Macromolecules **1998,** *31,* 1335−1340

Determination of Plateau Moduli and Entanglement Molecular Weights of Isotactic, Syndiotactic, and Atactic Polypropylenes Synthesized with Metallocene Catalysts

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Received August 21, 1997; Revised Manuscript Received December 15, 1997

ABSTRACT: Metallocene catalysis was employed to prepare model polypropylenes (PP) with very high molecular weights and narrow molecular weight distributions (MWDs) of $M_w/M_n \approx 2$, typical for "single site" metallocene catalysts. The viscoelastic properties of PP melts were investigated by means of oscillatory rheometry. Arrhenius and WLF equations were applied to model the influence of temperature on PP rheology. With very high molecular weight polypropylene samples it became possible to determine the onset of the plateau zone, reflecting the rubber-like properties of PP. For the first time plateau moduli G_N°s and entanglement molecular weights M_es were determined and found to be depend upon stereoregularity. The entanglement molecular weights were found to be 6900 g/mol for isotactic PP, 7050 g/mol for atactic PP, and 2170 g/mol for syndiotactic PP. This influence of stereoregularity was attributed to the different conformations of syndiotactic PP with respect to isotactic and atactic PP in PP melts.

Introduction

Most conventional Ziegler catalysts represent multisite catalysts and form polypropylenes (PPs) with broad molecular weight distributions and considerable amounts of stereoisomer impurities. Peroxide-induced thermal degradation was used to achieve a narrow molecular weight distribution (MWD) of PP. To obtain a model PP for investigation of physical properties, extensive purification by means of solvent fractionation was required. Ultrahigh-molecular-weight, atactic PP was not available because most conventional catalysts produced rather ill-defined low-molecular-weight PPs having low stereoregularity and containing isotactic segments of various lengths. The discovery of single-site metallocene catalysts has revolutionized polyolefin technology and gives excellent control of the stereochemistry and molecular weight of PP without sacrificing the narrow MWD. Today, well-defined atactic PP, characterized by a random distribution of the two possible configurations of the stereogenic carbon atom of the repeat unit along the PP chain, as well as isotactic and syndiotactic PP are available over the entire feasible molecular weight range without sacrificing the narrow MWD and high stereoregularity. Recently, Resconi and co-workers[2,3] developed special metallocene catalysts for producing high-molecular-weight, atactic PP. Therefore, metallocene catalysis provides researchers with an excellent model PP, which is very useful for the study of the influence of stereoregularity and molecular weight on rheological behavior. Syndiotactic PP and isotactic PP have the same dependence of the zero shear viscosity η_0 as a function of the molecular weight, but syndiotactic PP exhibits a 10 times higher viscosity than isotactic PP.[4] An important material parameter represents the plateau modulus G_N°,[5] as one of the characteristic constants for each type of polymer. The plateau modulus reflects the molecular architecture of the polymers and is dependent on the entanglement molecular weight M_e, which is defined as the molecular weight between adjacent temporary entanglement points. The plateau modulus can also be correlated with unperturbed chain dimensions, such as the radius of gyration R_g.[6] Usually, the viscoelastic behavior can be determined by measuring the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ over a wide range of frequencies ω and temperatures T. The storage modulus $G'(\omega)$ is proportional to the energy storage in a cycle deformation reflecting a certain degree of elasticity of the system. The loss modulus $G''(\omega)$ is proportional to the dissipation or loss energy as heat in a cycle deformation, reflecting a certain degree of viscosity of the system. There are two primary methods for determining the plateau modulus from the viscoelastic behavior of polymer melts. First, the plateau modulus can be obtained from the frequency where the minimum of the loss tangent tan δ (tan $\delta = G''/G'$) is located.[7−9]

$$G_N^\circ = G'(\omega)_{\tan\delta_{\min}} \tag{1}$$

The loss tangent δ is defined as the ratio of the loss modulus $G''(\omega)$ and the storage modulus $G'(\omega)$ and therefore represents the ratio of viscosity and elasticity. The $G'(\omega)$-value at the frequency ω where the minimum of tan δ is located represents the maximum elasticity of the system. While eq 1 is purely empirical, eq 2 is based on the use of the fluctuation−dissipation theorem, which combines the correlation function of the relaxation function (the fluctuation part) and the power spectrum of this function (dissipation part).[10] Moreover, this theorem is applied to that part of the relaxation function which is called the flow transition, $G_{FT}(t)$, and which includes the plateau, as well as the flow regions. This leads to the following equation for the plateau modulus:

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S0024-9297(97)01270-9 CCC: $15.00

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

where G_e is the equilibrium modulus, which we set to zero, and $G_{FT}(0)$ is the highest value of the relaxation function of the flow transition, which corresponds to the time zero. The plateau modulus reflects the unrelaxed, fully elastic response of the material corresponding to the flow transition. This is illustrated in Figure 1.

One problem which arises from the use of eq 2 is the separation of $G''_{FT}(\omega)$ from the measured $G''(\omega)$-function and the corresponding extrapolation of these data to ∞. For polymers with high molecular weights and a sufficiently narrow MWD this procedure can be performed easily, as will be shown below. A plot of $G''(\omega)$ versus the natural logarithm of the angular frequency indicates that these polymers exhibit a well pronounced maximum which is followed by a linear decrease and an onset of the main transition. In this case a linear extrapolation and integration can be performed which corresponds to eq 2. An important condition for this equation is the assumption that the $G''(\omega)$ curve has a pronounced maximum in a linear-natural logarithm plot. This enables reasonable extrapolation to high frequencies. Both high molecular weights and a narrow MWD facilitate this integration method: a broad MWD prevents the maximum of $G''(\omega)$ with respect to higher frequencies, because the transition between the plateau zone and the terminal flow region takes place over decades of frequencies. The plateau zone is more pronounced at higher molecular weights, because the terminal relaxation time shifts toward lower frequencies with increasing molecular weight. Another problem of determining the plateau modulus G_N° is related to the nature of the polymer. It is possible to determine the plateau modulus for amorphous polymers by dynamic oscillatory measurements. This was done for some amorphous polymers by both methods (eqs 1 and 2). The situation changes for semicrystalline polymers, particularly for the industrially important polyolefins. For instance, these methods for determining the plateau modulus cannot be used for polyolefins, because it is impossible to measure $G'(\omega)$ and $G''(\omega)$ of the plateau zone of these polymers. The window of rheological measurements of polyolefins is comparatively small, due to a crystallization temperature (~423−438 K) for PP. Degradation takes place at high temperatures above 513 K. Therefore, it was not possible to measure a significant onset of a plateau zone. Due to the very broad MWD of most conventional isotactic and syndiotactic PP samples, it was impossible to determine the plateau modulus by both methods. The determination of G_N° was only possible for atactic, amorphous PP. The value of the plateau modulus of atactic PP was determined, ranging from 420.000 up to 860.000 Pa, by rheological methods and scattering techniques.[11−14] From the variation in the data of the plateau moduli, an inconsistency is observed for atactic PP. Moreover, it should be noted that most conventional stereoirregular PPs were not true atactic PP with a Bernoullian distribution of the two configurations of the stereogenic carbon atom along the polypropylene chain. In fact, most conventional—so-called atactic—PPs contained significant amounts of stereoregular sequences. To overcome this problem, model polymers were prepared by living anionic diene polymerization followed by hydrogenation.[15−17] Although such hydrogenated polydienes represent polyolefins, it was not clear how they compare to uniform polyolefins prepared by means of metallocene catalysts. Stereoregularity is expected to influence chain entanglements and consequently the plateau modulus. In fact, this was observed for poly(methyl methacrylate) (PMMA) with different stereoregularities.[18,19] The plateau moduli of the semicrystalline syndio- and isotactic PPs were not reported in the literature until recently. The objectives of this research were the synthesis and rheological investigation of PPs with very high molecular weights and narrow MWDs, to determine the influence of stereoregularity on both plateau modulus and entanglement molecular weight.

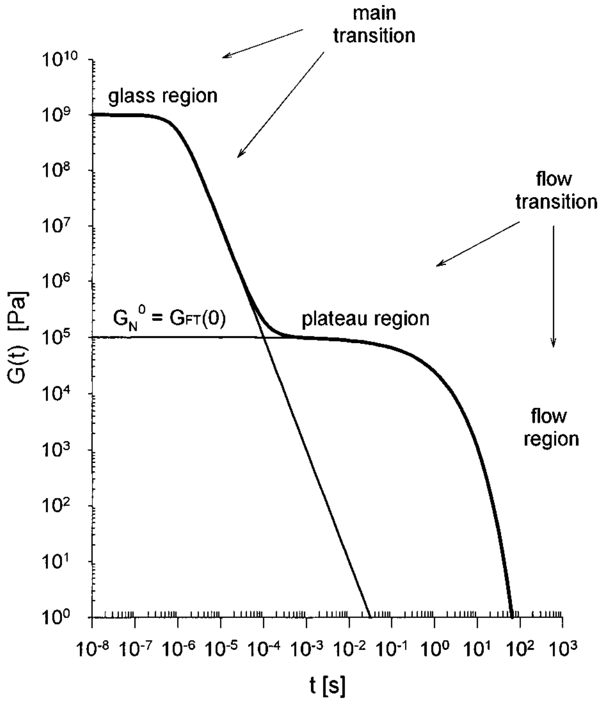

Figure 1. Schematic representation of relaxation function G(t) for an amorphous polymer. The plateau modulus G_N° can be determined by linear extrapolation of the flow transition modulus to small times.

Experimental Section

Polymer Synthesis. *rac*-Dimethylsilylenebis(2-methylbenz[*e*]indenyl)zirconium dichloride (MBI) was obtained from BASF AG, methylalumoxane (MAO) was obtained from Witco GmbH, and propene (polymerization grade) from BASF AG was used without further purification. Toluene was distilled over a Na/K alloy prior to use and injected directly in the reactor. Isotactic polypropylene (i-PPM9) was synthesized using MBI/MAO at 283 K in a mixture of liquid propene and toluene. Polymerization was carried out in a 1.6-L Buechi glass autoclave equipped with a torion valve. A combination of inner and outer cooling was used to keep the polymerization temperature constant at 283 K. After the temperature in the reactor was equilibrated, argon was removed by passing a continuous flow of propene (100 g/h) at 2 bar of pressure through the glass autoclave. The metallocene solution (in toluene, 20 mmol/L of MAO) was injected into the reactor. The catalyst concentration was 2 μmol/L with an Al/Zr molar ratio of 2000. The polymerization was quenched by precipitating polypropylene in a 3-fold excess of 10 wt % acidic methanol. The precipitated polymer i-PPM9 was filtered, washed with CH_3OH, and dried in a vacuum at 333 K to constant weight. Atactic polypropylene (a-PPM36) was synthesized using trimethyl(pentamethylcyclopentadienyl)titanium (Cp^*TiMe_3) activated with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) in liquid propene at 228 K. Polymerization was carried out in a glass-lined reactor, which had been flame-dried in vacuo. Stock

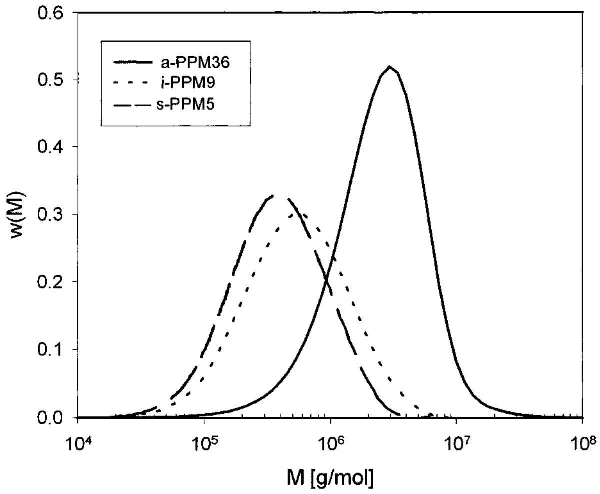

Figure 2. High-temperature size exclusion chromatography (HT-SEC) curves of three polypropylene samples. The solvent was 1,2,4-trichlorbenzene at 413 K.

solutions (ca. 10^{-5} mol/L) of Cp^*TiMe_3 and $B(C_6F_5)_3$ in toluene were freshly prepared. Propene was purified by being passed through P_2O_5 and 4-Å molecular sieves and was stored over $Et_2AlOC_6H_{13}$. The 1-L glass reactor vessel was filled with 500 mL of liquid propene at 223 K. Typically, 120 μmol of Cp^*TiMe_3 was injected followed immediately by 120 μmol of $B(C_6F_5)_3$. The propene started to boil and thus kept the temperature at 228 K. The reaction was stopped after 4 min by injecting 5 mL of methanol. The polymer was precipitated from methanol, redissolved in 1 L of diethyl ether, and precipitated from 8 L of methanol. The product was dried at 333 K for 24 h. The metallocene-based high-molecular-weight syndiotactic polypropylene (s-PPM5) was supplied by FINA.

Molecular Characterization. The molecular weights M_w and M_n and the polydispersity M_w/M_n were determined by means of high-temperature size exclusion chromatography (HT-SEC), using 1,2,4-trichlorobenzene (TCB) as solvent and 0.2 wt % Irganox 1010 as stabilizer. The HT-SEC was calibrated with isotactic PP standards of narrow MWD. The HT-SEC traces are displayed in Figure 2. ^{13}C NMR spectra were recorded on a Bruker ARX 300 spectrometer operating at 75.4 MHz at 400 K in $C_2D_2Cl_4$ solution, with 6000 scans, a 2-s delay, and an acquisition time of 1.5 s. The NMR spectra did not indicate the presence of branching. The content of triads was calculated from the pentads, indicating the grade of stereoregularity. DSC measurements were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter, equipped with a liquid nitrogen subambient accessory. The PP melting temperature, T_m, or the glass transition temperature, T_g, was measured using the second heating curve (heating rate 20 K/min) of 8-mg samples. Polymer densities were measured at 298 K and atmospheric pressure using a micropycnometer (Quantachrome). The changes in density as a function of temperature and pressure were determined with a Gnomix pvT Apparatus (Boulder, CO). The sample cell contained about 1 g of polymer and mercury as a confining fluid. The measurements were performed in the isothermal mode; that is, the sample was held at a certain temperature, and the pressure was continuously raised from 10 to 200 MPa with pressure, volume, and temperature being recorded in steps of 10 MPa. The specific volume corresponding to $p = 0$ MPa was extrapolated by the Tait equation using the pVT software (Gnomix). Subsequently, this procedure was repeated for temperatures between 303 and 543 K in steps of approximately 10 K. The molecular weights, polydispersities, and melting and glass transition temperatures of the synthesized i-PPM9, a-PPM36, and s-PPM5 are listed in Table 1. The stereoregularities of the three polypropylenes are listed in Table 2. The values given in Table 2 for a-PPM36 deviate slightly from the ideal values of the triade distribution corresponding to the Bernoulli statistic.

Table 1. Molecular Characterization of the Polypropylenes

polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (K)	T_m (K)	ρ^a (g/cm^3)
i-PPM9	365 000	871 000	2.4	nd^b	432	0.766
s-PPM5	231 000	483 000	2.1	nd	412	0.762
a-PPM36	1 890 000	3 670 000	1.9	276.9		0.765

[a] At reference temperature $T_0 = 463$ K. [b] Not determined.

Table 2. Stereoregularities of the Polypropylenes

polymer	mm^a (%)	mr^a (%)	rr^a (%)
i-PPM9	98.7	0.7	0.6
s-PPM5	0.7	6.3	93.0
a-PPM36	30.2	52.8	17.0

[a] Calculated from the pentad distribution using ^{13}C-NMR data.

Rheology. For the oscillatory measurements, the PP powder was dried under vacuum at 333 K for several days. The sample was cold-compressed and then annealed for 30 min at 483 K in a vacuum and compression-molded at 483 K to form a small disk 25 mm in diameter and with a thickness of about 1 mm. The rheological behavior was studied using dynamic oscillatory tests performed with a Rheometrics Mechanical Spectrometer RMS 800 with a parallel plate geometry 25 mm in diameter. The angular frequency ω varied from 10^2 to 10^{-2} rad s^{-1}, and the temperature ranged from 493 to 443 K for i-PPM9 and s-PPM5. In the case of a-PPM36, the temperature was varied between 513 and 303 K. All PP samples were studied under nitrogen atmosphere in order to avoid thermooxidative degradation. The isotherms were shifted to obtain master curves at the reference temperature $T_0 = 463$ K using the program LSSHIFT.[20] In the case of s-PPM5 the rheological behavior was studied using an additional creep experiment on a Bohlin CVO rheometer with parallel plate geometry (PP 25 mm) and a shear stress of 200 Pa at 463 K. The retardation spectrum L(λ) was calculated from the creep compliance $J(t)$ by using the nonlinear regularization program NLREG.[21] The dynamic compliances $J'(\omega)$ and $J''(\omega)$ were calculated from the retardation spectrum L(λ) and transformed to the corresponding $G'(\omega)$ and $G''(\omega)$ data using the standard formula given by Ferry.[5]

Results and Discussions

In general, the rheology of polymer melts depends strongly on temperature. It is well-known that in the case of thermorheological simplicity, isotherms of $G'(\omega)$ and $G''(\omega)$ (or other material functions) can be superimposed by horizontal shifts along the frequency axis ω:

$$G'^{('')}(\omega a_T, T_0) = G'^{('')}(\omega, T) \tag{3}$$

where a_T is the horizontal shift factor and T_0 is the reference temperature. All measured isotherms of i-PPM9, a-PPM36, and s-PPM5 could be superimposed along the frequency axis. Usually, two semiempirical equations, the Arrhenius and the WLF equation, are used to evaluate the temperature dependence of the shift factors. First, there is the Arrhenius equation,

$$\log a_T = \frac{E_A}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{4}$$

where R is the universal gas constant ($R = 8.314$ J mol^{-1} K^{-1}) and E_A is the activation energy of flow. Second, there is the Williams–Landel–Ferry (WLF) equation,

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \tag{5}$$

Table 3. WLF Parameters[a] and Arrhenius Activation Energy of Flow[a]

polymer	c_1	c_2 (K)	c_1c_2 (K)	E_{Arr} (kJ/mol)	E_{WLF} (kJ/mol)
i-PPM9	1.86	194.25	362.40	38.68	39.50
s-PPM5	3.92	335.70	1315.94	50.61	49.36
a-PPM36	2.91	253.50	737.68	nc[b]	39.23

[a] Reference temperature $T_0 = 463$ K. [b] Not calculated.

where c_1 and c_2 are the WLF parameters.

Analyzing the temperature dependence of a_T, we found Arrhenius behavior for isotactic PP and syndiotactic PP samples. It is also possible to describe the temperature dependence of isotactic PP and syndiotactic PP melts by the WLF equation with high accuracy. The values of a_T for i-PPM9 and s-PPM5 are comparatively small in contrast to those of other thermoplastic polymers such as polystyrene (PS), but they are in the range of those of other isotactic and syndiotactic PP samples.[4] The calculated Arrhenius activation energies of flow E_As of isotactic PP and syndiotactic PP samples have values typical for both types of polypropylenes, in accordance with earlier observations.[4,22] Analyzing the temperature dependence of a_T for the atactic polypropylene a-PPM36, we found only WLF behavior over a wide range of temperatures. For this reason no calculated Arrhenius activation energy of flow is listed in Table 3. The WLF equation is normally thought to be valid in the temperature range between T_g and $T_g + 100$ K, but some authors such as Lomellini[23] or Kulkarni[24] suggest the validity of the WLF equation up to $T_g + 300$ K. The measurement using a-PPM36 is a good example to demonstrate the validity of the WLF equation up to $T_g + 230$ K. It can be assumed that the wide temperature range of a-PPM36 is responsible for the observed WLF behavior. If the temperature range of the semicrystalline samples were as large as in the case of the atactic sample, only WLF behavior would probably be detectable. The WLF parameter, the WLF energies of flow, and the Arrhenius activation energies of flow are listed in Table 3.

Analyzing the WLF parameters c_1 and c_2 of the three polypropylenes we found similar values for isotactic PP and atactic PP, while the c_1 and c_2 values of the syndiotactic PP sample are clearly higher. In Figures 3−5 the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ and tan $\delta(\omega)$ for i-PPM9, s-PPM5, and a-PPM36 are shown as functions of reduced frequency ($\omega\ a_T$) at the reference temperature $T_0 = 463$ K.

In the case of isotactic PP there is only a small window useful for rheological measurements, because of oxidative degradation above 513 K and an onset of crystallization below 433 K. As a result of the small experimental window and the slight temperature dependence of isotactic PP melts, a master curve with a relatively small range of frequencies has been obtained. For i-PPM9 $G''(\omega)$ is proportional to ω in the terminal zone and consequently the slope is 1 in a double logarithmic plot. However, the storage modulus G' shows a deviation from the slope 2. As a consequence the terminal zone is not finally reached, because the high-molecular-weight fractions in the polymer sample are not fully relaxed. i-PPM9 shows a clear onset of the plateau zone toward higher frequencies. A minimum in the loss tangent curve cannot be observed. A determination of the plateau modulus G_N^0 is not possible by using eq 1. The master curve of s-PPM5 obtained by oscillatory measurements shows significant deviation from the i-PPM9-master curve, because the $G'(\omega)$ and $G''(\omega)$ curves coincide in the range of lowest measured frequencies in the oscillatory test. Even for the $G''(\omega)$ curve there is no frequency range where $G''(\omega)$ is proportional to ω. The experimental window for $G'^{('')}(\omega)$ of the s-PPM5 sample could be expanded by a creep measurement at the reference temperature $T_0 = 463$ K (see Experimental Section). A shear rate of 1.2×10^{-4} s^{-1} was calculated from the creep experiment, so that the region of linear viscoelasticity was found. The calculated dynamic moduli $G'(\omega)$ and $G''(\omega)$ from the creep measurement overlap with the directly measured $G'(\omega)$ and $G''(\omega)$ from the master curve in a broad frequency range. The small deviations between the two curves may result from using two different types of rheometers rather than a violation of the linear superposition principle. There are high-molecular-weight fractions in the sample s-PPM5 as can be seen from two or three relaxation processes from the resulting "super"-master curve. These high-molecular-weight fractions are not detectable by high-temperature size exclusion chromatography (HT-SEC), probably due to loss by filtration. Nevertheless, s-PPM5 is a linear polymer, because the terminal flow zone, where G' is proportional to ω^2 and G'' is proportional to ω, is reached at very low frequencies. The onset of the plateau can also be clearly detected. The minimum of the loss tangent curve is similar to that of isotactic PP not observable toward higher frequencies. A determination of the plateau modulus is not possible by using eq 1. In contrast to the case for the semicrystalline PP (i-PPM9 and s-PPM5), the master curve of the atactic PP a-PPM36 spreads over 9 decades of frequencies. The terminal flow region is not reached, because the rheological experiments were stopped at a temperature of $T = 513$ K. The rubber-elastic plateau region is clearly pronounced. As was mentioned before, the minimum of the loss tangent tan δ can be observed for this polymer. Both equations for determination of the plateau modulus can be used for a-PPM36. The plateau modulus G_N^0 of a-PPM36 was determined to be 415 000 Pa by means of eq 1. From eq 2 the plateau modulus can be obtained by integration of the loss modulus over the frequency axis. In Figure 6 loss moduli $G''(\omega)$ in a linear scale are shown as a function of reduced fre-

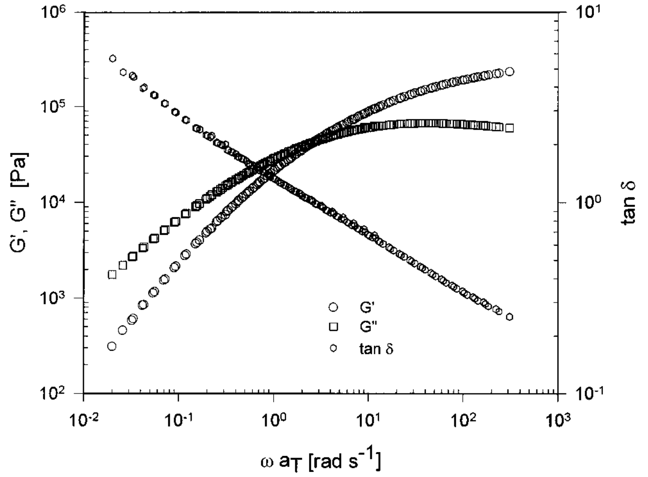

Figure 3. Mastercurve of the storage modulus $G'(\omega)$, the loss modulus $G''(\omega)$ and the loss tangent tan δ of the isotactic polypropylene (iPPM9) versus reduced angular frequency ωa_T at the reference temperature $T_0 = 463$ K.

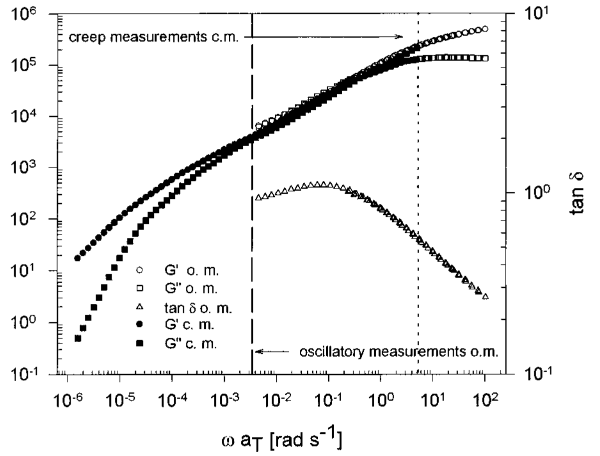

Figure 4. Master curve of the storage modulus $G'(\omega)$, the loss modulus $G''(\omega)$, and the loss tangent tan δ of syndiotactic polypropylene (sPPM5) versus reduced angular frequency ωa_T at the reference temperature $T_0 = 463$ K. Dashed lines display limits of oscillatory and creep measurements at the same reference temperature $T_0 = 463$ K.

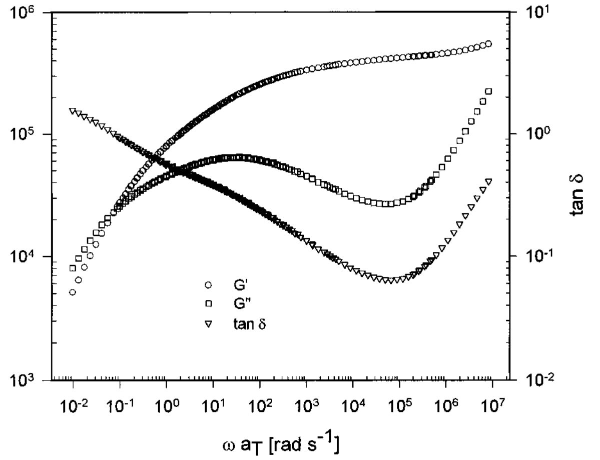

Figure 5. Master curve of the storage modulus $G'(\omega)$, the loss modulus $G''(\omega)$, and the loss tangent tan δ of atactic polypropylene (aPPM36) versus reduced angular frequency ωa_T at the reference temperature $T_0 = 463$ K.

quency (ω a_T) in natural logarithmic scale at the reference temperature $T_0 = 463$ K for i-PPM9, s-PPM5, and a-PPM36.

In this plot, maxima can be observed in the loss moduli $G''(\omega)$ for all three samples. In the case of a-PPM36, the data points of the onset of the glass transition are not shown. Using the maxima of the three curves, there are enough data points to extrapolate $G''(\omega)$ to zero reasonably for high angular frequencies in a linear, natural logarithm plot. We have linearly extrapolated $G''(\omega)$ to zero for high angular frequencies, because there is a linear dependence of the flow transition at high angular frequencies, as can be seen in the case of the atactic sample. There is a large difference of the integration areas between the syndiotactic and the isotatic/atactic samples, while the difference between atactic and isotactic PP is not pronounced. The integration areas of isotactic PP and atactic PP are almost the same, resulting in similar plateau moduli for isotactic PP and atactic PP samples. More data points of $G''(\omega)$ toward higher frequencies are desirable but are only available for PP with even higher molecular weights. For these PPs, the molecular weight limitations are a result of state of the art catalyst technology, which is at present unable to produce molecular weights two or three times higher than those of the PP samples used in this investigation. The G_N° values derived by the integration method are given in Table 4. The plateau modulus G_N° is connected with the entanglement molecular weight M_e:

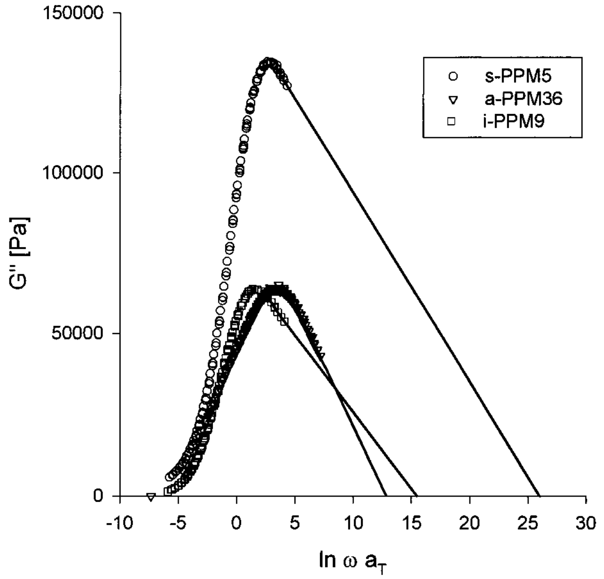

Figure 6. Loss moduli $G''(\omega)$ of the three PPs versus reduced angular frequency ωa_T in a linear, natural logarithm plot at the reference temperature $T_0 = 463$ K.

Table 4. Plateau Moduli G_N°s and Entanglement Molecular Weights M_es of Polypropylenes with Different Stereoregularities

polymer	G_N° [a] (Pa)	G_N° [b] (Pa)	M_e [c] (g/mol)	M_w/M_e
i-PPM9	427 000		6 900	126
s-PPM5	1 350 000		2170	222
a-PPM36	418 000	415 000	7050	520

[a] Calculated from eq 2. [b] Calculated from eq 1. [c] Calculated from eq 6 ($T_0 = 463$ K).

$$G_N^\circ = \frac{\rho R T}{M_e} \tag{6}$$

R is the universal gas constant ($R = 8.314$ J mol^{-1} K^{-1}) and ρ is the density of the polymer at temperature T, at which the plateau modulus was measured. The data for melt density ρ were taken from pvT measurements. The plateau moduli G_N° and the calculated entanglement molecular weights M_e are listed in Table 4. The entanglement molecular weights were found to be 6900 g/mol for isotactic PP, 7050 g/mol for atactic PP, and only 2170 g/mol for syndiotactic PP.

It can be seen from the last column of Table 4 that the ratio of M_w/M_e is large ($M_w/M_e \gg 100$), so that the influence of molecular weight on the plateau modulus can be neglected. From Table 4 it is evident that in the case of a-PPM36 the plateau modulus has the same value determined by both methods (eqs 1 and 2). This demonstrates that the linear extrapolation is an effective way to calculate plateau moduli.

From Table 4 it is clear that stereoregularity has an enormous influence on both the plateau moduli and the entanglement molecular weight. The different plateau moduli of isotactic and syndiotactic PP may be responsible for their different melt rheology, recently reported in the literature.[4] In contrast to the case for isotactic PP and syndiotactic PP, only the plateau moduli of the atactic PP sample can be compared with those reported previously. Fetters and co-workers found for model atactic polypropylene plateau moduli between 470 000 and 520 000 Pa by rheological measurements. From SANS measurements plateau moduli of the same polymers were determined to be between 420 000 and 520 000 Pa.[6] Plazek et al.[12] determined the plateau modulus of model atactic PP to be 470 000 Pa by rheological measurements. The plateau modulus of 418 000 Pa for atactic PP, presented in this study, is in good agreement with these results.

Conclusions

The viscoelastic properties of very high molecular weight isotactic, syndiotactic, and atactic PP, prepared with metallocene catalysts, were investigated. The influence of stereoregularity on activation energy of flow E_{WLF}, plateau modulus G_N°, and entanglement molecular weight M_e was analyzed. The activation energies of flow E_{WLF}s of atactic and isotactic PP were found to be very similar. In contrast, syndiotactic PP showed a 10 kJ/mol larger activation energy of flow with respect to that of isotactic or atactic PP, respectively. The PP samples with very high molecular weight enabled the measurement of $G'(\omega)$ and $G''(\omega)$ over a range necessary to obtain a significant onset of the plateau zone. The plateau moduli G_N°s of isotactic, syndiotactic, and atactic PP were determined successfully by integration of the $G''(\omega)$ function, which was not possible for conventional PP samples with a broad MWD and much lower molecular weight. The plateau moduli of isotactic and atactic PP are very similar, whereas that of syndiotactic PP is three times larger. The calculated entanglement molecular weight M_e in the molten state of syndiotactic PP was only one-third of the calculated entanglement molecular weight of isotactic and atactic PP, respectively. The melt properties of all PP samples were markedly influenced by their stereoregularity. The solid-state conformations are well-known for isotactic PP (3_1 helix),[25] syndiotactic PP (2_1 helix corresponding to planar zigzag conformation),[26] and atactic amorphous PP (random coil). Similar plateau moduli, entanglement molecular weights, and activation energies of flow of isotactic and atactic PP indicate that also isotactic PP is likely to form a random coil conformation in the molten state. The significant differences of the rheological properties of syndiotactic PP with respect to those of isotactic and atactic PP may be due to the presence of predominantly all trans conformations in the melt. This was reported by Loos et al.[27] and confirmed by molecular-modeling investigations.[28] The observation of similar material characteristics of isotactic and atactic PP in the molten state in contrast to those of syndiotactic PP is in accord with similar observations obtained in pressure−volume−temperature (pvT) experiments.[29,30]

Acknowledgment. This work was supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (project # 03D0055), and by BASF AG, Ludwigshafen. Also we want to thank Witco Germany for supplying samples of MAO. We are grateful to Dr. Razavi from FINA for supplying us with the syndiotactic polypropylene sample sPPM5.

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MA971270D