The Effect of Syndioindex on the Thermal Properties of Syndiotactic Polypropylene

D. R. GEE and T. P. MELIA

A differential scanning calorimeter has been used to measure the heat capacity of four samples of syndiotactic polypropylene having syndioindices lying in the range 1·8 to 2·7 from 180° to 450°K. The equations

$$C = 0{\cdot}235 + 4{\cdot}76 \times 10^{-3}\,T \text{ abs. J.*deg}^{-1}\text{g}^{-1}$$

and

$$C_m = 1{\cdot}220 + 3{\cdot}40 \times 10^{-3}\,T \text{ abs.J.deg}^{-1}\text{g}^{-1}$$

represent the heat capacity of each of the four samples in the temperature ranges 180° to 260°K and 420° to 450°K, respectively. A glass transition (265° ±2°K), a first order transition of unknown origin (386°–406°K) and a melting transition (404°K–417°K) were observed in each sample. The absolute entropy of liquid, syndiotactic polypropylene at 450°K and one atmosphere pressure, 2·98 ± 0·06 abs.J.deg^{-1}*g*$^{-1}$*, has been calculated. The thermal properties of isotactic, atactic and syndiotactic polypropylene are compared and it is concluded that steric configuration has little effect on thermal properties in the liquid state.*

SINCE polypropylene can be synthesized in essentially the isotactic[1], atactic[2] and syndiotactic[3] forms it provides a suitable system on which to conduct an investigation into the effect of molecular configuration on thermal properties.

Heat capacity measurements on the isotactic and atactic forms of polypropylene have been carried out by several groups of workers[4–6] but the only measurements on syndiotactic polypropylene are those of Gee and Melia[7] on a sample with a syndioindex[8] of 2·85. The effect of changing syndioindex on the thermal properties of polypropylene has not been investigated.

In the present work heat capacity measurements have been made in the range 180° to 450°K on well characterized samples of syndiotactic polypropylene having syndioindices lying in the range 1·8 to 2·7. The relation of these results to those obtained with the isotactic and atactic isomers is discussed.

EXPERIMENTAL

Calorimetry

The differential scanning calorimeter used in the present investigation has been described previously[9,10]. The weight of syndiotactic polypropylene used was 25 mg. Heating rates of 4 deg. K/min were employed. The overall precision of the measurements is better than ± 2 per cent.

---

*1 abs.J = 4·184 cal.

Material

Samples 1, 2 and 4 were kindly given by Professor A. Zambelli of the Istituto di Chimica Industriale del Politecnico, Milan[8], and sample 3 by Dr R. F. Schaufele of the Esso Research Company, Linden, New Jersey, U.S.A. Sample 3 was prepared by Dr J. Boor and Dr E. A. Youngman[11] of the Shell Development Company, Emeryville, California, U.S.A.

Prior to their introduction into the calorimeter all four samples were pumped for two hours at 408°K, cooled to 373°K and maintained at this temperature *in vacuo* for sixteen hours. This procedure was adopted to ensure that all samples had the same thermal history. The densities of the annealed samples were measured dilatometrically. Assuming a unit cell density of 0·93 g cm^{-3} [12] and a value of 0·854 g cm^{-3} for the density of the amorphous phase[13], the volume fraction crystallinities of the four samples were calculated. The infra-red syndioindices were determined on the annealed samples[8]. Intrinsic viscosities were measured in tetralin at 408°K[14]. Characterization data for these polymers are summarized in *Table 1*.

Table 1. Characterization data for syndiotactic polypropylene

Sample No.	$[\eta]$ *dl* g^{-1}	$\overline{M}_v$	*Syndio-index*	*Density g* cm^{-3}	*Volume fraction crystallinity*
1	0·88	31 200	1·8	0·875	0·29
2	0·46	28 800	2·0	0·879	0·35
3	0·33	23 400	2·3	0·883	0·40
4	0·3	20 000	2·7	0·887	0·46

Infra-red syndioindex $= A_{11\cdot53}/\tfrac{1}{2}\,(A_{2\cdot32}+A_{2\cdot35})$

RESULTS AND DISCUSSION

The observed values of the heat capacity of samples 1–4 are plotted against temperature in *Figures 1–4* respectively. Between 180° and 260°K the heat capacity, C, of each of the four samples can be represented by the equation

$$C = 0\cdot235 + 4\cdot76 \times 10^{-3}\, T \text{ abs.J.deg}^{-1}\text{g}^{-1} \tag{1}$$

where T is the temperature in °K. The heat capacity of all samples in the liquid state, i.e. above T_m, can be represented by the equation

$$C_m = 1\cdot220 + 3\cdot40 \times 10^{-3}\, T \text{ abs.J.deg}^{-1}\text{g}^{-1} \tag{2}$$

where C_m is the heat capacity of the fused syndiotactic polymer, which is assumed[15] to be equal to the heat capacity of amorphous syndiotactic polypropylene, C_a, at temperatures below the melting point. Below 180° K it was assumed that the heat capacity of syndiotactic polypropylene is the same as that of atactic polyproplene[4,5]. Such an approach is justified by the fact that below 240°K the heat capacity of syndiotactic polypropylene

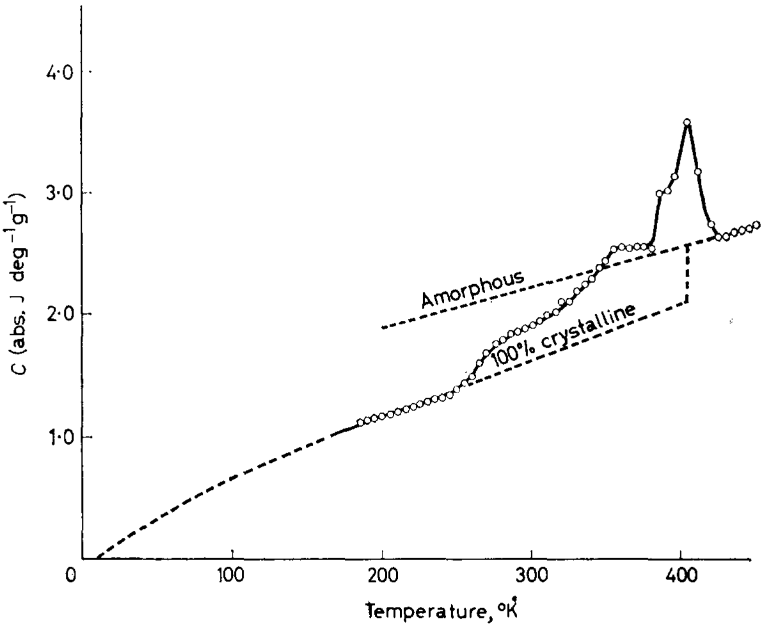

Figure 1—Observed heat capacities for sample 1 (syndioindex = 1·8)

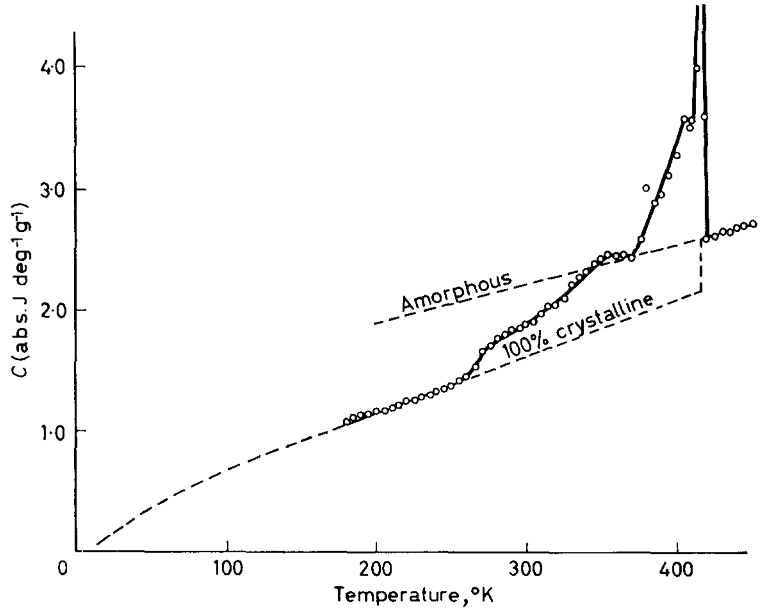

Figure 2—Observed heat capacities for sample 2 (syndioindex = 2·0)

is virtually indistinguishable from that of atactic polypropylene. It is therefore unlikely that significant deviations will occur at lower temperature since the molecular vibrations are short enough to be independent of chain order, crystallite size and steric configuration.

Inspection of *Figures 1–4* reveals the occurrence of three transitions in all the samples studied. This is in agreement with our earlier observations[7] on a polypropylene sample with a syndioindex of 2·85. The first transition, which can be recognized by the change in slope of the heat capacity versus temperature curve in the 260°K region, is attributed to the glass transition which has been found in this region by other methods[11]. The second, which is a first order transition having heat capacity maxima in the range 385° to 405°K, probably corresponds to the transition from the zig-zag planar conformation into the twofold helical conformation. However, we have no direct evidence on this point. The existence of both forms has been established by Natta and co-workers[16]. The third, which has heat capacity maxima in the range 404° to 417°K is the melting transition. The glass transition temperature (T_g) observed for the four samples, 265° ± 2°K, appears to be independent of the degree of syndiotacticity of polypropylene. The two first order transitions become more distinct as the syndioindex increases. For samples with syndioindex greater than 2·0 (samples 3 and 4) the peak in the heat capacity versus temperature curve corresponding to the crystal–crystal transition occurs at 405° ± 2°K. The highest melting points observed, 417° ± 1°K (samples 2 and 4), are in good agreement with previously published values[7,17]. The low value observed with sample 3 may be associated with its different method of preparation[11].

Since the crystal–crystal and melting transitions coalesce in all four samples no attempt has been made to assign values to their separate latent heats. Both contributions are included in the heat of fusion $\Delta H_f^{\star}$, calculated by means of equation 6 of ref. 7. Similarly, the entropy of fusion of semi-crystalline syndiotactic polypropylene is calculated from equation 7 of ref. 7. The results are presented in *Table 2*.

Table 2. Comparison of thermal properties of four syndiotactic polypropylene samples

Sample No. *Property*	*1*	*2*	*3*	*4*
Syndioindex	1·8	2·0	2·3	2·7
$\Delta H_f^{\star}$ (abs.J.g^{-1})	26·9	37·5	41·7	47·8
$\Delta S_f^{\star}$ (abs.J.deg.$^{-1}$g^{-1})	0·070	0·102	0·123	0·140
T_m (°K)	404	416	407	417
T_g (°K)	265	263	263	267
T_{tr} (°K)‡	(386)	405	403	406
Calorimetric entropy at 450°K (abs.J.deg^{-1}g^{-1})	2·89	2·91	2·92	2·93
S_0^0 (abs.J.deg^{-1}g^{-1})	0·03	0·03	0·03	0·02
S_{450}^0 (abs.J.deg^{-1}g^{-1})	2·92	2·94	2·95	2·96

‡Temperature at which crystal $\rightleftharpoons$ crystal transition occurs.

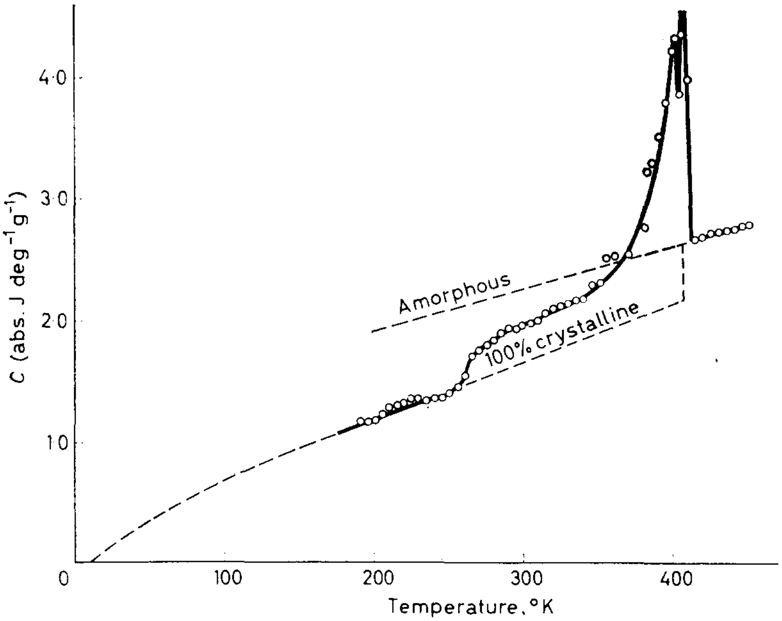

Figure 3—Observed heat capacities for sample 3 (syndioindex=2·3)

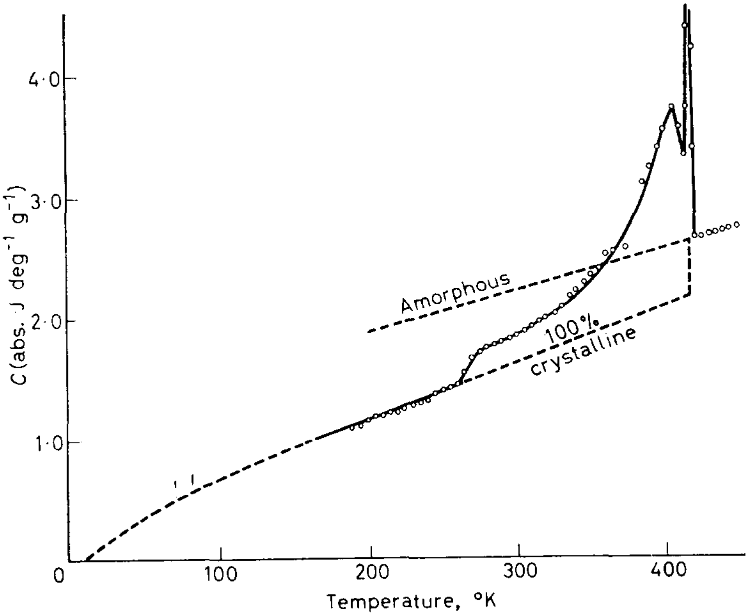

Figure 4—Observed heat capacities for sample 4 (syndioindex=2·7)

For samples with a syndioindex greater than 2·0 (samples 3 and 4), the heat of fusion of 100 per cent crystalline, syndiotactic polypropylene, ΔH_f, estimated from the expression[18]

$$\Delta H_f = \Delta H_f{}^{\star} / x \tag{3}$$

where x, the volume fraction crystallinity (*Table 1*), is $105{\cdot}5 \pm 2{\cdot}3$ abs.J.g^{-1} for both samples. This compares with the value of $102{\cdot}0 \pm 5{\cdot}0$ abs.J.g^{-1} recalculated from previously published data[7] using the more recent value[12] of 0·93 cm^3 g^{-1} for the unit cell density of 100 per cent crystalline. syndiotactic polypropylene. A similar calculation yields $0{\cdot}302 \pm 0{\cdot}006$ abs.J.deg.$^{-1}$g^{-1} for the entropy of fusion of the 100 per cent crystalline polymer. It should be noted that the ratio $\Delta H_f / \Delta S_f$ is not equal to T_m because the latent heat and entropy contributions from the crystal–crystal transition are included in the values quoted above.

Because the thermal properties of polymers are strongly crystallinity dependent this factor must be eliminated before the effect of molecular configuration can be deduced. For example, in order to compare the absolute entropies at 450°K, S^0_{450}, of the four samples under consideration account must be taken of their different residual entropies. The best way of doing this is to calculate the residual entropy, $(S^0_0)_a$, of the completely amorphous polymer at 0°K using the equation

$$(S^0_0)_a = \Delta S_f - \int_{T_g}^{T_m} (C_a/T)\,\mathrm{d}T + \int_{T_g}^{T_m} (C_c/T)\,\mathrm{d}T \tag{4}$$

where C_c, the heat capacity of 100 per cent crystalline, syndiotactic polypropylene, is obtained by a linear extrapolation of heat capacity data from below the glass transition temperature to the melting point. The calculated residual entropy may then be used in conjunction with the expression

$$S^0_{450} = \frac{\text{Calorimetric entropy}}{\text{at } 450^\circ\text{K}} + (1-x)(S^0_0)_a \tag{5}$$

to evaluate the absolute entropy of each sample at 450°K. The results are presented in *Table 2*.

The close coincidence between the four values of S^0_{450} indicates that the degree of syndiotacticity of polypropylene has no direct effect on thermal properties. However, it has an indirect effect in that the degree of syndiotacticity determines the crystallinity of the polymer and this in turn affects the thermal properties.

Previously published data[4,5] yield 2·94 abs.J.deg^{-1}g^{-1} for the absolute entropy of atactic polypropylene at 450°K. This is consistent with the fact that the syndiotactic and atactic isomers have similar densities[13,19] and also with n.m.r. observations[20] which indicate that atactic polypropylene has a good deal of syndiotactic character.

Although syndiotactic polypropylene has a lower melting point[5] (417° versus 450°K) and heat of fusion[5] (106 versus 215 abs.J.g^{-1}) than isotactic polypropylene it is interesting to note that the absolute entropies of these two isomers at 450°K are quite similar (2·94 versus 2·98 abs.J.deg^{-1}g^{-1}). This is consistent with the fact that the amorphous polymers have similar densities at 450°K[13]. This again illustrates the fact that steric configuration has little direct effect on thermal properties in the liquid phase where packing considerations are less important.

We are indebted to the Science Research Council for a grant in aid of this investigation.

Department of Chemistry and Applied Chemistry,
University of Salford,
Salford 5, Lancashire.

(*Received May 1968*)

REFERENCES

[1] NATTA, G. *J. Polym. Sci.* 1955, **16**, 143

[2] NATTA, G., PINO, P., MAZZANTI, G. and CORRADINI, P. *Proceedings* of the Fourth World Petroleum Congress, Rome, 1955

[3] NATTA, G., PASQUON, I. and ZAMBELLI, A. *J. Amer. chem. Soc.* 1962, **84**, 1488

[4] DAINTON, F. S., EVANS, D. M., HOARE, F. E. and MELIA, T. P. *Polymer, Lond.* 1962, **3**, 286

[5] PASSAGLIA, E. and KEVORKIAN, H. K. *J. appl. Polym. Sci.* 1963, **34**, 90

[6] WILKINSON, R. W. and DOLE, M. *J. Polym. Sci.* 1962, **58**, 1089

[7] GEE, D. R. and MELIA, T. P. *Makromol. Chem.* 1968, **116**, 122

[8] ZAMBELLI, A., NATTA, G. and PASQUON, I. *J. Polym. Sci.* 1963, **C4**, 411

[9] O'NEILL, M. J. *Analyt. Chem.* 1964, **36**, 1238
O'NEILL, M. J., JUSTIN, J. and BRENNER, N. *Analyt. Chem.* 1964, **36**, 1233

[10] CLEGG, G. A., GEE, D. R., MELIA, T. P. and TYSON, A. *Polymer, Lond,* 1968, **9**, 501

[11] BOOR, J. and YOUNGMAN, E. A. *J. Polym. Sci.* 1966, A1, **4**, 1861

[12] CORRADINI, P., NATTA, G., GANIS, P. and TEMUSSI, P. A. *J. Polym. Sci.* 1967, **C.16**, 2477

[13] NATTA, G. and PAGORARO, M. *R. C. Accad. Lincei,* 1963, **34**, 100

[14] MORAGLIO, G. *Chim. e Industr.* 1959, **41**, 879

[15] KARASZ, F. E., BAIR, H. E. and O'REILLY, J. M. *Polymer, Lond.* 1967, **8**, 547

[16] NATTA, G., PERALDO, M. and ALLEGRA, G. *Makromol. Chem.* 1964, **75**, 215

[17] BOOR, J. and YOUNGMAN, E. A. *J. Polym. Sci.* 1965, **B.3**, 577

[18] MELIA, T. P. *J. appl. Chem.* 1964, **14**, 461

[19] DANUSSO, F. and MORAGLIO, G. *Chim. e Industr.* 1959, **41**, 748

[20] CHIERICO, A., DEL NERO, G., LANZI, G. and MOGNASCHI, E. R. *European Polymer Journal,* 1966, **2**, 339