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A Reexamination of G_N^0 and M_e of Syndiotactic Polypropylenes with Metallocene Catalysts

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Introduction

The rheological behavior of polymer melt in the plateau zone is fundamentally affected by the entanglement coupling between molecular chains.[1] The most important parameter is the entanglement molecular weight, M_e, as one of the characteristic constants for each type of polymer. M_e is defined as the average molecular weight between entanglement points and depends on the plateau modulus G_N^0, which can be determined by measuring the dynamic moduli G' and G'' in an oscillatory shear experiment. Recently, Larson et al.[2] carefully review and clarify the different definitions of entanglement spacing. However, the experimental determination of the plateau modulus had not been discussed in-depth in the literature. There are three kinds of methods for estimating G_N^0 from the viscoelastic behavior of polymer melt. First, the plateau modulus G_N^0 could be directly obtained from the pseudoequilibrium modulus, if the storage modulus G' was absolutely independent of frequency in the plateau zone, which needs the exceedingly high molecular weight.[1,3] Second, the majority of the values of G_N^0 reported in the literature was obtained from the area of the terminal loss modulus peak by numerical integration[1,4,5]

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{+\infty} G''(\omega) \, d \ln \omega \qquad (1)$$

or by a modified equation.[6] Both high molecular weight and narrow molecular weight distribution (MWD) facilitate this integration method. The integration method is a classical and more extensively used method.[1,4,5] Third, G_N^0 can be obtained by relating itself with some viscoelastic characteristic parameters, such as the storage modulus G' at the minimum of loss tangent $\tan \delta_{min}$,[7,8] the maximum in terminal loss modulus G''_{max},[1,9–13] and the crossover modulus G_c,[14,15] where the G' and G'' curves intersect each other and $G' = G'' = G_c$. The last sort of method was mainly employed

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Table 1. Characterization of Syndiotactic Polypropylenes

sample	supported by	M_w (g/mol)	M_w/M_n	rr (%)	rrrr (%)
s-PP32	kaolinite	320 000	2.08	92.8	76.5
s-PP36		363 000	2.30	93.7	78.9
s-PP44	silica	443 000	2.23	95.4	81.2
ref 21		150 000	1.4	91.6	
ref 19		180 000	2.2		86.3
ref 18		483 000	2.1	93.0	

for some condensation polymers with too high molecular weight to be prepared, or for some semicrystalline polymers with very narrow window of rheological measurement, or as a tool to supply and confirm the results obtained by the integration method.

The stereoregularity is expected to influence chain entanglements and consequently the G_N^0. Recently, the influence of stereoregularity on the chain entanglements,[16–19] the chain dimensions and dynamic properties,[4,19,20] and the miscibility of blends[21–24] have attracted considerable academic interest. The syndiotactic polypropylene (*s*-PP) has been reported to exhibit a substantially larger G_N^0 than *i*-PP and *a*-PP (1.35 vs 0.42 MPa in ref 18). However, there are several inconsistent reports of values of the plateau modulus and chain dimensions of *s*-PP in the theoretical and experimental investigations.[4,19,21,25,26] In the present paper, three kinds of *s*-PPs with very high molecular weights and narrow MWDs were synthesized by using a metallocene catalyst supported by silica or kaolinite. The viscoelastic properties were investigated in an oscillatory shear measurement, and then the G_N^0 and M_e are reexamined by the integration method; the other different methods for estimating entanglement spacings are also discussed.

Experimental Section

Preparation of Syndiotactic Polypropylenes. Syndiotactic polypropylenes were prepared with a syndiospecific metallocene catalyst adduct supported. The adduct, $Ph_2C(Cp)$-$(Flu)ZrCl_2 \cdot Et_2O \cdot LiCl$, was synthesized and supported according to the procedure of CN96109534.2[27] and CN97115170.9,[28] respectively. The supports were silica (Divison 955) or kaolinite. The polymerization was carried out in 70 °C using a 5 L stainless steel reactor equipped with a mechanical stirrer. Under a nitrogen atmosphere, given amounts of triisobutylaluminum (TIBA), the supported catalyst, and propylene were added to the reactor. The polymerization was terminated by venting the monomer after 2 h. White *s*-PPs particles were obtained by drying under reduced pressure at 60 °C.

Characterization of *s*-PP Samples. The molecular weight (MW) and molecular weight distribution (MWD) were measured by GPC in *o*-dichlorobenzene at 135 °C with a Waters 150C apparatus. The ^{13}C NMR spectra of *s*-PPs were measured in 10% *o*-dichlorobenzene solutions at 125 °C with a Bruker AM400 spectrometer. The racemic pentad contents for three *s*-PPs are listed in Table 1. The contents of racemic dyads for these *s*-PPs are above 90%,[18,19,21] calculated from the pentad distribution. All the molecular characterizations of those *s*-PPs in refs 18, 19, and 21 are also listed in Table.1. It can be found that the degree of syndiotacticity and the width of the

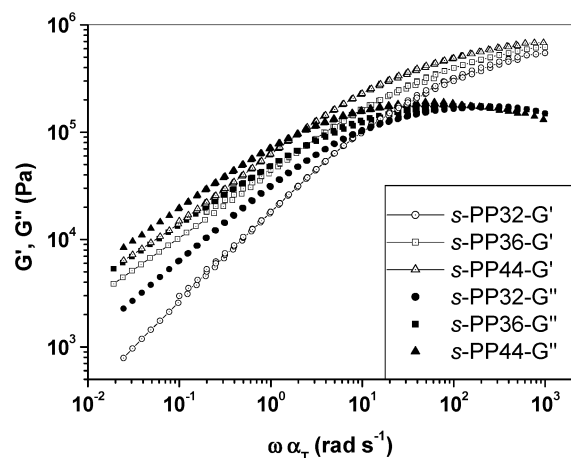**Figure 1.** Master curves of the dynamic moduli G' and G'' for the three *s*-PPs. The reference temperature is 190 °C.

Figure 2. Loss moduli G'' in a linear scale are shown as a function of reduced frequency in natural logarithmic scale at the reference temperature $T_0 = 190$ °C for the three *s*-PPs.

molecular weight distribution of our polymers are comparable with those in the literature.

Rheological Measurements. Dynamic rheological measurements were carried out on a Rheometrics SR 200 dynamic stress rheometer. The samples were melt-pressed at 190 °C into 1 mm thick plates and then were cut into small disks of about 25 mm diameter. Before rheological measurements, the samples were dried under vacuum at 100 °C for 24 h to completely remove the moisture. These measurements were then run with 25 mm parallel plate geometry and a 1 mm sample gap. Thermal stability of samples during the rheological testing was checked by a time sweep, where the selected samples gave a stable G' signal for at least 60 min at 250 °C. The dynamic viscoelastic properties were determined with frequencies from 0.1 to 500 rad/s, by using the strain values determined with a stress sweep to lie within the linear viscoelastic region (LVR). All measurements were carried out in a nitrogen atmosphere in the temperature range from 170 to 250 °C.

Result and Discussion

Figure 1 shows the master curves of the dynamic moduli G' and G'' for the three *s*-PPs. The reference temperature is 190 °C. The shift factor is plotted in terms of the Arrhenius equation, giving an average value of the apparent activation energy for flow of $E_a = 51.5$ kJ/mol, which is in good agreement with the values of 49−58 kJ/mol reported previously.[18,21,29] The master curve includes the terminal zone and rubbery plateau zone. The terminal zone shifts progressively to the low-frequency side with increasing molecular weight.[3,6] However, because the high molecular weight fractions in the *s*-PPs have not fully relaxed, the terminal zone is not finally reached, which is similar to the reports in the literature.[18,19,21]

In Figure 2, loss moduli G'' in the linear scale are shown as a function of reduced frequency in natural logarithmic scale at the reference temperature $T_0 = 190$ °C for the three *s*-PPs. In this plot, a well-developed maximum value of G'' at high frequency can be observed
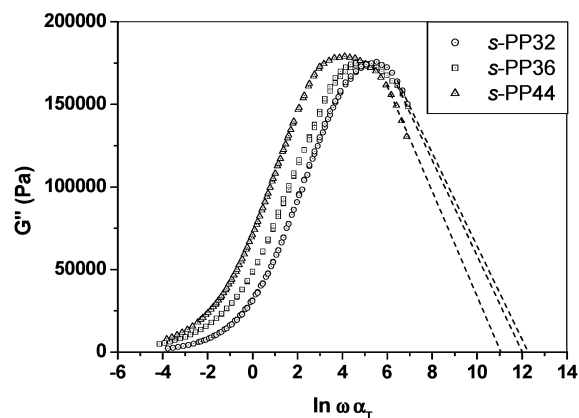
for all the *s*-PPs. The assumed high-frequency portion of the terminal peak is shown by the dashed line. The plateau modulus G_N^0 was calculated by using eq 1, and the values are listed in Table 2, giving a range from 8.2 $\times 10^5$ to 9.1×10^5 Pa for the three *s*-PPs (0.87 ± 0.05 MPa). However, because of the uncertainty of the moduli at the high-frequency region due to the machine compliance,[30,31] and some guesswork needed for extrapolating G'' to zero at high angular frequencies in a linear vs natural logarithm plot,[1] these values must be regarded as only tentative. Onogi et al.[3] found that no serious error was introduced when the value of ω_{max} (at which the loss modulus G'' takes its maximum) was taken as one of the integration limits or when the whole curve was assumed to be symmetric. On the basis of the experimental results, Wu[6] simplified eq 1 and then indicated that the plateau modulus G_N^0 was determined by

$$G_N^0 = \frac{4}{\pi} \int_0^{\omega_{max}} G'' \, \mathrm{d} \ln \omega \tag{2}$$

where ω_{max} is the frequency at G''_{max}. The values for three *s*-PPs estimated by eq 2 are also listed in Table 2. It is clear that the values obtained by both methods are reasonably consistent, which verifies the assumed linear extrapolation at high angular frequencies in Figure 2. However, G'' does not fulfill the ideal symmetry condition, which was illustrated by the recent theory of Likhtman and McLeish[32] (Figure 7, the power law $\omega(\alpha)$ of $G''(\omega)$ with $\alpha = -1/4$ as $\omega \gg \omega_{max}$), so the values calculated by eq 2 are a little smaller than those by eq 1.

The high molecular weight isotactic and syndiotactic PPs with a narrow MWD and high stereoregularity are still not available until recently. Eckstein et al.[18] reported a value of 1.35 MPa of the G_N^0 for a *s*-PP that is much greater than our value of 0.87 MPa. As shown in Figure 6 of ref 18, it lacks enough data points for

Table 2. Plateau Moduli G_N^0s of Syndiotactic Polypropylenes Estimated by Different Methods ($T_0 = 190$ °C)

| sample | G_N^0 (Pa) | | | | G''_{max} (Pa) | E_a (kJ/mol) |
	eq 1	eq 2	eq 3	eq 4		
s-PP32	825 000	860 000	626 000	849 000	176 000	49.9
s-PP36	889 000	803 000	623 000	845 000	175 000	55.4
s-PP44	909 000	873 000	637 000	865 000	179 000	49.0
ref 21			676 000	918 000	190 000	53
ref 19			623 000	845 000	175 000	
ref 18	1350 000		481 000	652 000	135 000	50.6

s-PP to extrapolate G'' to zero for high angular frequencies in a linear, natural logarithm plot. Raju and co-workers[10] validated both experimentally and theoretically (see Figure 1 and Table VII in ref 10) that it is about 3−4 decades the displacement from the ω_{max} to the frequency of the intercept of extrapolating G'' to zero at high frequencies. The criterion is supported by Likhtman and McLeish.[32] They illustrated the power law $\omega(\alpha)$ in the dynamic loss modulus $G''(\omega)$ with $\alpha = -1/2$ (the pure reptation + Rouse theory) as $\omega > \omega_{max}$ and with $\alpha = -1/4$ (addition of contour length fluctuations and constraint release) as $\omega \gg \omega_{max}$. This conclusion means that the frequency will increase 2−4 decades when the G'' decreases 1 decade as $\omega > \omega_{max}$. However, the difference of two frequencies for *s*-PP in Figure 6 of ref 18 is about 10 decades (about 23 in the natural logarithm plot), which means $\alpha = -1/10$. The gradual slope of the extrapolation line will unquestionably enlarge the area of integration and render an overestimation of G_N^0. In contrast, if eq 2 had been used for calculating the G_N^0 of their *s*-PP, the value would be obviously lower than 1.35 MPa. In fact, in their paper, the *a*-PP with M_w/M_e of 520 had enough data points at high frequencies for the extrapolation and has a plateau modulus of 0.42 MPa that is in good agreement with the values reported previously,[5] whose curve is evenly symmetric. Then the values estimated by both methods of eqs 1 and 2 should be similar to each other.

Another way to estimate the G_N^0 is the equation of relating the G''_{max} and G_N^0 suggested by Raju and co-workers.[10]

$$G_N^0 = 3.56 G''_{max} \tag{3}$$

G''_{max} is the maximum in terminal loss modulus G''. A similar equation was presented by Marvin−Oser[9]

$$G_N^0 = 4.83 G''_{max} \tag{4}$$

This is based on a shifted Rouse model for the terminal spectrum. As an important aspect of this method, it is unnecessary to have data of a sample with a very narrow MWD.[1] Although the distribution of entanglement strand lengths influences the calculation, neither the MWD nor the magnitude of the M_W affects the result as long as all the molecular species are large enough to participate in entanglements. Equation 4 is also supported by recent BSW relaxation time spectrum,[11,12] and the front factor is equal to 4.8 for all the molecular weights of both polystyrene and polybutadiene.[13]

As can be seen from Table 2, the values of the G''_{max} of 1.75×10^5 Pa in this study are in good agreement with those results in the literature,[19,21] except the lower value of 1.35×10^5 Pa in ref 18. Moreover, Fetters et al.[4] pointed out that some branched polymers were present in the *s*-PP sample of ref 18. Recent results show that the branched polymers have lower modulus than the linear polymers at high frequencies.[33,34] All the values of G_N^0 obtained by eqs 3 and 4 are listed in Table 2. It can be seen that the results obtained by Marvin−Oser equation and BSW theory are in good agreement with that of the integration methods of eqs 1 and 2. However, if using the data of ref 18, one would obtain a front factor of $G_N^0/G''_{max} = 1350000/135\,000 = 10$! Even if using the data of G''_{max} of 175000 Pa in refs 19 and 21 and our paper, one would obtain a front factor

of $G_N^0/G''_{max} = 1350000/175\,000 = 7.7$. No theories supported such higher front factor, which indicates that there has been a severely incorrect extrapolation procedure in Figure 6 of ref 18 from another aspect.

Conclusions

The viscoelastic property of three *s*-PP samples with very high molecular weights has been investigated in an oscillatory measurement. The main results of this rheological analysis can be briefly stated as follows:

The plateau modulus G_N^0 and the entanglement molecular weight M_e are the important material parameters that one needs to calculate the tube parameters in "tube" models for entangled polymer melts and solutions. The G_N^0 value of 0.87 ± 0.05 MPa for *s*-PP in this Note was estimated by using the integration method, and the M_e value of 3370 g/mol was calculated by using the same equation ($M_e = \rho RT/G_N^0$) and the same values of parameters (ρRT) in ref 18. Unfortunately, the "generally accepted literature" G_N^0 for *s*-PP was obviously overestimated due to the incorrect extrapolation procedure. The Marvin−Oser equation and BSW theory support our results, and those results in refs 19 and 21 also support our value of G_N^0.

It should be cautious to use the extrapolation procedure in the integration method of eq 1 determining the plateau modulus. It should be effective to use Raju's criterion[10] (about 3−4 decades the displacement from the ω_{max} to the frequency of the intercept of extrapolating G'' to zero at high frequencies in the linear, natural logarithm plot) for checking up the extrapolation of the G'' at high frequencies. This is supported by Likhtman and McLeish.[32] The other methods presented in the Introduction could be used for supplying and confirming the results obtained by the integration method.

References and Notes

(1) Ferry, J. D. In *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; Chapter 13.
(2) Larson, R. G.; Sridhar, T.; Leal, L. G.; McKinley, G. H.; Likhtman, A. E.; McLeish, T. C. B. *J. Rheol.* **2003**, *47*, 809−818.
(3) Onogi, S.; Masuda, T.; Kitagawa, K. *Macromolecules* **1970**, *3*, 109−116.
(4) Fetters, L. J.; Lohse, D. J.; Garcia-Franco, C. A.; Brant, P.; Richter, D. *Macromolecules* **2002**, *35*, 10096−10101.
(5) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639−4647.
(6) Wu, S. *Macromolecules* **1985**, *18*, 2023−2030.
(7) Wu, S.; Beckerbaur, R. *Polymer* **1992**, *33*, 509−515.
(8) Lomellini, P. *Polymer* **1992**, *33*, 1255−1260.
(9) (a) Marvin, R. S.; Oser, H. *J. Res. Natl. Bur. Stand.* **1962**, *66B*, 171. (b) Oser, H.; Marvin, R. S. *J. Res. Natl. Bur. Stand.* **1963**, *67B*, 87.
(10) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1668−1676.
(11) Baumgaertel, M.; Schausberger, A.; Winter, H. H. *Rheol. Acta* **1990**, *28*, 400−408.
(12) Baumgaertel, M.; Derosa, M. E.; Machado, J.; Masse, M.; Winter, H. H. *Rheol. Acta* **1992**, *31*, 75−82.
(13) Carri, G. A.; Winter, H. H. *Rheol. Acta* **1997**, *36*, 330−344.
(14) Wu, S. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 723−741.
(15) Nobile, M. R.; Cocchini, F. *Rheol. Acta* **2001**, *40*, 111−119.

(16) Wu, S.; Beckerbauer, R. *Polym. J.* **1992**, *24*, 1437−1442.

(17) Fuchs, K.; Friedrich, C.; Weese, J. *Macromolecules* **1996**, *29*, 5893−5901.

(18) Eckstein, A.; Suhm, J.; Friedrich, C.; Maier, R.-D.; Sassmannshausen, J.; Bochmann, M.; Mülhaupt, R. *Macromolecules* **1998**, *31*, 1335−1340.

(19) Jones, T. D.; Chaffin, K. A.; Bates, F. S.; Annis, B. K.; Hagaman, E. W.; Kim, M.-H.; Wignall, G. D.; Fan, W.; Waymouth, R. *Macromolecules* **2002**, *35*, 5061−5068.

(20) Arrighi, V.; Batt-Coutrot, D.; Zhang, C. H.; Telling, M. T. F.; Triolo, A. *J. Chem. Phys.* **2003**, *119*, 1271−1278.

(21) Yamaguchi, M.; Miyata, H. *Macromolecules* **1999**, *32*, 5911−5916.

(22) Maier, R. D.; Thomann, R.; Kressler, J.; Mülhaupt, R.; Rudolf, B. *J. Polym. Sci., Part B*: *Polym. Phys.* **1997**, *35*, 1135−1144.

(23) Silvestri, R.; Sgarzi, P. *Polymer* **1998**, *39*, 5871−5876.

(24) Marquardt, J.; Thomann, R.; Thomann, Y.; Heinemann, J.; Mülhaupt, R. *Macromolecules* **2001**, *34*, 8669−8674.

(25) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Part B*: *Polym. Phys.* **1999**, *37*, 1023−1033.

(26) Pütz, M.; Curro, J. G.; Grest, G. S. *J. Chem. Phys.* **2000**, *114*, 2847−2860.

(27) Chen, W.; Zhang, L.; Jing, Z. H.; Liu, K.; Wang, J. W. (RIPP, SINOPEC) CN 96109534.2, 1998.

(28) Sun, C. Y.; Chen, W.; Cui, C. M.; Hou, M. X.; Jing, Z. H. (RIPP, SINOPEC) CN 97115170.9, 1999.

(29) Eckstein, A.; Friedrich, C.; Lobbrecht, A.; Spitz, R.; Mülhaupt, R. *Acta Polym.* **1997**, *48*, 41−46.

(30) Raju, V. R.; Smith, G. G.; Marin, G.; Knox, J. R.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1979**, *17*, 1183−1195.

(31) Wood-Adams, P. M.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. *Macromolecules* **2000**, *33*, 7489−7499.

(32) Likhtman, A. E.; McLeish, T. C. B. *Macromolecules* **2002**, *35*, 6332−6343.

(33) Milner, S. T.; McLeish, T. C. B.; Young, R. N.; Hakiki, A.; Johnson, J. M. *Macromolecules* **1998**, *31*, 9345−9353.

(34) Liu, C. Y.; Li, C. X.; Chen, P.; He, J. S.; Fan, Q. R. *Polymer* **2004**, *45*, 2803−2814.