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Relation between *PVT* measurements and linear viscosity in isotactic and syndiotactic polypropylenes

Elena Rojo, Mercedes Fernández, Maria Eugenia Muñoz, Anton Santamaría*

Department of Polymer Science and Technology and POLYMAT, Faculty of Chemistry, University of the Basque Country,
P.O. Box 1072, E-20080 San Sebastian, Spain

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Abstract

Pressure–Volume–Temperature (*PVT*) data of an isotactic and a syndiotactic PP are fitted to a modification of the Simha–Somcynsky equation of state (S–S), to calculate characteristic parameters, such as V^*, T^*, P^* and the solubility parameter δ. The hole fraction of the S–S model and the free volume are deduced from these parameters. The application of a modified Doolittle equation and a modified Berry–Fox equation to estimate viscosity, leads to extract novel conclusions on the differences between both types of PPs. An equation which accounts for the effect of temperature on the characteristic ratio of syndiotactic PP is presented.

Keywords: Characteristic ratio; Free volume; Syndiotactic polypropylene

1. Introduction

The knowledge of *PVT* behaviour is important, because many features of polymers depend on pressure and on the associated changes in volume. Besides the technical importance of determining the specific volume as a function of pressure and temperature in injection moulding process, *PVT* data allow to obtain reduced equations of state, cohesive energy, internal pressure and free volume, contemplated in the theories of molecular liquids. The pioneering work of Batschinski [1] showing the variation of viscosity with specific volume is one of the basis for well known papers, like those of Doolittle [2], Williams et al. [3] and Hildebrand [4], devoted to correlate viscosity and free volume. This subject currently deserves a substantial interest in the field of polymer melts [5–12].

In the particular case of polypropylene (PP), the recent use of metallocene or single site catalysts lets to produce highly syndiotactic samples. The almost perfect stereoregularity reached, gives rise to a peculiar viscoelastic response; in particular syndiotactic polypropylenes (sPP) exhibit Newtonian or linear viscosities about 10 times larger than isotactic samples (iPP) [13,14].

On the other hand, few papers refer to *PVT* measurements of syndiotactic PPs. Some experimental *PVT* data are given in the literature [15–18], but, as far as we know, only two papers [19,20] take advance of a equation of state model to obtain the characteristic parameters P^*, T^* and V^*, from which the cohesive energy and the solubility parameter δ can be determined: in both papers the Flory–Orwoll–Vrij free volume theory [21] is used. We also remark that a PALS (positron annihilation lifetime spectroscopy) study [22] gives data of the mean local free volume of syndiotactic PP, although these are not combined with *PVT* data.

This work is organised as follows: *PVT* data of an isotactic and a syndiotactic PP are analysed using the Simha–Somcynsky equation of state [23], modified by Utracki and Simha [10], which allows to calculate V^*, T^*, P^* and δ. From this model we also obtain other thermodynamical parameters, such as the hole fraction of the Simha–Somcynsky [23] model and the free volume. Both the parameters are used to determine the linear

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* Corresponding author. Tel.: +34 943 018184; fax: +34 943 015270.
E-mail address: antxon.santamaria@ehu.es (A. Santamaría).

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viscosity, applying, respectively, a modified Doolittle equation [12] and a modified Berry–Fox equation [11]. Novel conclusions on the differences between both types of PPs are attained from the application of these models.

2. Experimental part

A syndiotactic polypropylene from Fina, as well as a commercial isotactic polypropylene provided by Repsol YPF have been investigated. The molecular characteristic of the samples are presented in Table 1.

PVT behaviour was measured in a *PVT* apparatus of the piston die technique made by Haake. Measurements were carried out using the isobaric cooling mode procedure in the pressure range of 200–1600 bar using a cooling rate of 5 °C/min. The test was repeated for number of times necessary to make sure a volume difference $\leq 0.05\%$ between two measurements.

Dynamic or oscillatory measurements in the linear viscoelastic regime were carried out in a ARES (Advanced Rheometric Expansion System) in the temperature range 130–190 °C at ambient pressure. The experimental error was checked by repeating the measurements at least four times: the repeatability was within 3%.

The real part of the complex viscosity η', plotted as a function of frequency, at different temperatures, is displayed in Fig. 1. The well-known Briedis–Faiteĺson model was used to calculate the Newtonian viscosity η_0:

$$\eta' = \eta_0/(1+(\omega\tau_0)^{\alpha}) \tag{1}$$

where η_0 is the linear or Newtonian viscosity, τ_0 a relaxation time and α a non-linearity index. The standard deviation was $\sigma < 0.005$.

Table 1
Molecular characteristics of the investigated polypropylenes

	M_w (g/mol)	M_w/M_n	mmmm%	rrrr%
iPP	22,4300	4.2	93	
sPP	18,1300	3.95		77

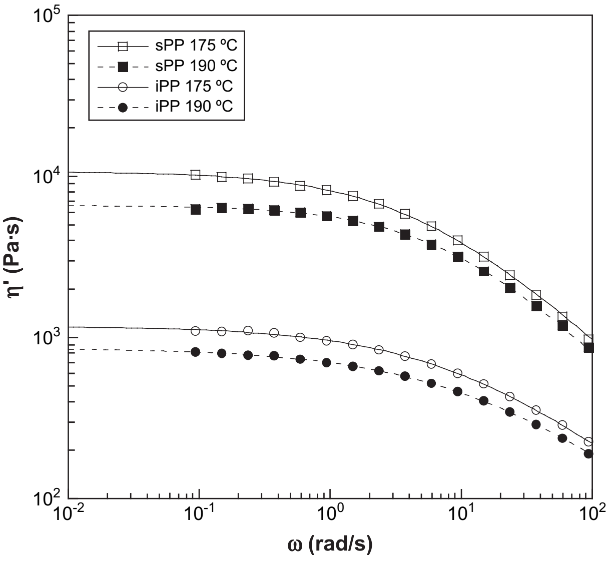

Fig. 1. The real part of the complex viscosity as a function of frequency at $T = 175$ and 190 °C (circles are used for iPP and squares for sPP). The lines correspond to the Briedis–Faiteĺson model (see Section 2). Similar results are obtained for the rest of temperatures ranging from 130 to 190 °C.

3. Results and discussion

Fig. 2 shows the specific volume as a function of temperature, at a constant pressure $P = 400$ bar. The glass transition temperature and the crystallization process of both, isotactic and syndiotactic PPs, are observed. For the purposes of our work, the relevant data are those obtained in the molten state. Similar results are obtained in isobaric cooling experiments at different pressures (see Section 2), which allow to determine the specific volume at atmospheric pressure, via extrapolation of the Tait equation [24].

The specific volume at atmospheric pressure as a function of temperature is included in the inlet of Fig. 2. Experimental data are fitted to Simha–Somcynsky approximation at zero reduced pressure [23]:

$$\ln \tilde{V} = a_0 + a_1 \tilde{T}^{3/2} \tag{2}$$

where $\tilde{V} = V/V^*$ and $\tilde{T} = T/T^*$ are reduced variables defined according to the equation of state models for dense liquids [21]. According to recent results obtained by Utracki and Simha [10], the following values are taken for the adjustable parameters: $a_0 = -0.10346$ and $a_1 = 23.854$. The characteristic volume V^* and the characteristic temperature T^*, obtained from the fitting to experimental values of Fig. 2, are presented in Table 2. The Simha–Somcynsky equation of state in the full range of pressures is used to evaluate the characteristic pressure P^*, also shown in Table 2:

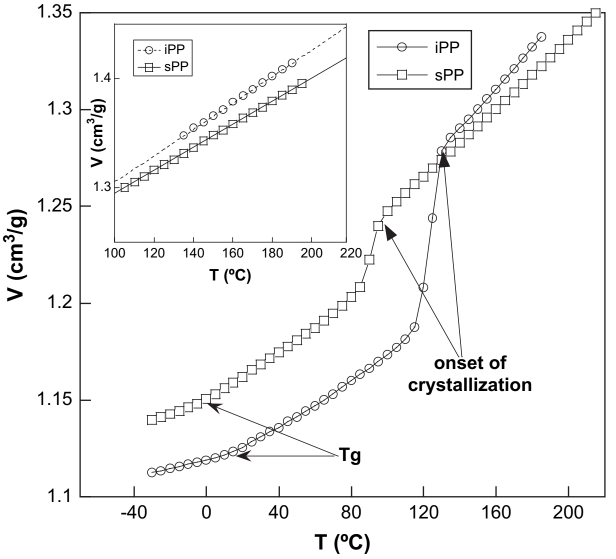

Fig. 2. The specific volume as a function of temperature at a pressure of 40 MPa. The glass transition and crystallization temperatures are marked. The specific volume at the atmospheric pressure, determined via extrapolation of the Tait equation and adjusted to the Simha–Somcynsky model (see Section 3), is shown in the inlet. Same symbols as in Fig. 1.

Table 2
Thermodynamical parameters obtained using Simha–Somcynsky equation of state

	P^* (MPa)	V^* (cm^3/g)	T^* (K)	M_0 (g/mol)	δ (MPa)$^{1/2}$
iPP	555.2	1.1883	9009	38.6	15.84
sPP	573.8	1.1951	9533	39.3	16.53

$$\ln \tilde{V} = a_0 + a_1\tilde{T}^{3/2} + \tilde{P}[a_2 + \tilde{T}^2(a_3 + a_4\tilde{P} + a_5\tilde{P}^2)] \tag{3}$$

The following numerical values have been proposed: $\tilde{P} = P/P^*$ and $a_0 = -0.10346$, $a_1 = 23.854$, $a_2 = -0.132$, $a_3 = -333.7$, $a_4 = 1032.5$, $a_5 = -1329.9$.

The employed equation of state predicts the following expression [25–27] for the molecular weight of the statistical (or effective) segment M_0, in the case of high molecular weight systems:

$$M_0 = \mathrm{R}T^*/3P^*V^* \tag{4}$$

On the other hand, the Simha–Somcynsky theory provides an expression for the cohesive energy density, $\tilde{U}$, [28]:

$$\tilde{U} \equiv U/P^*V^* = -(1/2)y(y\tilde{V})^{-2} \tag{5}$$

where U is the internal energy and y the occupied site fraction.

Then the solubility parameter δ can be obtained by considering that:

$$\delta^2 = \mathrm{CED} = \mathrm{C\tilde{E}D}P^*; \quad \mathrm{C\tilde{E}D} = \tilde{U}/\tilde{V} \tag{6}$$

CED is the internal energy of a given liquid per unit volume.

The corresponding values of the solubility parameter are included in Table 2. Actually this table is a compendium of the respective thermodynamical parameters of isotactic and syndiotactic PPs, corresponding to Simha–Somcynsky equation of state. The molecular weight of the effective segment M_0 (proportional to the lattice cell volume) is practically the same for both polypropylenes. In fact the most significant difference concerns the solubility parameter (related to the cohesive energy density as shown in Eq. (6)), which is higher for the syndiotactic sample, in agreement with the data obtained by Maier et al. [19] and Menke et al. [20], using the Flory–Orwoll–Vrij equation of state. The solubility parameter is directly proportional to the density [21]. As can be deduced from the results shown in Fig. 2, the densities of our samples (at $T = 200$ °C and atmospheric pressure) are $\rho_{\mathrm{iso}} = 0.700$ g/cc and $\rho_{\mathrm{syndio}} = 0.717$ g/cc; these values can be compared with δ values of Table 2. It is seen that δ increases with ρ, although a linear dependency between both the parameters is not observed.

Within this context, the viscosity–density relationship, which is on the basis of the work of Batschinski [1], opens the door to the liaison between *PVT* measurements and viscosity. As a first approach, it can be said that the high viscosity of syndiotactic PPs, with respect to isotactic PPs, mentioned in the Section 1, is a consequence of the different *PVT* behaviour found for both polypropylenes. In particular, the low specific volume values and high solubility parameter values of syndiotactic sample lead to envisage an enhanced viscosity for this sample.

In the lattice models for liquids, it is assumed that the free volume is distributed as randomly located holes in a close-packed site arrangement [21]. The lattice-hole model developed by Simha and Somcynsky [23] introduces the concept of a temperature and pressure-dependent hole fraction, h, which has been correlated with transport properties [29,30]. This useful parameter can be estimated using the reduced volume $\tilde{V} = V/V^*$ and the reduced temperature $\tilde{T} = T/T^*$ in the equation:

$$h = h_0 + \frac{h_1}{\tilde{V}} + h_2\tilde{T}^{3/2} + \frac{h_3}{\tilde{V}^2} + h_4\tilde{T}^3 \tag{7}$$

where, following Utracki and Simha [10], the adjustable parameters are: $h_0 = 1.203$, $h_1 = -1.929$, $h_2 = 10.039$, $h_3 = 0.729$, $h_4 = -218.42$.

The free volume is related to the hole fraction by the equation $V_{\mathrm{f}} = Vh$. Actually, V_{f} is used to define the "relative free space" V_0/V_{f} (where V_0 is the occupied volume) in the correlation proposed by Doolittle and Doolittle [2]:

$$\eta_0 = A_1 \exp\left(A_2V_0/V_{\mathrm{f}}\right) \tag{8}$$

where A_1 and A_2 are adjustable parameters.

Utracki initiated the search for a general form of the viscosity behaviour as a function of T and P, based on the free volume approach [5,6,8–10], which has been followed by successive efforts in this direction. We draw the attention to the equation proposed by Sedlacek et al. [12], which is actually a modification of Eq. (8), to adapt it to the Simha–Somcynsky theory:

$$\ln \eta_0 = \ln C_1 + C_2 \ln(h'/h) \tag{9}$$

where C_1, C_2 and h' are adjustable parameters.

Within the context of our work, the interest of this equation lies in the facility it offers to investigate the correlation between the viscosity and the hole fraction h, determined by means of *PVT* data, as shown in Eq. (7). As can be seen in Fig. 3 excellent correlations between experimental viscosity and the hole fraction model at different temperatures are observed for both isotactic and syndiotactic polypropylenes. The corresponding values of the adjustable parameters are shown in Fig. 3. For both the polymers very good fittings are obtained with $h' = 1$, indicating that the hole fraction correcting factor h' of Eq. (9), introduced by Sedlacek et al. [12], is useless in this case. Under these conditions, the parameter C_1 is the viscosity at maximum free volume ($h = 1$), which we judge to be equivalent to the structure sensitive factor F, defined in the earlier literature on polymer viscosity [31,32]:

$$\eta_0 = F\zeta \tag{10}$$

where ζ is a temperature or density dependent friction factor.

According to Berry and Fox results [33], F is directly proportional to the molecular weight and to the radius of gyration in the unperturbed state, S^2. The same proportionality can be assumed for the parameter C_1. Considering the molecular weights presented in Table 1, we can assume that, in our case, the parameter C_1 is rather affected by S^2. Therefore, the smaller

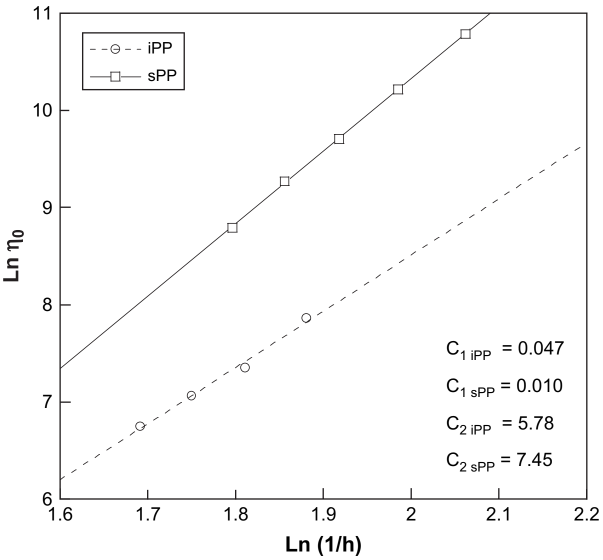

Fig. 3. Application of Eq. (9) for the Newtonian viscosity determined experimentally (see Section 2) and the hole fraction obtained using Eq. (7). Same symbols as in Fig. 1.

C_1 value found for syndiotactic PP would obey to a lower radius of gyration, with respect to isotactic PP. However, the characteristic ratio C_∞, which is directly proportional to S^2, has been reported to be higher (see below) for syndiotactic PPs. Therefore, with the results we have in hand, no conclusions on the conformational differences between syndiotactic and isotactic chains can be extracted from the hole fraction model.

The magnitudes of the parameter C_2 have been analysed for different polymers [12,34], observing a parallel increase of this parameter and the activation energy of flow. This relation is confirmed when we compare the C_2 values, presented in Fig. 3, with the corresponding activation energies of isotactic ($E_a = 40$ kJ/mol) and syndiotactic ($E_a = 50$ kJ/mol) polypropylenes reported in the literature [13,14,35]. When we compare the syndiotactic and the isotactic sample, the variation of both the parameters, C_2 and E_a, is very similar: $(C_2)_{\text{sPP}}/(C_2)_{\text{iPP}} = 1.29$ and $(E_a)_{\text{sPP}}/(E_a)_{\text{iPP}} = 1.25$. This result indicates a similitude between the temperature effect on the hole fraction and on the viscosity.

A different approach to the use of *PVT* data to investigate the viscosity of polymers, lies on the evaluation of the parameters involved in the basic $\eta_0 = F\zeta$ expression. The development of this equation, initiated by Berry and Fox [33], leads to the following expression, as explained by Yamamoto and Furukawa [11]:

$$\log \eta_0 = \log\left(\frac{N_A}{6}\right) + \log\left(\frac{C_\infty^3 \langle l_0^2 \rangle}{m_0}\right) + 3.4 \log\left(\frac{M_w}{2M_e}\right) + \log \zeta(\rho);$$

$$\log \zeta(\rho) = -10.6 + \frac{1}{2.303}\left[\frac{1}{f_g + \alpha_f (T - T_g)}\right] = -10.6 + \frac{1}{2.303}\left[\frac{1}{V_f}\right] \tag{11}$$

where N_A is Avogadro's number, C_∞ is the characteristic ratio, $\langle l_0^2 \rangle$ is the mean square length, m_0 is the molecular weight of the statistical skeletal bond, M_w is the weight average molecular weight and M_e is the entanglement molecular weight.

The free volume at ambient pressure is obtained from the hole fraction (determined using the Simha–Somcynsky equation of state), considering $V_f = Vh$, as explained above. The rest of the parameters of Eq. (11), except the characteristic ratio, are presented in Table 3. The C_∞ values reported in the literature lie in the range 4.15–6.2 for isotactic and 6.1–9.2 for syndiotactic polypropylenes [36–39]. The viscosity results obtained from Eq. (11) are compared with the experimental data, determined as described in the Section 2, in Fig. 4. As can be seen in Fig. 4a, the agreement between the theoretical and the experimental results is good for isotactic PP, using a temperature independent $C_\infty = 6$ value, which is within the interval given in the literature. However, for sPP no satisfactory agreement between theory and experimental results can be obtained using any of the C_∞ values reported in the literature. As an example, a clear deviation is noticed for syndiotactic PP in Fig. 4a, using a temperature independent $C_\infty = 6.7$ value. We remark that the difference between theory and experimental results increases as temperature decreases, giving a deviation which grows from 12% to 30%. These values clearly exceed the experimental error indicated in Section 2. We have to point out, that according to literature [21], the temperature coefficient of C_∞, $k = \mathrm{d}\ln C_\infty/\mathrm{d}T$, is 0 for isotactic PP; that is to say its characteristic ratio is constant in a wide range of temperatures in the melt state. As far as we know, only the old paper of Inagaki et al. [40] refers to a variation of C_∞ with temperature for a syndiotactic PP, giving $k = -0.7 \times 10^{-3}$ per degree, in the temperature range 30–135 °C, which is out of the interval considered in our work. Our results of Fig. 4a oblige us to introduce a temperature dependent C_∞ as an adjustable parameter to fit sPP experimental data to Eq. (11). Best fits are shown in Fig. 4b, where the following equation has been used to provide the proper C_∞ values to adjust the data:

$$C_\infty = 2.92 \exp(-0.002)T \tag{12}$$

Therefore, under the assumptions presumed in our work, a tentative temperature coefficient value $k = -2 \times 10^{-3}$ per degree is derived for syndiotactic PP, in the range of temperatures 130–190 °C.

It is shown that Eq. (11), proposed by Yamamoto and Furukawa [11] as a modification of the Berry–Fox model, is suitable to correlate thermodynamic and *PVT* measurements with viscosity results and in particular to deepen in the differences between iPP and sPP melts. A corollary of the obtained results is that Eq. (11) can be employed as an indirect way to

Table 3
Values of the parameters employed in Eq. (11)

	$\langle l_0^2 \rangle$ (Å^2)	m_0 (g/mol)	M_e (g/mol)
iPP	1.53	21	5500
sPP	1.53	21	2700

The values of the characteristic ratio C_∞ are indicated and discussed in the text.

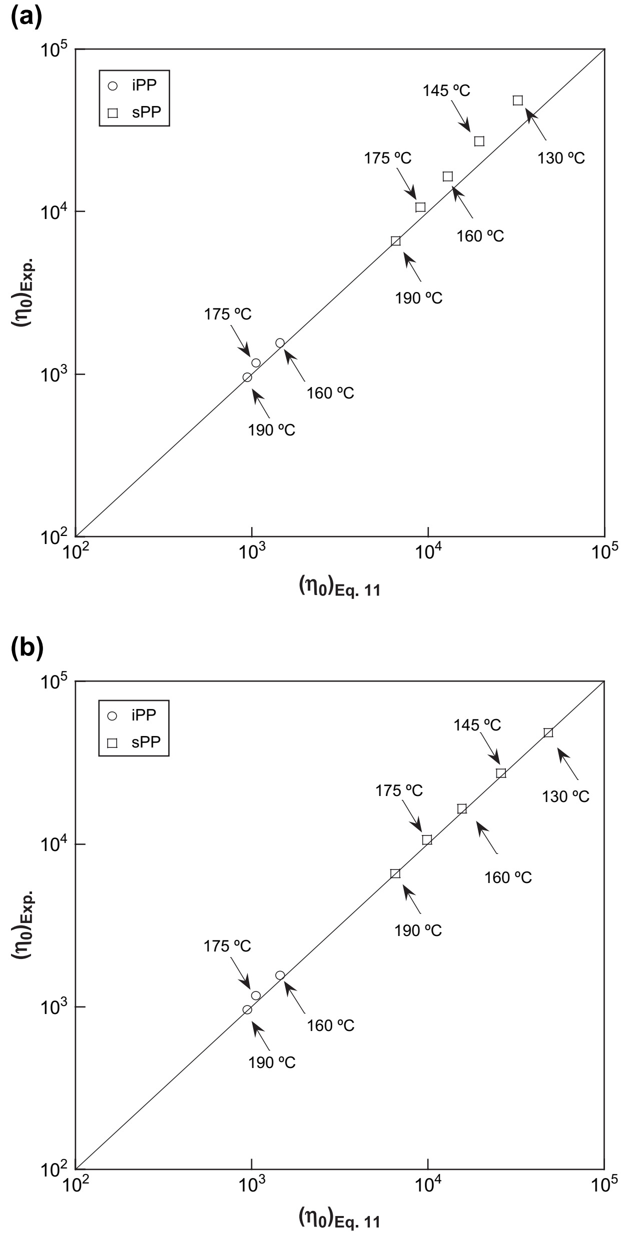

Fig. 4. Experimental η_0 values versus η_0 values obtained from Eq. (11). The line indicates exact coincidence between experimental and theoretical values. Same symbols as in Fig. 1 are used. (a) The η_0 values of Eq. (11) are obtained using temperature independent characteristic ratios for respective polypropylenes and (b) the η_0 values of sPP are obtained from Eq. (11) using the temperature dependent C_∞ of Eq. (12) (see Section 3).

determine the characteristic ratio at different temperatures. As could be expected, considering aforementioned literature results, we observe that C_∞ is independent of temperature for isotactic PP. But significantly enough, the characteristic ratio decreases exponentially with temperature in the case of syndiotactic PP.

4. Conclusions

The characteristic thermodynamical parameters V^*, T^*, P^* and the solubility parameter, δ, of an isotactic and a syndiotactic polypropylene, are obtained by fitting the *PVT* data to the Simha–Somcynsky equation of state. This allows to determine the hole fraction and the free volume, which are used in a modified Doolittle equation and a modified Berry–Fox equation to evaluate the linear viscosity. The analysis of the effect of temperature on hole fraction confirms the higher susceptibility of syndiotactic PP in the viscosity–temperature relationship. The Yamamoto and Furukawa model is employed as an indirect way to evaluate the characteristic ratio of both samples at different temperatures. Confirming literature results, it is observed that C_∞ is independent of temperature for isotactic PP. However, for the first time, an equation which accounts for the effect of temperature on C_∞ of syndiotactic PP, at $T > T_m$, is presented.

Acknowledgment

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