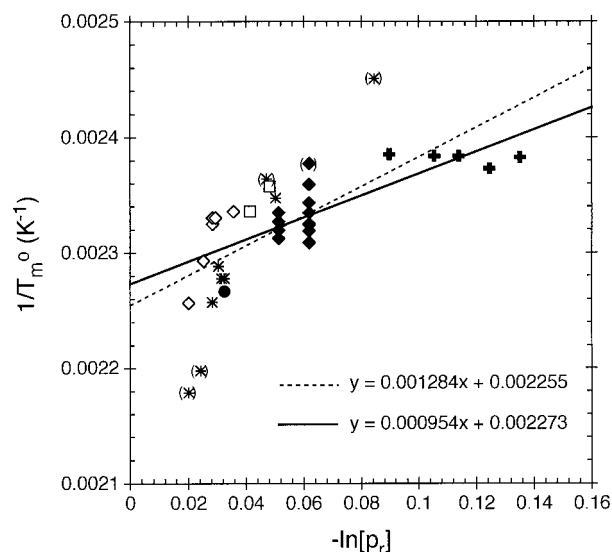
There are two ways of estimating the  $(T_m^o)_{100\%}$  value based on the data listed in Table I: the direct calculation method [this can be done because the values of  $T_m^o$ ,  $\Delta H_f^o$  (taken as the average value of the literature data), and  $p_r$  are known] and the extrapolation method [this can be done through the plot of  $1/T_m^o$  vs.  $-\ln p_r$  with the y intercept being  $1/(T_m^o)_{100\%}$  and the slope being  $R/\Delta H_f^o$ ]. We analyzed the data taken from the literature based on the first method and report the results in columns 10 and 11 in Table I. Col-

umn 10 summarizes the calculated  $(T_m^o)_{100\%}$  values based on the actual reported  $\Delta H_f^o$  values. The calculated  $(T_m^o)_{100\%}$  values range from 159.9 to 176.2°C, and the average value is  $168.7 \pm 4.1^\circ\text{C}$ . Column 11 summarizes the  $(T_m^o)_{100\%}$  values estimated based on the average  $\Delta H_f^o$  value (i.e.,  $7.8 \text{ kJ mol}^{-1}$ ). The calculated  $(T_m^o)_{100\%}$  values are in the range of 160.5–175.9°C (the values in parentheses are excluded), and the average value is  $168.0 \pm 4.5^\circ\text{C}$ .

We also analyzed the data taken from the literature using the second method by plotting  $1/T_m^o$  as a function of  $-\ln p_r$  (as shown in Fig. 1). With the exclusion of the data points marked in parentheses, the least-squares line fit shown in Figure 1 as the solid line (the correlation coefficient of the fit  $r^2 = 0.61$ ) through the bulk of the data gave the  $(T_m^o)_{100\%}$  and  $\Delta H_f^o$  values of  $166.7^\circ\text{C}$  and  $8.7 \text{ kJ mol}^{-1}$ , respectively. However, if all of the data points are included in the extrapolation, the least-squares line fit shown in Figure 1 as the broken line (the correlation coefficient of the fit  $r^2 = 0.50$ ) through the bulk of the data gave the  $(T_m^o)_{100\%}$  and  $\Delta H_f^o$  values of  $170.4^\circ\text{C}$  and  $6.5 \text{ kJ mol}^{-1}$ , respectively.

Apparently, both methods give very comparable  $(T_m^o)_{100\%}$  values ( $168.0^\circ\text{C}$  in the first method vs.  $166.7^\circ\text{C}$  in the second). In addition, the  $\Delta H_f^o$  value of  $8.7 \text{ kJ mol}^{-1}$  that is estimated based on the extrapolation method is satisfactory when considering that the average value of the raw data is  $7.8 \text{ kJ mol}^{-1}$ . It is worth noting that estimation of the  $(T_m^o)_{100\%}$  values using the Flory theory for the depression of the melting point in copolymers<sup>29,30</sup> is fairly justified by the work of Schmidtke et al.,<sup>18</sup> who found that s-PP does not thicken as much during crystallization and annealing. This finding further suggests that the isotactic defects should be totally, or at least partially, excluded from the crystals.

A number of authors<sup>9,13,17</sup> applied the Flory theory for the depression of the melting point in copolymers<sup>29,30</sup> to their data. Uehara et al.<sup>17</sup> analyzed their data based on the first method and arrived at the  $(T_m^o)_{100\%}$  value of  $168 \pm 2^\circ\text{C}$ , which is in very good agreement with our result. Balbontin et al.<sup>13</sup> utilized the extrapolation method and found the  $(T_m^o)_{100\%}$  value of  $213.8^\circ\text{C}$ . Because their estimated  $\Delta H_f^o$  value of  $1.4 \text{ kJ mol}^{-1}$  was clearly too low, their  $(T_m^o)_{100\%}$  value seems unrealistically high. Miller and Seeley<sup>9</sup> reported a  $(T_m^o)_{100\%}$  value of approximately  $220^\circ\text{C}$ . We found this very questionable, because they did not report this value in their original publication.<sup>10</sup> To

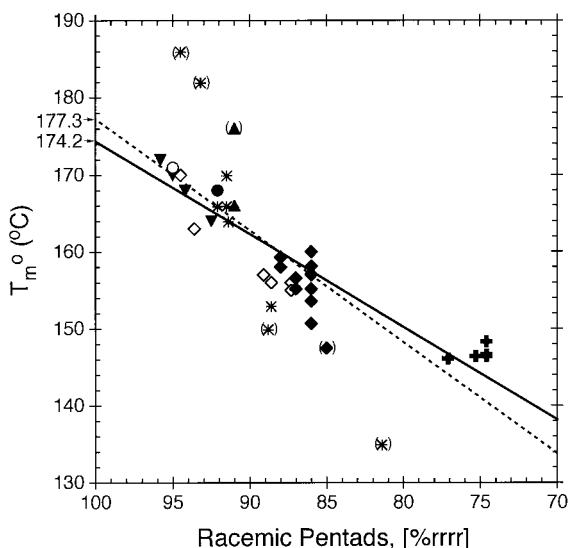


**Figure 1** The determination of the equilibrium melting temperature of a 100% syndiotactic polypropylene (s-PP) sample [ $(T_m^o)_{100\%}$ ] by means of the Flory theory for the depression of the melting temperature in copolymers through the plot of  $1/T_m^o$  versus  $-\ln p_r$ , where  $p_r$  is substituted by the racemic dyad content. The least-squares fit with  $r^2 =$  (—) 0.61 or (---) 0.50. (□) Haftka and Koennecke,<sup>12</sup> (\*) Balbontin et al.,<sup>13</sup> (●) Marigo et al.,<sup>14</sup> (◆) Rodriguez-Arnold et al.,<sup>15,16</sup> (◇) Uehara et al.,<sup>17</sup> and (+) Supaphol and Spruiell.<sup>20</sup>

make our point certain, we recalculated the  $(T_m^o)_{100\%}$  value based on their original data ( $\Delta H_f^o = 3.1 \text{ kJ mol}^{-1}$  and  $p_r = 0.72$ ) and found it to be abnormally high ( $424.4^\circ\text{C}$ ). Even when the average  $\Delta H_f^o$  value of  $7.8 \text{ kJ mol}^{-1}$  was used instead, the resulting  $(T_m^o)_{100\%}$  value was still too high ( $237.3^\circ\text{C}$ ). Along with the fact that a small amount of i-PP crystals were found in their WAXD patterns,<sup>9,10</sup> their original  $T_m^o$  value seems to be overestimated (because of the contribution of the crystals of isotactic counts).

Recently, De Rosa et al.<sup>19</sup> questioned the applicability of the Flory theory for the depression of the melting point in copolymers<sup>29,30</sup> to determine the  $(T_m^o)_{100\%}$  value in s-PP. Based on the fact that isotactic defects (which are present in an s-PP sample) are found to be at least partly tolerably included within the crystals,<sup>31</sup> the assumption of total exclusion of the isotactic defects from the s-PP crystals adopted in previous analyses has to be contested; and this may result in a higher value of the calculated  $(T_m^o)_{100\%}$ . However, it will be interesting to utilize other theories of melting point depression in copolymer crystals<sup>32,33</sup> to estimate the  $(T_m^o)_{100\%}$  value of s-PP. Because addi-





**Figure 2** The determination of the equilibrium melting temperature of a 100% syndiotactic polypropylene (s-PP) sample [ $(T_m^o)_{100\%}$ ] by means of the extrapolation of the equilibrium melting temperatures ( $T_m^o$ ) of the s-PP samples shown in Table I as a function of the syndiotactic pentad content [%rrrrr]. The least-squares fit with  $r^2 =$  (—) 0.83 or (---) 0.66. (○) Galambos et al.,<sup>11</sup> (\*) Balbontin et al.,<sup>13</sup> (●) Marigo et al.,<sup>14</sup> (◆) Rodriguez-Arnold et al.,<sup>15,16</sup> (◇) Uehara et al.,<sup>17</sup> (▲) Schmidtke et al.,<sup>18</sup> (▼) De Rosa et al.,<sup>19</sup> and (⊕) Supaphol and Spruiell.<sup>20</sup>

tional work is needed to apply these theories to the data summarized in Table I, this investigation is a matter for future research.

De Rosa et al.<sup>19</sup> proposed a direct graphical extrapolation method to obtain  $(T_m^o)_{100\%}$  values based on a plot of observed  $T_m^o$  values versus the syndiotactic pentad content [%rrrrr]. We plotted the  $T_m^o$  values as summarized in column 7 in Table I as a function of the syndiotactic pentad content [%rrrrr] (column 4), as shown in Figure 2. With the exclusion of the data points marked in parentheses, the least-squares line fit shown in Figure 2 as the solid line (the correlation coefficient of the fit  $r^2 = 0.83$ ) through the bulk of the data resulted in the  $(T_m^o)_{100\%}$  value of 174.2°C. However, if all of the data points are included in the extrapolation, the least-squares line fit shown in Figure 2 as the broken line (the correlation coefficient of the fit  $r^2 = 0.66$ ) through the bulk of the data gave the  $(T_m^o)_{100\%}$  value of 177.3°C. When compared to the reported value by De Rosa et al.<sup>19</sup> (182°C), our result of 174.2°C seems reasonably acceptable (when taking into account that this value was estimated based on an unbiased compilation of the literature data).

Comparison of the  $(T_m^o)_{100\%}$  value calculation based on the Flory theory for the depression of the melting point in copolymers<sup>29,30</sup> and the estimation based on the direct extrapolation method indicates comparable results (168.0 vs. 174.2°C) within the estimated experimental error. It is not certain at this point which method is the best for the estimation of the  $(T_m^o)_{100\%}$ , but the method based on the Flory theory at least has a theoretical basis for the linear dependence of the extrapolated quantity.

## CONCLUSIONS

The literature data on the thermodynamic properties of s-PP were critically reviewed. The  $(T_m^o)_{100\%}$  of a completely syndiotactic PP, which was estimated based on the Flory theory for the depression of the melting point in random copolymers, was found to be 168.0°C. The use of the Flory theory in the estimation of the  $(T_m^o)_{100\%}$  value was evidently justified by the work of Schmidtke et al.,<sup>18</sup> who found no thickening of crystals upon crystallization and annealing. The thermodynamic  $\Delta H_f^o$  of a perfect crystal of completely syndiotactic PP was estimated to be 8.7 kJ mol<sup>-1</sup> whereas the average value of the literature data was 7.8 kJ mol<sup>-1</sup>.

Contrary to the findings by Schmidtke et al.,<sup>18</sup> Auriemma et al.<sup>31</sup> reported that isotactic defects are found to be at least partially tolerably included within the crystals. As a result, the assumption of the total exclusion of the isotactic defects from the s-PP crystals, which was the basis in the utilization of the Flory theory in the estimation of  $(T_m^o)_{100\%}$  and  $\Delta H_f^o$  values, must be questioned. As a result, a graphical extrapolation of the plot of the observed  $T_m^o$  value versus the syndiotactic pentad content [%rrrrr] was proposed by De Rosa et al.<sup>19</sup> Based on this method, a  $(T_m^o)_{100\%}$  value of 174.2°C was found. It is necessary to mention that the most significant drawback of this method is the lack of theoretical reasoning of a linear relationship between the  $T_m^o$  value and the racemic pentads [%rrrrr].

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