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THERMAL PROPERTIES OF SYNDIOTACTIC POLYSTYRENE *

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ABSTRACT

Syndiotactic polystyrene was unknown until about 1986 when it was first synthesized. As with isotactic polystyrene, syndiotactic polystrene is a semicrystalline polymer with a melting point of between 264 and 272°C. The heat of fusion for 100% crystalline syndiotactic polystyrene is 53.2 J g^{-1} with typical syndiotactic polystyrene samples being about 50% crystalline. The heat capacity for syndiotactic polystyrene is the same as that of atactic and isotactic polystyrene. The crystal form of syndiotactic polystyrene changes from orthorhombic to monoclinic when material which has been precipitated from solution is heated. Upon crystallizing from the melt, only the monoclinic form is obtained. The crystallization kinetics have also been studied. Syndiotactic polystyrene crystallizes much more rapidly than isotactic polystyrene. It appears to initially crystallize very rapidly after which a melt recrystallization process occurs.

INTRODUCTION

The early development of polystyrene is, in fact, the development of atactic polystyrene. Figure 1 shows that atactic polystyrene is characterized by the phenyl rings having a random orientation relative to the polymer chain backbone. In the 1950s a method was developed for the synthesis of isotactic polystyrene, which is characterized by having all of the phenyl rings on the same side of the polymer backbone (Fig. 1). The production of isotactic polystyrene gave the first crystallizable form of polystyrene. The relatively high melting point (240°C) gives isotactic polystyrene good solvent resistance and added strength at temperatures above T_g. Attempts to commercialize isotactic polystyrene met with limited success, due in large part to the relatively slow crystallization rate.

In the last three years, several authors have described the preparation of syndiotactic polystyrene [1–4]. Syndiotactic polystyrene differs from the

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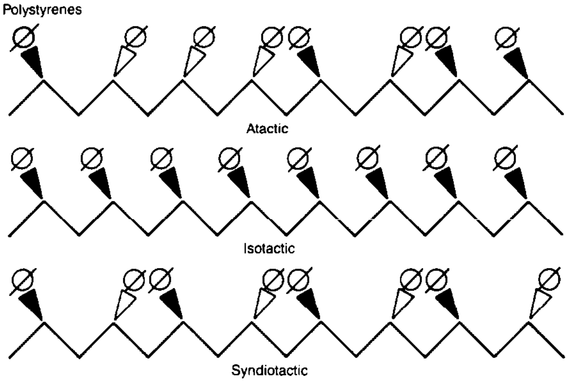

Fig. 1. Polystyrene structures, structures for atactic, isotactic and syndiotactic polystyrene.

other forms in that the phenyl rings alternate regularly from side to side of the polymer backbone (Fig. 1). This regular structure allows syndiotactic polystyrene to crystallize and should give it many of the same advantages (in particular, good solvent resistance) that isotactic polystyrene has. Over the past two years, there has been considerable interest in characterizing syndiotactic polystyrene. This paper discusses our efforts to characterize the level of crystallinity by thermal methods, the crystal structure of the polymer, and the heat capacity of the crystalline and amorphous forms. In addition, we will briefly discuss the crystallization rate of syndiotactic polystyrene.

EXPERIMENTAL METHODS

Samples of syndiotactic polystyrene were supplied by The Dow Chemical Company, Midland, MI. The level of syndiotacticity was determined by NMR and, for all of the samples used in this study, was found to be greater than 95%. All molecular weights reported were determined by high temperature gel permeation chromatography, with atactic polystyrene samples being used as standards. Heat of fusion and crystallization data were obtained using a Du Pont 910 or 912 differential scanning calorimeter (DSC). For heat of fusion data, samples were scanned at 10 °C $\min^{-1}$ from 20 to 300 ° C. For crystallization experiments or experiments attempting to quench the sample, the resin was initially heated to 320 ° C. It was found that this temperature was required to remove all traces of crystallinity from the system.

Heat capacity data were obtained using a Perkin–Elmer DSC-2C, with data reduction being performed using Perkin–Elmer Specific Heat software. The data were collected using a heat step method over 10 ° C steps at a scan rate of 10 ° C $\min^{-1}$ with two-minute isothermal steps before and after the scan. A typical scan sequence would include an empty pan, a sapphire standard for calibration, and the sample. Three heat capacity values were obtained at each temperature.

High-resolution X-ray diffraction data of selected syndiotactic polystyrene samples were obtained using a Huber Guinier X-ray camera in the subtraction mode and asymmetric arrangement. Cu $K\alpha_1$ radiation was used. The X-ray tube was operated at 40 kV, 20 mA and the sample exposure time was ~ 70 h. An internal standard of As_2O_3 was used to calibrate the diffraction peak positions. Diffracted intensities were collected on CEA Reflex 15 single emulsion X-ray film. A K.-E. Johansson densitometer (step size, 20 μm) was used to digitize the diffraction data.

The Dow-developed simultaneous DSC/XRD was used to monitor the effect of temperature on syndiotactic polystyrene crystalline structure. The instrument design consists of an XRD system utilizing Guinier optics and a position sensitive proportional counter (PSPC) in addition to a DSC with both computerized control and data acquisition. The PSPC is held in a fixed position and collects simultaneously 20–25° two-theta of diffracted radiation. Temperature control in the DSC cell is within 0.1°C from 25 to 600°C. Cu $K\alpha_1$ radiation was used. The X-ray tube was operated at 40 kV, 20 mA and the data collection time (for each XRD pattern) was 3 min. The DSC cell was heated at a rate of 1°C min^{-1} from 80 to 290°C. Each X-ray pattern spanned a 3°C temperature range.

RESULTS AND DISCUSSION

The DSC trace for a quenched sample of syndiotactic polystyrene with an M_w of 159000 is illustrated in Fig. 2. The glass transition is observed at about 90°C, slightly lower than the value of 95°C observed for higher

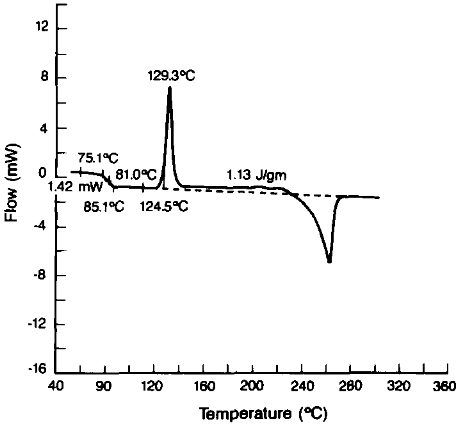

Fig. 2. DSC scan for a sample of syndiotactic polystyrene (M_w = 159000) which has been quenched from the melt.

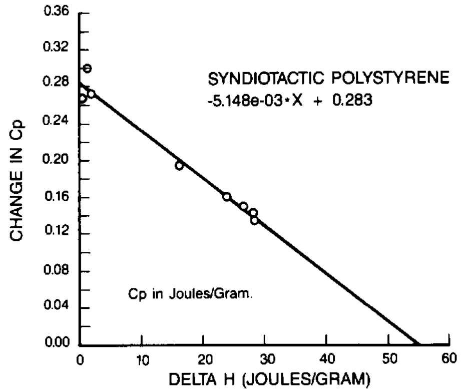

Fig. 3. *C*p change at *T*g versus heat of fusion for syndiotactic polystyrene.

molecular weight samples. The crystallization exotherm maximum is observed at 129 °C and the melting endotherm at 261° C. The peak melting temperature has been found to be as high as 272° C, with values in the neighborhood of 265 ° C being more common.

It is important to be able to determine the level of crystallinity in a syndiotactic polystyrene sample, and a DSC measurement of the heat of fusion would be one of the more convenient methods for this determination. However, it is first necessary to determine the heat of fusion for the completely crystallized polymer. Karasz et al. [5] have demonstrated that for a semi-crystalline polymer, the level of crystallinity may be determined by comparing either the heat of fusion for a sample to the heat of fusion for the completely crystallized material or from a comparison of the change in specific heat at the glass transition for the partially crystalline sample with that of the totally amorphous sample, the latter method giving the fraction of the amorphous phase. A plot of the change in C_p at T_g versus the observed heat of fusion for the same sample should be linear and provide the basis from which the heat of fusion for the 100% crystalline sample can be calculated. Figure 3 is a plot of the change in C_p at T_g vs. the heat of fusion with a straight line fitted to the data. For this particular sample the heat of fusion for completely crystalline syndiotactic polystyrene was found to be 55.0 J g^{-1}. For a series of different syndiotactic polystyrene samples, an average heat of fusion of 53.2 J g^{-1} has been found. In order to check the validity of the method, the same procedure was used to study a sample of isotactic polystyrene, and a heat of fusion of 90.5 J g^{-1} was found, which compares well with a literature value of 86.5 J g^{-1} [6]. Using the value of 53.2 J g^{-1}, it is now possible to determine the level of crystallinity in various samples of syndiotactic polystyrene. "As made" samples generally have a heat of fusion of 30–35 J g^{-1} which indicates a level of crystallinity of 55–65%. Melt crystallized syndiotactic polystyrene has a heat of fusion of

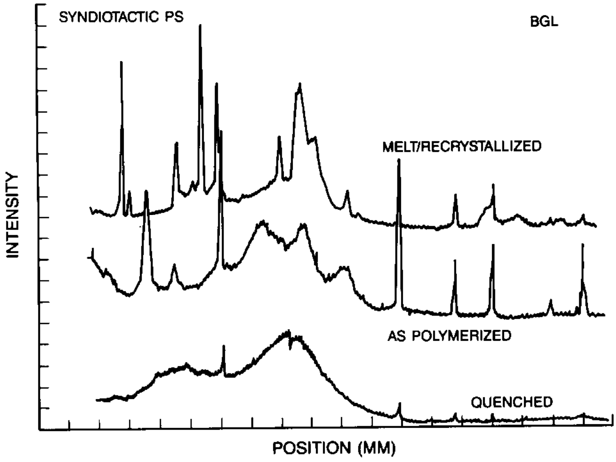

Fig. 4. X-ray patterns for syndiotactic polystyrene.

about 25–28 J g^{-1}, which indicates that the level of crystallinity is 47–53%. This indicates that syndiotactic polystyrene can crystallize to a relatively high level.

We have also examined the crystal structure using X-ray diffraction (XRD). Figure 4 illustrates the room temperature diffraction patterns for syndiotactic polystyrene recrystallized from the melt, for the polymer "as made" and for a quenched sample. Note that the small discrete peaks in the quenched sample are an internal standard (As_2O_3). These peaks also appear in the other two diffraction patterns. Originally we were somewhat surprised to find two different XRD patterns for syndiotactic polystyrene, depending on how the sample was crystallized: an orthorhombic structure for the as polymerized form and a monoclinic structure for the melt recrystallized material [7]. Table 1 lists the unit cell parameters for the two structures.

Subsequent studies on syndiotactic polystyrene demonstrated that the monoclinic structure can be formed by heating a sample containing the orthorhombic structure to temperatures above 175 °C. This structural transformation can be observed using the simultaneous DSC/XRD instrument. XRD patterns of an "as polymerized" sample containing (predominantly)

TABLE 1

Unit cell parameters for syndiotactic polystyrene

Orthorhombic	Monoclinic
a = 8.8 Å	a = 19.8 Å
b = 28.8 Å	b = 12.9 Å
c = 5.1 Å	c = 5.1 Å
	γ = 95°

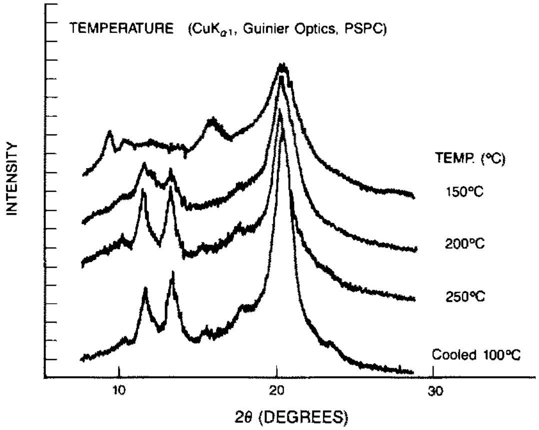

Fig. 5. DSC/XRD patterns of an "as made" syndiotactic polystyrene sample upon heating.

the orthorhombic structure are pictured in Fig. 5 as a function of temperature. Clearly the diffraction patterns which are observed at temperatures below 150 °C are markedly different from those above 200 °C. These data illustrate the transition from the orthorhombic to monoclinic crystal form in syndiotactic polystyrene during heating. However, it appears that this structural transformation is not reversible upon cooling. Recently, we have observed a conversion from the monoclinic form to the orthorhombic form only upon dissolution and subsequent precipitation of the polymer. The DSC scan given in Fig. 6 for an "as made" sample of syndiotactic polystyrene shows an endotherm at about 162 °C, which corresponds to the temperature where the change in structure is observed in the X-ray pattern. A rescan of the same material, now crystallized from the melt, does not show this endothermic event. Based on molecular modeling studies they

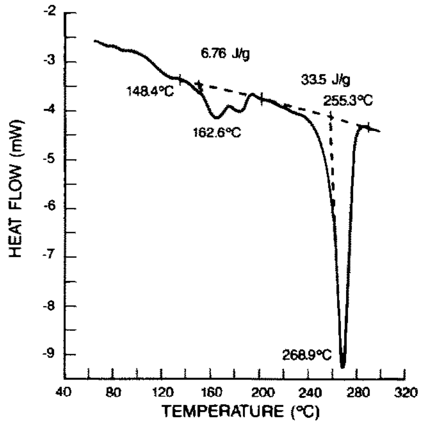

Fig. 6. DSC/SCAN of "as made" syndiotactic polystyrene.

TABLE 2

Comparison of specific heats for atactic, syndiotactic, and isotactic polystyrene [a]

Temp. (°C)	Atactic (Meas)	Atactic [b]	Q SPS (Meas)	Ann SPS (Meas)	Q ISO [b]	Ann Iso [b]
25.0	1.214	1.193	1.241	1.213	1.194	1.189
50.0	1.273	1.300	1.347	1.311	1.301	1.301
125.0	1.851	1.868		1.767		1.765
155.0	1.926	1.944		1.927		1.911
195.0	2.135	2.045		2.084		2.105

[a] Abbreviations: Q = Quenched; Ann = Annealed; SPS = Syndiotactic; ISO = Isotactic.
[b] = See refs. 5 and 8. C_p values in J g^{-1}-°C.

have performed, Doherty and Hopfinger [8] have recently suggested that a conformational change in syndiotactic polystyrene occurs. Their modeling studies suggest that only an all-trans form or a trans-trans-gauche-gauche form are possible, with the all-trans form being the more stable.

We have also made some initial studies of the heat capacity of syndiotactic polystyrene using the DSC method described in the experimental section. Table 2 lists the heat capacity data determined in this work for atactic polystyrene and quenched and annealed syndiotactic polystyrene. Also listed are literature values of atactic polystyrene and quenched and crystallized isotactic polystyrene [5,9]. From the data presented, it is apparent that all three forms of polystyrene have very similar heat capacities.

For isotactic polystyrene, the major problem for commercial development was the slow rate of crystallization. We had found that syndiotactic polystyrene crystallizes more rapidly and thus prompts a study of the crystallization kinetics. Isothermal studies were performed and Avrami plots were made and n values, which are characteristic of the nucleation type and crystal growth geometry, and rate constants were determined [10]. It was found that only over a 5°C range could consistent n values of about 2.5 be obtained. For the most part, it was found that at low (125–135°C) or high (235–260°C) temperatures inconsistent n values were obtained, ranging in value from 2 to 9. The difficulties with constant n values appear to be due to crystal perfection occurring during the crystallization process. Figure 7 shows the X-ray pattern for syndiotactic polystyrene as a quenched sample is heated. At low temperatures, a diffuse scattering pattern (similar to atactic polystyrene) is observed. Presumably this is due to the lower level of crystallinity and small average crystallite size which exists in this sample. However, the XRD pattern sharpens as the temperature is increased, indicating that as the sample is heated further crystallization and crystal perfection occurs. Wunderlich [10] has discussed crystal growth and perfection and suggests that this process occurs on a more regular basis than might be expected. As the temperature of the melt increases, a greater fraction of

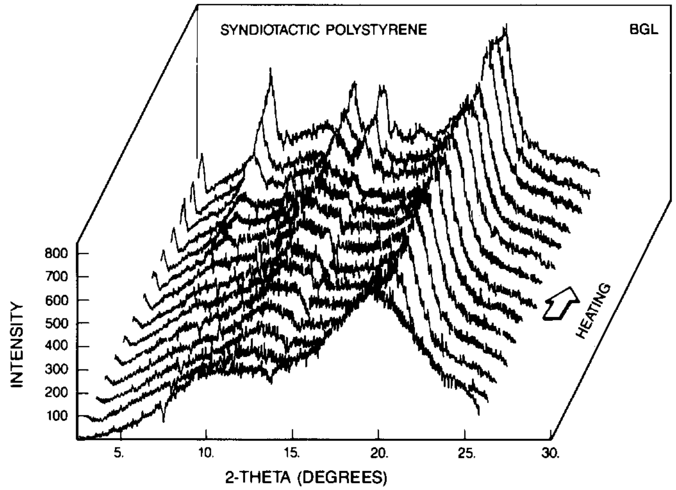

Fig. 7. DSC/X-Ray pattern of syndiotactic polystyrene during crystallization of a quenched sample.

the sample can crystallize including "kinks" in the chain which were excluded from crystallization at lower temperatures. This process permits the growth of larger, more perfect crystallites. For SPS the initial crystallization process is so rapid that crystallites with a high degree of imperfection are formed, so the perfection process can play a more important role in the overall crystallization process.

Because of the difficulties with the Avrami plots, it was decided to perform some nonisothermal crystallization studies. Samples of syndiotactic polystyrene (three different molecular weights, M_w) were either cooled from the melt or melted, quenched, and then heated at various rates. Data for the scan rates and the peak crystallization temperatures are presented in Table 3. On heating of quenched samples, there appears to be little difference

TABLE 3

Non-isothermal crystallization temperatures temperature of crystallization peak maximum

Low Temperatures			
Scan Rate	Molecular Weight ($\times 10^3$)		
	159	349	1100
1	111	133	139
5	121	145	143
10	127	150	153
Low Temperatures			
2.5	234	244	252
5	231	241	248
10	225	236	245

Scan rate in °C $\min^{-1}$

between the 349 000 and the 1 100 000 M_w samples with the 159 000 M_w samples appearing to crystallize more rapidly. At higher temperatures, there is a direct relation between molecular weight and peak crystallization temperature, with the higher molecular weights crystallizing at higher temperatures. We believe this is due to the increase in melt viscosity with molecular weight, the higher molecular weight samples having a higher melt viscosity, hence less mobility and a higher level of order remaining from the melted crystal structure. Thus, when cooled there is less rearrangement necessary upon crystallization; and hence, these samples crystallize more rapidly than lower molecular weight samples.

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