

# Fusion enthalpy and entropy of syndiotactic polystyrene

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The fusion enthalpy and entropy of a highly syndiotactic polystyrene sample were determined by melting point depression in the presence of diluents. Three solvents were used to ascertain the presence, if any, of polymorphic modifications: dioctyl phthalate, diphenylsulphone and diphenyldiketone (benzil). The results were compared with those of the corresponding isotactic stereoisomer. Comparative observations were also made about crystallinity degree and crystallization rate of the two polymers.

(Keywords: polystyrene; polymorphic modifications; crystallization)

## INTRODUCTION

The knowledge of fusion enthalpy and entropy is fundamental to crystalline polymer characterization. Such thermodynamic parameters can be correlated with changes in molecular configurations relative to the melting of the purely crystalline phase.

It is well known that a reliable method that allows the determination of these quantities rests on the Flory's theory of polymer solutions<sup>1,2</sup>. The  $\Delta H_u$  value of the fusion enthalpy of a monomeric unit can be obtained by a graphical solution of the equation

$$\left(\frac{1}{T_m} - \frac{1}{T_m^\circ}\right) \frac{1}{v_1} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} \left(1 - \frac{BV_1}{R} \frac{v_1}{T_m}\right) \quad (1)$$

where  $T_m^\circ$  and  $T_m$  are the melting points (K) of the polymer in the pure state and in solvent mixtures at volume fractions  $v_1$ .  $V_1$  and  $V_u$  are the molar volumes of the solvent and of the monomeric unit at  $T_m$ ,  $R$  is the gas constant, and  $B$  is the polymer-solvent interaction parameter.

This equation has been derived from equilibrium thermodynamic considerations. It gives reliable  $\Delta H_u$  values as the melting points of polymer-diluent mixtures approach the equilibrium conditions<sup>3</sup> and the solvents used have no adverse influence on the thermal stability of the polymer, or on the structure of its separated crystalline phase.

It is also known that the methods normally used to measure melting points can hardly approach the equilibrium conditions and that, nevertheless, the final results may be sufficiently accurate. In this work the polymer examined has a high melting point, in a range of temperature ( $\approx 270^\circ\text{C}$ ) in which some thermal decomposition, common also to other styrenic polymers<sup>4</sup>, has been shown. As a consequence, the d.s.c. method has been used as the most appropriate method for melting point determination.

## EXPERIMENTAL

### Polymer sample

The polymer sample of syndiotactic polystyrene (*syn*-PS) was synthesized with proper titanium based catalysts at the G. Donegani Research Institute of Montedison S.p.A.<sup>5</sup>. The intrinsic viscosity,  $[\eta]$ , of the sample, measured in orthodichlorobenzene at  $135^\circ\text{C}$ , was  $1.55 \text{ dl g}^{-1}$ , which indicates a viscosimetric average molecular weight of about 600 000, according to the equation  $[\eta] = 1.183 \times 10^{-4} M_v^{0.71}$  which was found valid for atactic polystyrene, and should hold also for the isotactic isomer<sup>6</sup>. The *syn*-PS sample investigated had a very high steric purity, checked by n.m.r.

### Solvents

The solvents used were pure grade products. They were selected on the basis of the following two main features: a high thermal stability (boiling point and/or decomposition temperature higher than  $300^\circ\text{C}$ ), and different chemical structures in order to watch any possible polymorphic change in the separated polymer phase. The solvents chosen were dioctyl phthalate, diphenylsulphone, and diphenyldiketone (benzil). The specific volume of these solvents was determined in the range of 30 to  $270^\circ\text{C}$  by dilatometric measurements (see below).

### Polymer-solvent mixtures

Polymer and solvents, in suitable ratios, were introduced and sealed in glass vials under vacuum. The vials were, then, cautiously heated to  $270^\circ\text{C}$  in a silicon oil bath to obtain homogeneous melts without perceptible polymer degradation. The treatment did not last more than 3 h.

### Dilatometric measurements

The specific volume measurements vs. temperature of solvents,  $v_{sp,1}$ , and of *syn*-PS,  $v_{sp,2}$ , in the molten state were carried out by capillary dilatometers, using apparatus

**Table 1** Experimental data for  $\Delta H_u$  evaluation of *syn*-PS (A = dioctyl phthalate, B = diphenylsulphone, C, D = benzil (diphenyldiketone))

Mixture	$T_m$ (K)	$10^3/T_m$	$W_2$	$v_{sp1}$	$v_{sp2}$	$v_1$
A1	533.7	1.8737	0.905	1.254	1.075	0.109
A2	528.3	1.8929	0.800	1.247	1.071	0.226
A3	521.1	1.9190	0.692	1.237	1.066	0.341
A4	516.2	1.9372	0.597	1.230	1.063	0.438
A5	509.9	1.9612	0.503	1.221	1.058	0.532
A6	507.5	1.9704	0.401	1.218	1.057	0.639
B1	529.6	1.8882	0.900	0.943	1.072	0.089
B2	520.8	1.9201	0.789	0.935	1.066	0.190
B3	511.7	1.9542	0.706	0.926	1.059	0.267
B4	504.2	1.9833	0.590	0.920	1.055	0.377
B5	503.2	1.9872	0.504	0.919	1.054	0.462
B6	495.1	2.0197	0.395	0.912	1.048	0.572
C1	527.5	1.8957	0.882	1.047	1.071	0.116
C2	517.3	1.9331	0.800	1.035	1.064	0.196
C3	507.1	1.9719	0.692	1.023	1.057	0.301
C4	491.4	2.0350	0.610	1.008	1.047	0.381
C5	484.8	2.0627	0.496	1.000	1.042	0.494
C6	474.1	2.1092	0.392	0.990	1.035	0.598
D1	504.4	1.9825	0.692	1.021	1.055	0.301
D2	494.2	2.0234	0.603	1.010	1.047	0.388
D3	485.0	2.0618	0.502	1.000	1.042	0.489
D4	483.8	2.0669	0.481	0.998	1.040	0.509
<i>syn</i> -PS	542.1	1.0845	1.000	—	1.080	0.000

and filling techniques previously described in detail in refs 7 and 8. During the measurements, dilatometers were maintained at a constant temperature, in a silicon oil bath.

#### Melting point determinations

The melting points of solvent mixtures ( $T_m$ ) and of pure polymer ( $T_m^\circ$ ) were determined using a TA 3000 Mettler scanning calorimeter with a heating rate of 10°C/min. Runs were carried out on at least three samples, obtained by spot sampling, to ascertain the mixture homogeneity.

The 'peak temperature' was assumed to be the melting point. Reproducibility better than 1°C was generally obtained with samples having a single sharp peak. On the contrary, a lower reproducibility was obtained when two peaks or large premelting intervals were observed. In these cases, a new melting homogenization in vial was repeated, like the first one, obviously at the risk of some degradation.

## RESULTS AND DISCUSSION

Table 1 recapitulates the experimental results and all the data needed to determine  $\Delta H_u$  of *syn*-PS from equation (1). The specific volumes of the solvent, at the melting temperatures,  $T_m$ , of the various mixtures, were calculated by interpolating the experimental dilatometric data of each solvent determined from 30 to 270°C.

Conversely, some difficulties were met in determining the dilatometric data of amorphous *syn*-PS, in that its range of stability in the molten state was relatively narrow. In fact, at a few degrees below its melting point, *syn*-PS shows, unlike its isotactic counterpart (*iso*-PS), a very fast crystallization rate. At temperatures above its melting point appreciable polymer degradation took place instead. In order to increase the range in which the specific volume interpolation of amorphous *syn*-PS could

be made, our previous data of *iso*-PS and atactic PS (*a*-PS) (ref. 9) were also considered and compared. The three sets of data, within the limits of their experimental accuracy, fit well a single straight line, which was then considered the best relation to be used for the determination of the specific volumes of *syn*-PS, and consequently of the volume fractions  $v_1$  and the molar volume  $V_u$ .

Figure 1 reports the relations between melting points and composition, which represents the phase diagrams of the three polymer-solvent mixtures.

It should be noted that the three series of data allow good extrapolations to the same value of the melting point of the pure polymer, so that the presence of polymorphic modifications in the separated polymer phases can reasonably be excluded.

Figure 2 illustrates the plot of the graphical solution of equation (1) for each solvent used. The same figure also shows a reproducibility test carried out with benzil, i.e. the lower boiling solvent. As may be seen, the two series of data fit the same straight line well.

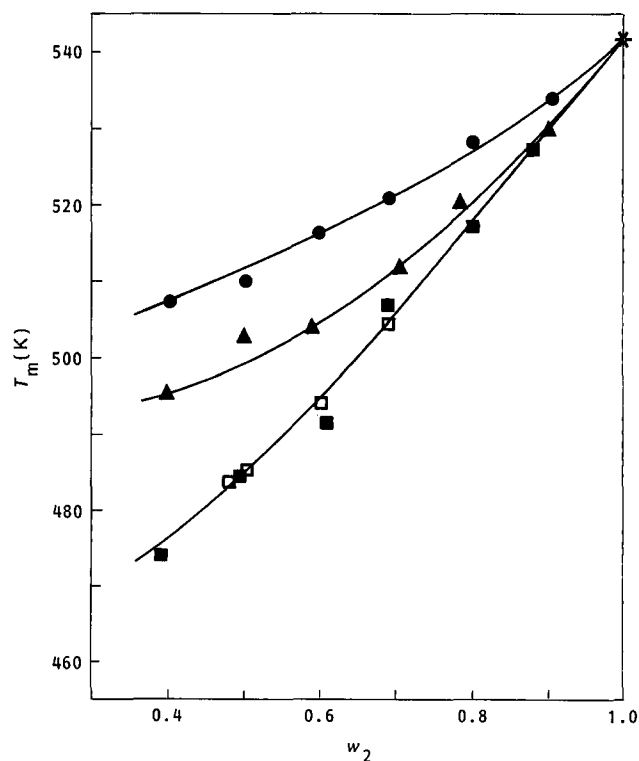
Through the graphical solutions, three  $\Delta H_u$  values can be independently calculated for *syn*-PS in the three solvents. From these, the following reliable mean value of fusion enthalpy of *syn*-PS can be obtained:

$$\Delta H_u = 2050 \pm 100 \text{ cal/unit}$$

From the  $T_m^\circ$  value of *syn*-PS (m.p. 269°C, Table 1), the fusion entropy can be directly deduced as:

$$\Delta S_u = \frac{\Delta H_u}{T_m^\circ} = 3.8 \pm 0.2 \text{ cal/K unit}$$

These enthalpy and entropy values can be compared to those previously determined for *iso*-PS (refs. 10–12):  $\Delta H_u = 2150 \pm 100 \text{ cal/unit}$ ,  $\Delta S_u = 4.2 \pm 0.2 \text{ cal/K unit}$  (melt-


**Figure 1** Melting points vs. polymer fraction of mixtures in different solvents: ●, dioctyl phthalate; ▲, diphenylsulphone; ■, □, benzil

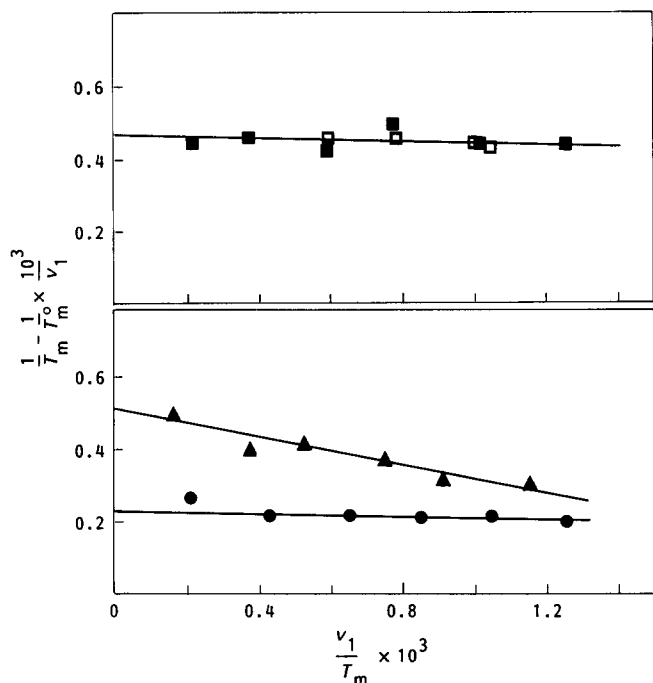


Figure 2 Plot of the data according to equation (1) for the three solvents considered

ing point 240°C). For fusion enthalpy, the difference is within the experimental accuracy, whereas for entropy the value of *syn*-PS should actually be slightly lower than that of *iso*-PS. The practical equality of  $\Delta H_u$  may be somewhat surprising, since the two values correspond to different crystalline structures, with different chain conformation and mode of packing<sup>13</sup> so that the difference in  $\Delta S_u$ , mainly originating from different values of the melting point, accounts for the difference in stability of the two structures.

From a number of d.s.c. measurements, the heat of fusion of pure *syn*-PS, crystallized under different thermal treatments, resulted in a narrow interval around the mean value of the apparent fusion enthalpy of 840 cal/unit, from which a degree of crystallinity of about 40%, in agreement with X-ray measurements<sup>13</sup>, can be calculated. Such a degree is quite similar to that normally found for *iso*-PS. This is also surprising, because with the *syn*-PS sample

investigated, which is of high steric purity, a high crystallization rate was observed, opposite to the low rate typical of *iso*-PS which was measured using samples of comparable high steric purity.

These contrasting properties, found experimentally, should be explained through a better knowledge of structural details relative to crystalline and amorphous phases involved, including those concerning the role of the phenyl side groups, frequently inferred to explain anomalies observed in the behaviour of *iso*-PS.

## CONCLUSION

The enthalpy and entropy of fusion of *syn*-PS and *iso*-PS are very similar, even if their entropy shows some difference probably due to the high melting point of *syn*-PS. Notwithstanding their very different crystallization rates and crystalline structures, the degree of crystallinity of the two stereoisomers reaches the same low value ( $\approx 40\%$ ) in spite of their very high steric purity. Finally, the polymer-solvent mixtures used do not promote any polymorphic transition or crystallinity improvement.

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