

## **Study of the solution properties of tactic polystyrenes**

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### **Summary**

Viscosity measurements are reported for syndiotactic polystyrenes in a molar mass range from 35,000 to 400,000 g/mol and standard fractions of narrowly distributed atactic polystyrenes in a molar mass range from 50,000 to 600,000 g/mol in trichlorobenzene at 135 °C. The correlation between molar mass and intrinsic viscosity of different polystyrene samples was investigated as well as their solution properties. The results demonstrate that the intrinsic viscosity of polystyrene in thermodynamically good solvents is independent of the type of tacticity of the polystyrenes investigated here. The dilute solution properties were compared with those for isotactic and atactic polystyrenes. The small differences in their solution viscosities may occur due to the different molar mass distributions of differently synthesized samples.

### **Introduction**

During recent years essential progress in Ziegler-Natta polymerization catalysis has been achieved by developing homogeneous group 4 metallocene catalysts combined with methylaluminoxane (MAO) (1). As an example, homogeneous titanium catalysts promote the polymerization of styrene to highly syndiotactic products (sPS) (2), whereas isotactic polystyrene (iPS) is yielded by employing heterogeneous titanium catalysts combined with alkylaluminium compounds. Recently we have developed catalysts of unprecedentedly high activity for the production of sPS (3).

Although in solid phase sPS is remarkably different from atactic polystyrene (aPS), to date no relationship between the viscosity of sPS solutions and molar mass has been found in the literature. Therefore there is some interest in answering the question as to which solution properties are exhibited by polystyrenes of different tacticities.

Table 1 contains some important technical data, such as the glass transition temperature  $T_g$ , melting temperature  $T_m$ , density, solubility, and degree of tacticity, which differ significantly from one another.

Table 1: Characteristics of polystyrenes differing in tacticity.

	$T_g$ (°C)	$T_m$ (°C)	density g/cm <sup>3</sup>	soluble in	degree of tacticity
sPS	100	270	1,12	TCB <sup>1</sup> , 135°C	96
iPS	100	230	1,08	toluene, 30°C	varied
aPS	100	217	1,06	toluene, 25°C	0

<sup>1</sup> trichlorobenzene (TCB)

## Experimental part

Toluene was purified by boiling over sodium/potassium alloy. Styrene was dried by stirring over CaH<sub>2</sub>. Cyclopentadienyltitaniumtrichloride (CpTiCl<sub>3</sub>) was purchased from Aldrich and recrystallized from toluene/pentane. Cyclopentadienyltitaniumtrifluoride (CpTiF<sub>3</sub>) and MAO were kindly supplied by H. W. Roesky et al. and H. Sinn et al. respectively (4), (5). The syndiospecific polymerization of styrene was performed by sequentially introducing toluene, a solution of MAO in toluene, styrene, and CpTiCl<sub>3</sub> into a thermostated glass reactor. The reaction was terminated by the addition of acidified ethanol. After washing with ethanol the sPS was dried in vacuo. The melting points of the s-PS samples were determined from the second heating runs by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-4 at a heating rate of 20 K/min. A Waters 150-C ALC was used to determine the weight average molecular mass by gel permeation chromatography (GPC). Solutions of sPS in 1,2,4-trichlorobenzene were passed through the columns at 135°C with a flow rate of 1 ml/min. Standard atactic polystyrene samples were applied for the calibration. The syndiotacticity was greater than 96 % as tested for all samples (dissolved in mixtures of 1,1,2,2-tetrachloroethane/1,1,2,2-tetrachloroethane-d<sub>2</sub>) by <sup>13</sup>C NMR on a Bruker MSL 300 spectrometer.

The atactic polystyrene standard samples were purchased from Pressure Chemical Co., Pittsburgh (USA). The samples had a narrow molar mass distribution ( $M_w/M_n = 1.06-1.30$ ) and the detailed characterisation data for these polymers from light scattering and viscometry measurements are described elsewhere (6).

The intrinsic viscosities for the samples were measured in trichlorobenzene (TCB) at 135°C using an Ubbelohde capillary viscometer. Each polystyrene solution underwent hot filtration and tempering for 15min before being measured.

## Results and Discussion

Table 2 summarizes the polymerization conditions and results of syndiospecific polymerization of styrene.

Table 2 Polymerization of styrene by  $\text{CpTiCl}_3/\text{MAO}$

sample No.	Catalyst	[Ti] (mol/l)	$T_p$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$M_w$ (g/mol)
1	$\text{CpTiCl}_3$	$2.5 \cdot 10^{-4}$	10	101	261/268	390000
2	$\text{CpTiCl}_3$	$2.5 \cdot 10^{-4}$	30	103	263/266	230000
3	$\text{CpTiCl}_3$	$2.5 \cdot 10^{-4}$	50	102	258/266	115000
4	$\text{CpTiF}_3$	$2.5 \cdot 10^{-5}$	70	102	247/258	35000

polymerization conditions:  $n_{\text{Al}}/n_{\text{Ti}} = 300$ ; toluene: 20 ml; styrene: 20 ml. [Ti]: amount of catalyst in mol of titanium.  $T_p$ : polymerization temperature.  $T_g$ : glass transition temperature of the sPS by DSC.  $T_m$ : melting temperature of the sPS by DSC.  $M_w$ : weight average molar mass of the sPS by GPC.

In order to prepare the required sPS samples of different molecular mass, we chose  $\text{CpTiX}_3/\text{MAO}$  (Cp = Cyclopentadienyl; X = Cl, F; MAO = methylaluminoxane) as the polymerization catalysts since they yield polystyrenes of decreasing molar mass when the polymerization temperature is increased. According to recent research the exchange of the chloro ligands in  $\text{CpTiCl}_3$  for fluoro ligands leads to an enormous increase in the polymerization activity defined as the polymer yield divided by the amount of the catalyst and polymerization time (3). For this reason the concentration of the catalyst applied was reduced by one order of magnitude in the case of  $\text{CpTiF}_3$ .

The characterization of sPS is complicated due to its insolubility in common solvents such as toluene. Therefore the measurements of the intrinsic viscosities had to be performed in TCB at  $135^{\circ}\text{C}$ . TCB is a thermodynamically good solvent at this elevated temperature. After the measurements the gelation behaviour was observed upon cooling the solutions to room temperature.

Figure 1 depicts the results of a syndiotactic and an atactic polystyrene sample measured in TCB at  $135^{\circ}\text{C}$ . The specific viscosity divided by the concentration is plotted versus the concentration. The experimental conditions applied yield a reproducible linear relationship between  $\eta_{\text{sp}}/c$  and  $c$ .

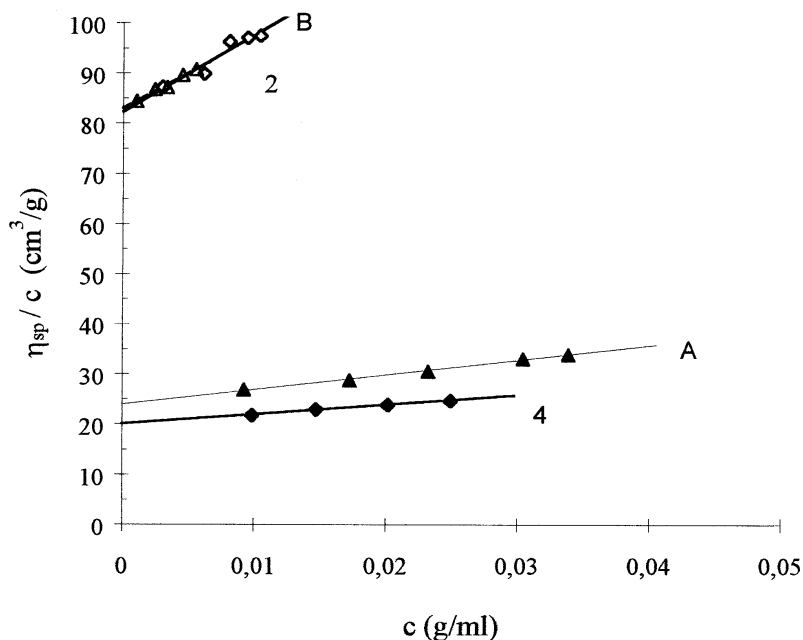


Fig. 1. Plot of  $\eta_{sp}/c$  vs.  $c$  for sPS (sample 4, 2) and aPS (A, B) with the molar mass 35000, 261000 and 46000, 260000 g/mol in trichlorobenzene (TCB) at 135°C.

Table 3 lists the values of the intrinsic viscosity  $[\eta]$  measured in TCB at 135°C and the molar mass  $M_w$ . We have calculated the molar masses  $M_w$  in table 2 with the equation [1] performed for aPS in orthodichlorobenzene at 135°C (7). The molar masses were comparable with those obtained by the GPC. The syndiotactic and the atactic polystyrenes had analogous intrinsic viscosities reflected in the molar masses.

Tab. 3: Results of the polystyrene samples measured.

	Sample	$[\eta]$ ml/g	$M_w$ by [1] g/mol	$M_w$ by GPC g/mol
sPS	4	20	35000	35000
	3	56	150000	115000
	2	83	261000	230000
	1	115	415000	390000
aPS	A	24	46000	
	B	83	260000	
	C	140	546000	

We established a high number of  $[\eta]$ - $M$ -relationships (6), (8), (9) for aPS in toluene, cis-decalin and trans-decalin over a broad range of molar mass from 800 to  $23 \cdot 10^6$  with narrow molar mass distributions at 25 °C. Brandrup (10) and Gianotti (7) published  $[\eta]$ - $M$ -equations for the calculation of the molar mass of aPS and sPS, respectively. We

determined the molecular masses of our aPS and sPS samples by GPC and viscosity measurements under constant conditions (TCB, 135 °C) and calculated the values of  $M_w$  by means of the following relationships (7), (6):

$$[\eta] = 0,01183 \cdot M_w^{0,71} \text{ (orthodichlorobenzene, 135 °C)} \quad [1]$$

$$[\eta] = 0,00862 \cdot M_w^{0,74} \text{ (toluene, 25 °C)} \quad [2]$$

Comparing the results it is evident that the molar masses calculated by Gianotti's equation [2] are in accord with our figures obtained by GPC.

Figure 2 is a double logarithmic plot of the intrinsic viscosity  $[\eta]$  versus mass-average molar mass  $M_w$  for polystyrene differing in tacticities. We compare the experimental results with the data for atactic (6) and for isotactic polystyrene (11).

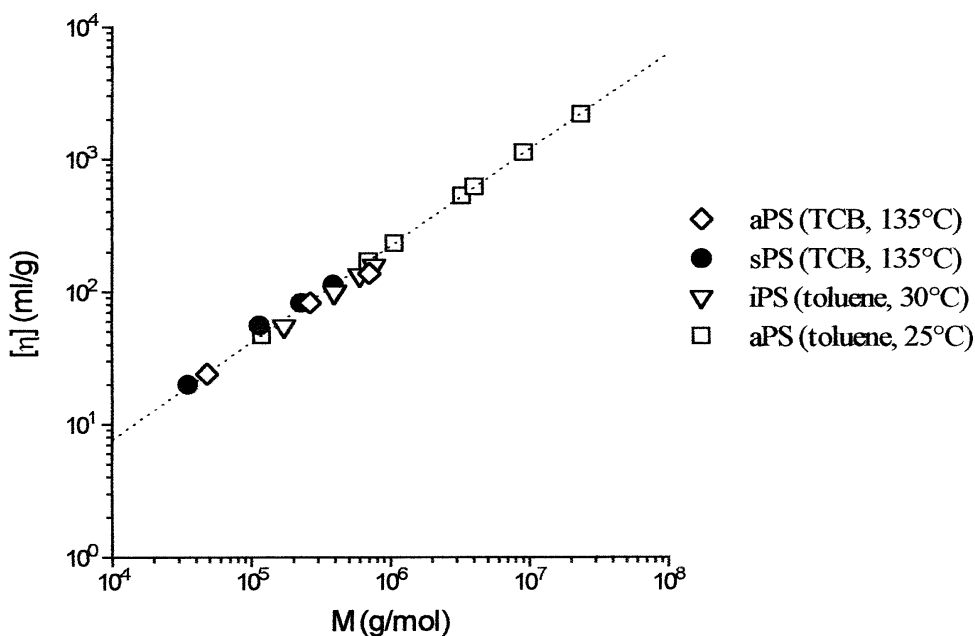


Fig. 2. Intrinsic viscosity  $[\eta]$  as a function of mass-average molar mass  $M_w$  of polystyrene with different tacticities in toluene at 25, 30°C and trichlorbenzene (TCB) at 135°C, respectively.

The data plotted in Fig.2 show that we obtained comparable slopes for all the various polystyrenes. From these findings it can be inferred that the solution structures are similar for all the polymers tested suggesting that they do not differ with respect to their hydrodynamic volume. But one can only assume an independence of hydrodynamic volume if advanced measurements were carried out for sPS. Further measurements for examples light scattering or osmometry were difficult because the sPS was only soluble in TCB at 135°C.

Our results extend those of G. Natta et al. (12) and Danusso et al. (13) who reported that there is no essential difference in the  $[\eta]$ -M-relationship for aPS and iPS.

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