

## Study of the thermal behavior of syndiotactic and atactic polystyrene by Raman spectroscopy

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**Abstract.** The glass properties and semi crystalline properties of polymers are observable by X-ray diffraction. Some previous works <sup>1, 2, 3</sup> were about determination of degree of crystallinity of sPS by various technologies, like for example DSC, XRD and Raman spectroscopy. The purpose of this paper is to show importance of Raman spectroscopy as analytical tool for the study of amorphous and semi-crystalline phase. The polymers on which our research is achieved, is amorphous polystyrene, shortened aPS, and semi crystalline polystyrene, sPS.

### 1 Introduction

A polymer is characterized by one or many phase transitions, as glass transition, crystallization or melting point. Each transition has characteristic temperature, which can be defined by vibrational spectroscopy, differential scanning calorimetry and so on. On other hand, the glass properties and semi crystalline properties of polymers are observable by X-ray diffraction. Some previous works were about determination of degree of crystallinity of sPS by DSC, XRD and Raman spectroscopy.

A lot of properties electrical, chemical, optical or physical can be explained by the chemical structure of polymer. For example, atactic polystyrene and syndiotactic polystyrene present differences about the regularity of their hydrocarbon chain. If the first has phenyl groups randomly distributed on both sides of the chain, the second has got a regular arrangement which the group has alternate positions along the chain. The amorphous or semi-crystalline character depends on reaction of polymerization. Actually, if reaction of polymerization is a radical polymerization, polymer will be amorphous. Whereas, polystyrene made by Ziegler-Natta polymerization is semi crystalline.

We propose to use Raman spectroscopy to characterize the crystallinity of polystyrene, in particular, amorphous and semi-crystalline phase. Usual method like

DSC and XRD will experimented to compare the data obtained with Raman spectroscopy.

### 2 Backgrounds

In the study of polymer, it is more important to measure of the glass transition temperature,  $T_g$ , and melting temperature  $T_m$ . Also, between the glass transition and the melting point, part of the hydrocarbon chain has enough energy to fall into crystalline arrangements. The temperature allowing this crystallisation phenom is noted  $T_c$ . So, the polymer behaviour is fonction of the temperature of treatment. The Figure 1 show behaviour of semi-crystalline polymer, with first field which correponds to glass transition, the second to rubber transtion and the last one is the melt field:

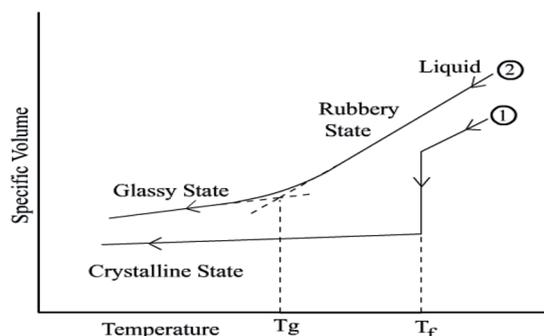


Fig. 1. State diagram of a semi-crystalline polymer

Furthermore, the literature of syndiotactic polystyrene index four polymorphs,  $\alpha$ ,  $\beta$ ,  $\gamma$  et  $\delta$ , can be grouped by pairs, according to the backbone conformation, the ( $\alpha$ ,  $\beta$ ) has a planar all-*trans* “zigzag” conformation whereas the other pair ( $\gamma$ ,  $\delta$ ) have a helical trans-trans, gauche-gauche conformation<sup>4</sup> Figure 2<sup>5</sup>, illustrate the two types of conformation that literature gives:

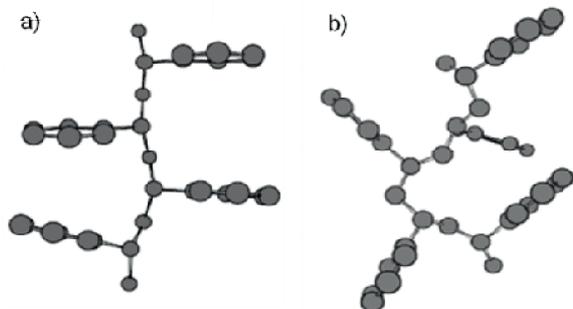


Fig. 2. a) in the  $\alpha$  and the  $\beta$  forms viewed along an axis perpendicular to the chain axis; b) in the  $\gamma$  and the  $\delta$  forms viewed along axis perpendicular to the chain axis

This paper present data observed of different transition phase and crystallinity rate. The purpose is to establish a correlation between Raman spectroscopy, DSC and XRD.

### 3. Experimental methods

#### 3.1 Differential Scanning Calorimetry (DSC)

The sample weight was approximately 15 mg. Only one scan rate was selected, 10 °C/min to assess the effect of recrystallization within the material during the scan (20-300 °C). The cooling is assured by N<sub>2</sub> gaz. In semi-crystalline polymers, DSC gives glass temperature, crystallization and melting point. Furthermore, the crystalline rate can be estimated by DSC using enthalpy.

#### 3.2 X-Ray Diffraction (XRD)

Usual X-Ray Diffraction equipment is used for this experiment, in order to determine cristallinity rate. The range of measurement extends from 10 to 30 degrees. The revolution speed is 1 rps. Experiments of DSC and XRD are made at institute of technology department of “Génie des Matériaux” in Forbach.

#### 3.3. Laser Raman spectroscopy

Raman spectra were taken with 785 nm line of a diode laser. Working at 785 nm eliminate fluorescent phenomenon important in polymers. This equipment is coupled with a microscope, and a 50x objective is used. The temperature can be adjusted between 30 and 300 °C in thermostat oven as shown in Figure 3<sup>6</sup>. All measurements were unpolarized.

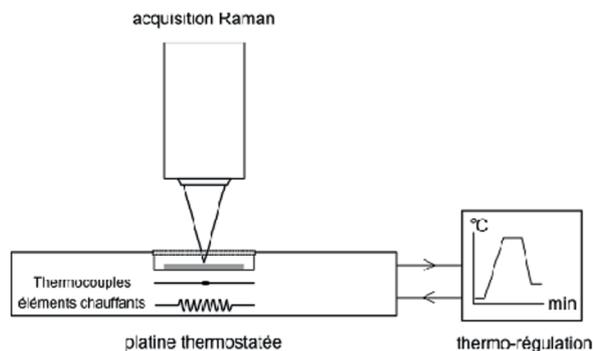


Fig. 3. Thermostat oven with micro Raman Spectroscopy

## 4. Results and discussion

### 4.1 Differential Scanning Calorimetry (DSC)

The first experiment was realized on an atactic polystyrene and a syndiotactic polystyrene. Only one temperature, corresponding to the glass transition is observed. On the second material, three transitions are observed (figure 4), and indexed in the table 1. The first temperature is at 100 °C, and corresponds to the glass temperature. The second is an exothermic peak and correspond to the rubber field, and the last transition is viscous state.

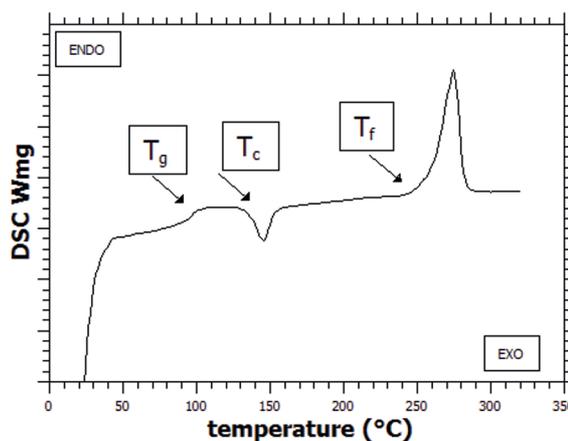


Fig. 4. DSC of sPS material. Arrows show the three different phase transitions in this polymer

Table 1. DSC data obtained for aPS and sPS polymers

	T <sub>g</sub> (°C) <sup>2</sup>	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/K)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/K)
aPS	96	-	-	-	-
sPS	100	146	5	275	22

Using a theoretical enthalpy of 100 % crystalline syndiotactic polystyrene equal to 82,6 J/K<sup>7</sup>, we can deduce the crystallinity of our material

### 4.2. X-Ray Diffraction (XRD)

Seok-Ho Hwang et al.<sup>8</sup> work about mechanical properties of sPS pure and sPS mixed poly(p-phenylene sulfide), they identified various peaks corresponding to crystallite  $\alpha$ , and other for crystallite  $\beta$ , like shown in Figure 7.

Typical X-Ray diffraction peaks of crystallite  $\alpha$  are obtained at  $2\theta = 6.62^\circ, 11.63^\circ, 13.44^\circ, 15.6^\circ$  and  $18^\circ$ . In the same way, the crystallite  $\beta$  is characterized by the peaks at  $2\theta = 6.1^\circ, 12.3^\circ, 18.6^\circ$  and  $20.28^\circ$ .

On XRD measurements, Figure 5, the same peaks are observed, but there is one more at  $29.31^\circ$ . However, for  $15 < 2\theta < 25$ , graph is a little bit ambiguity, because this experiment is made on pellets of syndiotactic polystyrene.

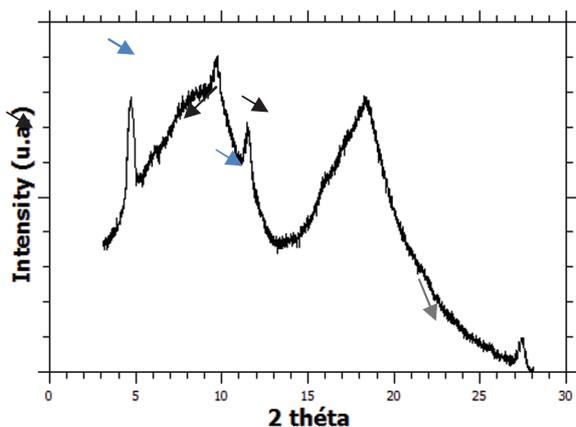


Fig. 5. X-ray diffraction of sPS. Blue arrows indicate different crystallite  $\alpha$  and black arrows correspond crystallite  $\beta$ . Grey arrow indicate one more peak

The XRD of a PS has no peaks as expected in an amorphous polymer.

### 4.3. Laser Raman spectroscopy

#### 4.3.1. Preliminary work

Raman spectra of atactic polystyrene and syndiotactic polystyrene were investigated, in order to determine signature of crystallinity.

The Raman spectrum of atactic polystyrene shows peaks which are different compared to Raman spectrum of syndiotactic polystyrene, as shows in figure 6.

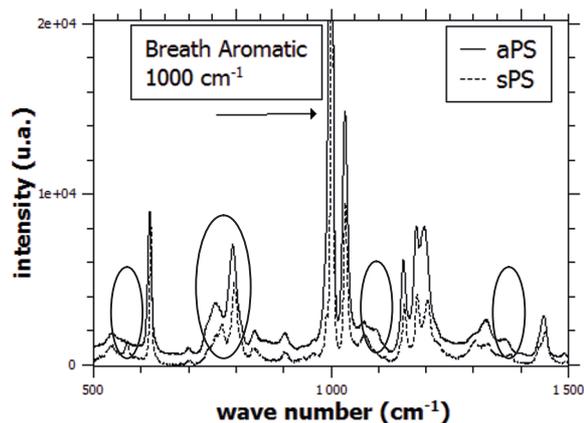


Fig. 6. Raman spectrum of aPS (black) and sPS (dash line). Circles show the main differences between aPS and sPS spectra

At first sight, differences are observed at  $575 \text{ cm}^{-1}$  with a supplementary peak for sPS. The field  $700\text{-}800 \text{ cm}^{-1}$  is really different, as around  $1100 \text{ cm}^{-1}$ , and beyond  $1300 \text{ cm}^{-1}$ .

Using Raman spectroscopy, Kobayashi et al.<sup>9</sup> observed that the  $\nu_1$  vibration is very sensitive to the local backbone conformation resulting in the presence of two distinct peaks at  $770\text{-}773$  and  $796\text{-}802 \text{ cm}^{-1}$  corresponding to all-trans conformations and mixed trans/gauche conformations, respectively.

In Figure 7, the part of Raman spectrum of sPS is given and shows peak position, of all-trans and trans-gauche.

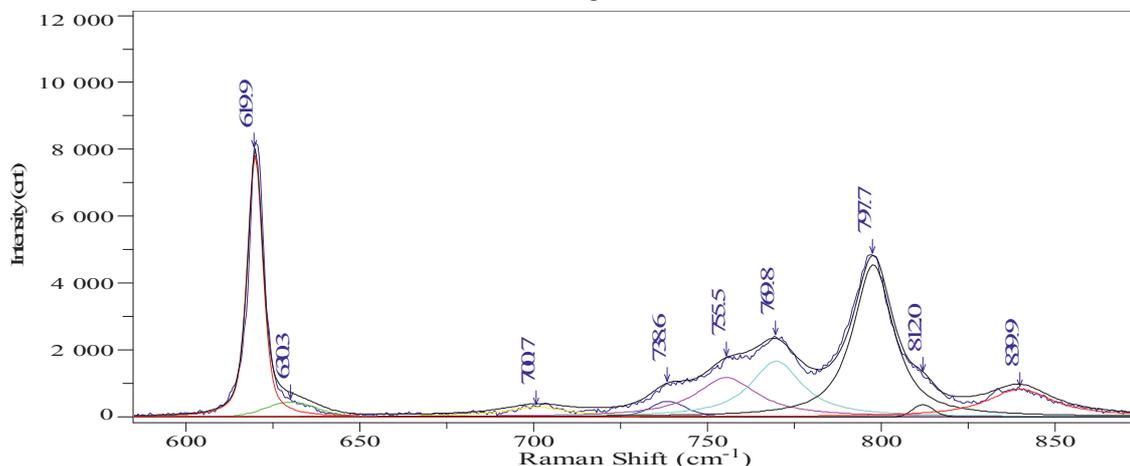


Fig. 7. Fitted Raman spectrum of sPS, from  $600$  to  $850 \text{ cm}^{-1}$  at room temperature

### 4.3.2. Crystallization temperature

In Figure 8, we focus on the spectra part from 700 to 800  $\text{cm}^{-1}$ . The peak observed at 770  $\text{cm}^{-1}$ , which is relating all-trans conformation, increases with temperature. Whereas the peak at 797  $\text{cm}^{-1}$ , which is associated trans-gauche conformation, reduces with temperature:

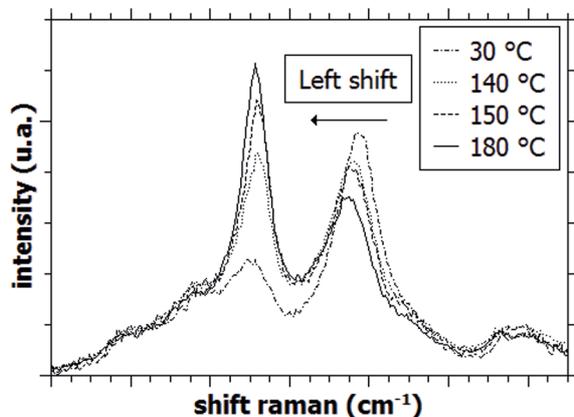


Fig. 8. Raman spectrum of sPS at 30 °C, 140 °C, 150 °C, and 170 °C

Moreover, we observe a shift of the band at 796  $\text{cm}^{-1}$  towards the low frequencies, corresponding to a compression of the liaison. The evolution of these peaks can be made in equation by the relation (1) and (2), which is a ratio of area. Results are represented on Figure 9.

$$R_{\text{all-trans}} = \frac{A_{770}}{A_{770} + A_{797}} \quad (1)$$

and

$$R_{\text{trans-gauche}} = \frac{A_{797}}{A_{770} + A_{797}} \quad (2)$$

We define the peak at 770  $\text{cm}^{-1}$ , as corresponding to all-trans conformation. And the other peak characterizes trans-gauche conformation. So, we can approximate proportion of each conformation in function of the temperature. We observe an intersection between the two equations at 149 °C, which is exactly the temperature of crystallization, given by DSC. On other hand, the change of slope for the both equation begins at 120 °C. This temperature is related to the end of vitreous part.

Consequently, below crystallize temperature, trans-gauche conformation is prevailing, whereas beyond  $T_c$ , all-gauche conformation is predominant. In addition, proportion established by equation (1) and (2), is constant in function of the temperature.

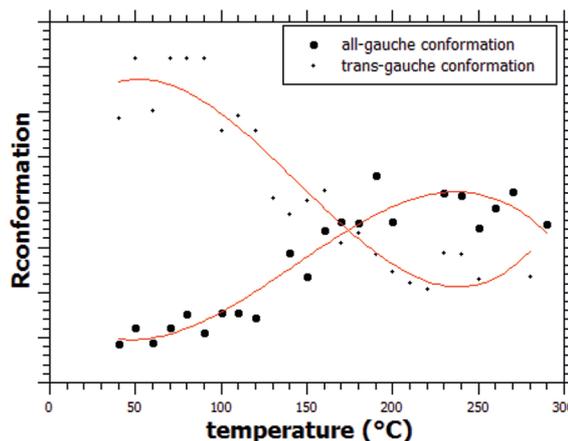


Fig. 9. Proportion of  $R_{\text{all-trans}}$  and  $R_{\text{trans-gauche}}$  as a function of temperature

### 4.3.3. Phase transitions

Five peaks on Raman spectra are interesting for study of the phase transitions, in particular that at 235  $\text{cm}^{-1}$ .

Normalized with the peak at 1000  $\text{cm}^{-1}$ , independent of the temperature, give equation (3):

$$R_{235} = \frac{A_{235}}{A_{1000}} \quad (3)$$

On Figure 10, we observe a linear ratio for temperature from 40 °C to 120 °C. After, a maximum is observed at approximately 135 °C. This temperature corresponds approximately to the crystallization temperature. Then, some intensity is observed without attribution. And finally, another maximum is observed at 270 °C, which is exactly the same temperature as melting temperature found in DSC.

Consequently, we define three temperature ranges, one from ambient temperature to 120 °C, equivalent the vitreous phase, and another field from 270 °C, matching the viscous phase. And between the two, we observe a rubber field. We confirm the results as the literature observations, with the three phase transition (Figure 1).

These observations are confirmed by the same type of ratio, ( $R_i = A_i / A_{1000}$ ), with the peak at 525  $\text{cm}^{-1}$ , which appear only from 120 °C, and with peak at 1316  $\text{cm}^{-1}$ .

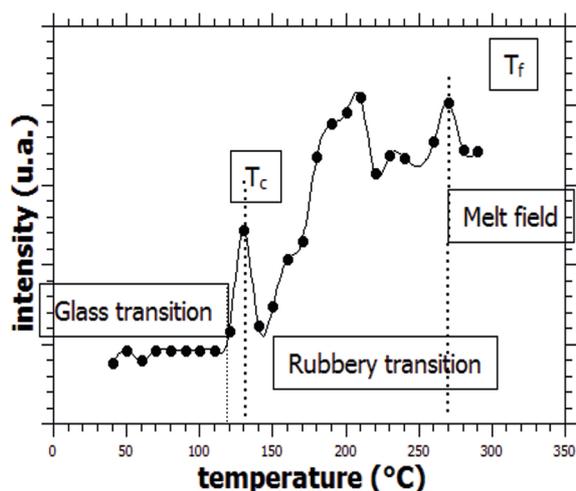


Fig. 10. Evolution of the 235 cm<sup>-1</sup> peak, normalized to the peak at 1000 cm<sup>-1</sup> with temperature.

#### 4.3.4. Crystallinity rate

DSC and XRD give the crystallinity rate, we would like to establish a relationship between this property and Raman spectroscopy. So, we compare the three values obtained by the three different methods.

In DSC, we use theoretical enthalpy to estimate the crystallinity of polystyrene. In XRD, peaks are the consequence of presence crystalline phase. In Raman spectroscopy, we consider the peak at 1316 cm<sup>-1</sup>.

On account of, it is maximal for 275 °C, at melting point, dividing the value at ambient temperature by this value, equation (4), we can approach  $\chi_c$ :

$$\chi_c = (R_c 30\text{ °C} / R_c 275\text{ °C}) * 100 \quad (4)$$

with

$$R_c = A_{1316} / A_{1000} \quad (5)$$

So, the crystallinity is indexed in table 2:

Table 2. Crystallinity rate estimated by DSC, XRD and Raman spectroscopy

DSC	DRX	Raman Spectroscopy
4,1%	6%	4,3%

Current investigation is undergoing to obtain different crystallinity ration.

## 5 Conclusion

In this work, a comparison of Raman spectra of amorphous polystyrene and semi-crystalline polystyrene has been investigated.

Raman bands in the 700 to 800 cm<sup>-1</sup> present peak sensitive to the crystallinity and the conformation. The study in function of temperature allows determining the state diagram of syndiotactic polystyrene. In particular, peaks at 770 and 797 cm<sup>-1</sup> give the crystallization temperature, similarly, the all-trans and trans-gauche conformation have each one a prevalence field according to our work the temperature.

Moreover, the evolution of the three peaks, those at 235, 525 and 1316 cm<sup>-1</sup> give phase transition, glass, rubber and viscous field. The state diagram of semi-crystalline polymer is known by literature, and data obtained by Raman spectroscopy can establish it and can be correlated with DSC and XRD. On other hand, we estimate crystallinity ratio. Investigation is currently done to obtain various crystallinity ratio by annealing in order to confirm our hypothesis.

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