Influence of Tacticity on the Rheology of Syndiotactic Polypropylene

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ABSTRACT

The development of new, metallocenes and post-metallocenes catalysts has allowed in recent years the formulation of new classes of crystalline polyolefines where the typical mechanical properties of crystalline materials (high rigidity and high stress to break) are associated with those of an elastomer (high deformability, high ductility). The study of the rheology of polyolefins based on homogenous metallocenic catalyst has been mainly devoted to the understanding material process performance. However, rheology is a useful tool to highlight the details of the polymer microstructure, such as the chemical stereo-regularity or the degree of chain branching. In this work, we have examined the relation between rheology and molecular structure (tacticity) of a series of syndiotactic polypropylenes (sPP) with different degrees of tacticity. Small-amplitude oscillatory rheometry tests were performed in the melt phase using an ARES rheometer. In this way, the plateau modulus, and consequently the molecular weight between entanglements could be calculated by different methods. The results are discussed in terms of their dependence upon the degree of tacticity of the polymer chain.

INTRODUCTION

Mechanical properties like high rigidity, high stress to break and elastomeric properties like high deformability and ductility have made the crystalline elastomers an attractive and promising class of innovative materials for applications in different areas[1-3].

Among crystalline polyolefins, syndiotactic polypropylene (sPP) has shown interesting and unexpected elastic properties[1]. In the case of sPP, the crystallization behavior is strictly related to the degree of tacticity of the polymer[4], that is, to the local molecular architecture. In turn, a change in tacticity generates changes in the molecular weight between entanglements, M_e, of the polymer in the melt phase[5]. Since M_e is directly related to the viscoelastic plateau modulus of the melt[6], it is expected that information on the degree of tacticity can be extracted from linear viscoelastic measurements in the melt state. This experimental route has been already used in the past. In particular, for the case of polypropylene, Eckstein[7]et al., 1998 showed that the M_e value of syndiotactic PP determined from plateau modulus measurements is considerably different from that obtained for both isotactic and atactic samples. More generally, dramatic differences in the melt viscoelastic response between sPP and the corresponding isotactic and atactic polymers can be found in the literature[8].

In this work the linear viscoelastic response of a series of syndiotactic polypropylenes of varying tacticity has been studied by using oscillatory rheometry. The plateau modulus of the samples has been determined by standard calculation methods thus allowing for the determination of the entanglement molecular weigth. The latter has been compared to the stereoregularity properties of the different samples.

MATERIAL AND METHODOLGY

Samples of sPP with different degrees of tacticity were used for the viscoelastic study. The relevant properties of the polymers are reported in Table 1. The samples labelled Spp-8 and Spp-8 are commercial polymers (supplied by Montell Technology) The others come from laboratory synthesis using metallocene catalysts[9]. It can be noted from Table 1 that samples are characterized by varying degrees of tacticity (rrrr), melting temperature (T_m) and molecular weight (M_w).

All viscoelastic tests were performed on an ARES rotational rheometer (TA Instruments) equipped with 8 mm diameter parallel plate geometry.

Dynamic frequency sweep tests were performed at different temperatures for all polymer samples after confirming the linearity by dynamic strain sweep tests. At the lowest temperatures, where crystallization can take place, the "Multi Wave Test" mode of the instrument was used[10] in order to minimize the experimental time and avoid the crystallization-induced changes in the viscoelastic properties.

Table1. List of polymer samples and properties.

Polymer samples	Tacticity [rrrr] (%)	T_m (°C)	M_w (g/mol)
sPP-3	93.0	149	213000
sPP-8	87.0	136	509000
sPP-9	78.0	124	193000
sPP-11	70.6	100	297000
sPP-12	60.1	77	241000

RESULTS AND DISCUSSION

Viscoelastic master curves for the samples were determined at the reference temperature of 200°C. In all cases, master curves were obtained by applying Time Temperature Superposition (TTS) to data obtained at different temperatures. The vertical shift correction was also applied by using the temperature dependence of the density for sPP as determined by Royo et al [13].

Two typical examples of linear viscoelasticity master curves of the sPP samples are shown in Figs 1-2. In Figure 1, the viscoelastic response of sPP-3 is reported. In this case, due to the high melting temperature, the plateau region could not be reached, and only the modulus cross-over could be observed. Conversely in Figure 2, which refers to sample sPP-12, measurements could be extended to much lower temperatures, thus allowing for the determination of the whole plateau region. For the other samples (not shown here) intermediate results were found.

The determination of the plateau modulus was accomplished with different methods, as suggested by the literature[11], depending on the extension of the experimentally determined viscoelastic response. In the case where only the cross-over modulus could be determined, the plateau modulus was obtained from the empirical relation[12]:

$$\log\left(\frac{G_N^0}{C_{co}}\right) = 0.38 + \frac{2.63\log\left(\frac{M_w}{M_n}\right)}{1+2.54\log\left(\frac{M_w}{M_n}\right)} \qquad (1)$$

Where G_N^0 is the plateau modulus, G_{co} the cross-over modulus, and (M_w/M_n) is the polydispersity index (PI).

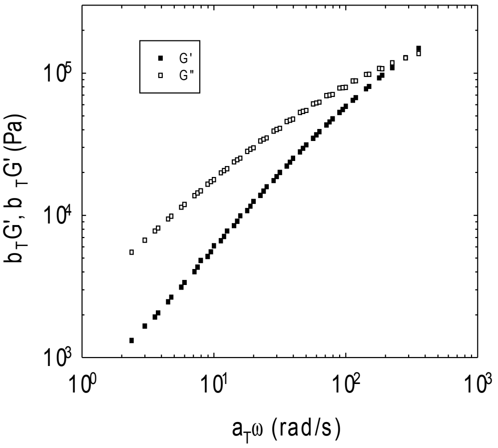

Figure1. Linear viscoelasticity of sPP-3 at 200°C.

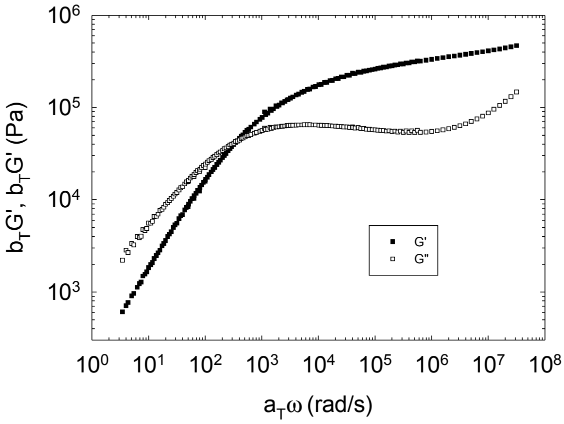

Figure 2. Linear viscoelasticity of sPP-12 at 200°C.

If data are sufficiently extended so as to include the relative loss modulus maximum, direct integration of the loss modulus can be used:

$$G_N{}^0 = 4/\pi \int_0^{\omega_{\max}} G'' d\ln\omega = 4/\pi \int_0^{\omega_{\max}} G''/\omega d\omega$$

(2)

In this case, the simplified version of the integral method is used[5], which assumes symmetry of the *G"* curve around its maximum, thus avoiding integration over the problematic high frequency region.

Finally, if the whole plateau region is available (such as in the case of Figure 2), the most reliable method of picking the plateau modulus as the elastic modulus corresponding to the minimum of $\tan\delta = G''/G'$, can be applied.

Once the plateau modulus is calculated from one of the above mentioned methods, the molecular weight between entaglements, M_e, can be obtained as:

$$M_e = \frac{\rho RT}{G_N^0} \quad (3)$$

where ρ is the mass density, *R* the universal gas constant and *T* the absolute temperature. Values of the plateau moduli obtained from the different methods and of the corresponding M_e are summarized in Table 2 for all samples.

Table-1: List of polymer samples and their properties

Sample	[rrrr] %	cross-over		*G"* integration		tanδ minimum	
		G_N^0 (Pa)	M_e (Da)	G_N^0 (Pa)	M_e (Da)	G_N^0 (Pa)	M_e (Da)
sPP-3	93.0	1.35×10^6	2080	/	/	/	/
sPP-8	87.0	9.60×10^5	2920	/	/	/	/
sPP-9	78.0	4.99×10^5	5610	/	/	/	/
sPP-11	70.6	5.88×10^5	4760	6.62×10^5	4230	/	/
sPP-12	60.1	3.54×10^5	7914	3.18×10^5	8820	3.32×10^5	8430

The dependence of the molecular weight between entanglements upon tacticity is also graphically reported in Figure 3. It is apparent that M_e is extremely sensitive to the degree of stereo-regularity of the polymer chain. In particular, an increase of the molecular weight between entanglements is observed upon decreasing the degree of syndiotactic tacticity. This result quantitatively confirms the more qualitative indication previously found[7].

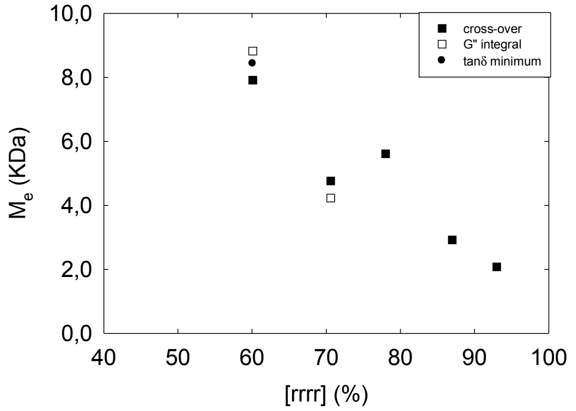

Figure 3. Relationship between tacticity and entanglement molecular weight at 200°C.

CONCLUSION

The linear viscoelastic measurements performed on sPPs of different stereoregularity show that the plateau modulus, and therefore the molecular weight between entanglements, significantly depend upon on the degree of tacticity of the polymer chain. In particular it was shown that M_e decreases with increasing the degree of tacticity. The results demonstrate that viscoelasticity is a powerful tool determines the local details of the molecular architecture of crystalline elastomers.

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